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Mark Steven Erickson

_Louisiana State University and Agricultural & Mechanical College_

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Synthesis of novel metallocenes: Asymmetric hydrogenation catalysts to conductive polymers

Erickson, Mark Steven, Ph.D.
The Louisiana State University and Agricultural and Mechanical Col., 1992
SYNTHESIS OF NOVEL METALLOCENES:
ASYMMETRIC HYDROGENATION CATALYSTS TO CONDUCTIVE POLYMERS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Mark Steven Erickson
B.A., Hamline University, 1984
December 1992
DEDICATION

To my mother Caralou,
my father Norman,
and my brothers Brian and Jeff

and

for my wife Kathryn
and our children
Monica
Christopher
and
Stephanie
Kurt Vonnegut wrote a book called *Cats Cradle*. In his book he describes a religion called Bokanism. In the book of Bokan, it is written that we all have a *karass*, which is a cast of characters in our lives. "If you find your life tangled up with somebody else's life for no logical reasons," writes Bokonon, "that person may be a member of your *karass*." This dissertation is dedicated to my *karass*.

My father Norman and mother Caralou; brothers Brian and Jeff; my wife Kathy and our children Monica, Christopher, and Stephanie; my in-laws: Bernie, Sue, Jane, Patty, and Kim Stricker; Grandma Esther Erickson and Great Aunt Helga Westerlind; uncles Gary Erickson and Jim Beers, aunts Shari Erickson and Lynn Michael; cousins Chrissy and Paul Michael, Missy and Marnie Erickson, Kim, Sheila, and Dawn Beers; also Grandma and Grandpa Beers and Uncle Elliot Michael who passed away recently, have all been the strength and stability in my life.

I also wish to dedicate this dissertation to my friends for life, Chris Larson, Jeff Williams, James Capra, Dave Miller, Kale Hedstrom, Tim Halpine, Sue Lundquist, Chris Janzen, Rich Kelly, Steve Clark, Al Trojnar, Lorna Wong, Paul Verhagen, Rich Eckman, Mike Vitale, Dave Timmons, Mary Jo Phillips, Mike and Melinda Oliver, Linda Spiegel, Dave Brown, John Ozevek, Kathy Bender, Donn Smith, Colin and Chris Rickenbach, Jeff Sodemann, Sara and John Murphy, and Steve Lundahl; Dr. Olaf Runquist, my first research advisor, who first taught me how to perform research and believed in me enough to convince me to go on to graduate school; my track and cross-country coach Chuck Wallin who taught me how to reach for my goals, friends and former colleagues at Medtronics, Pat Cahalan, Al Jevne, and Eileen Halverson who helped me get a start in industry and treated me like family; friends and former colleagues at IBM, Steve Fuerniss, Carl
Diener, Jim Loftus, Lynn Martinowitz, and Bernd Appelt who made me feel comfortable at IBM and taught me how to deal with the red tape at Big Blue; Tom Watson who saved my life one afternoon; Kathy Nathan who helped me see myself; and all of my friends mentioned in the acknowledgements. It would take a whole book to describe how they all have influenced my life. They all mean the world to me and I want them to know that they are all part of this work. They will always be on my mind and in my heart.
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ABSTRACT

The goal of this research was to synthesize conductive polymers based on repeating ferrocene units. During the course of this study, the design of the conductive polymers evolved from the initial model based on "stacked" ferrocenes where ethano bridged cyclopentadienyl rings are linked by iron(II), to the latest ferrocene-diene model where ferrocene units were linked by double bonds. In the pursuit of these elusive monomers, attempts at their synthesis led down dead-end routes, even though new molecules were synthesized. Some of these dead-ends proved productive as in the synthesis of chiral titanocene derivatives. All the work reported in this dissertation had the eventual goal of synthesizing potential monomers for ferrocene conducive polymers.

This dissertation is divided into three chapters. Chapter one describes the attempted synthesis of thiophene derivatives where a cyclopentadienyl ring is fused to the [c]-face. Although the target molecule was never synthesized, a convenient and safe new synthesis of 3,4-dibromo-2,5-dimethyl thiophene was developed along with the synthesis and full characterization of 3-bromo-4-trimethylsilyl-2,5-dimethylthiophene. Chapter two describes the design of asymmetric hydrogenation catalysts and the convenient synthesis of chiral titanocene derivatives. Chapter three summerizes the history of our attempts to prepare ferrocene containing conductive polymers and describes the synthesis of ferrocenophenes and diethano bridged bis(cyclopentadienyl) compounds for use as monomeric precursors to conductive polymers based on repeating ferrocene units.
CHAPTER ONE.

Synthesis of Thiophene Derivatives: Attempts to Synthesize [c]-Annulated Cyclopentadienyl Thiophenes

1.1 Introduction.

Thiophene is a six π-electron aromatic heterocyclic compound. Thiophenes are known to form metal complexes of various hapticity.\textsuperscript{1-3} The goal of this project was to synthesize cyclopentadienyl [c]-annulated thiophenes as ligands for various transition metals. The resulting transition metal complexes would be interesting on both theoretical and practical standpoints because the transition metal can freeze-out resonance structures by complexing with the π-system of the most prevalent or reactive resonance structures, and the transition metal complexes can be used as precursors to monomers for conductive polymers.

The synthesis of 4H-cyclopenta[c]thiophene,\textsuperscript{4} 1.1, and 1,3-dimethyl-4H-cyclopenta[c]thiophene,\textsuperscript{5} 1.2, was reported previously (Figure 1.1). In each case, the cyclopentadienyl was fused to the thiophene using a technique developed by Ellison and co-workers.\textsuperscript{6} The anions of 1.2 and 1.3 have been synthesized, but to date, their respective metal complexes have not been reported. Analogous iron(II) complexes of the anions of cyclopenta[b]thiophenes have been reported.\textsuperscript{7} The interest in the metal complexes lies in the site of metal complexation, which can take place on either the thiophene ring or cyclopentadienyl ring. This is metal dependent when benz-annulated thiophenes are considered, but what about cyclopenta[c]thiophenes? Also, if the metal complexes η\textsuperscript{5} to the cyclopentadienyl,
what happens to the $\pi$-electrons in the thiophene? Are all the $\pi$-electrons still delocalized or will the thiophene have some diradical character?

Figure 1.1 Examples of known [c]-annulated thiophenes 1.1 and 1.2 with the proposed pentamethylcyclopenta[c]thiophene, 1.3.

Deprotonation of 1.2 and relevant proposed resonance structures are illustrated in Figure 1.2. The most interesting of the resonance structures is 1.2c and 1.2d. If a diradical character were to exist, would the metal complexes undergo intermolecular cyclizations or would the bis(cyclopenta[c]thiophene) metal complexes undergo intramolecular ring closures? Structure 1.2c may also undergo intramolecular coupling. X-ray crystal structures of non-classical thiophenes provide evidence for the existence of highly strained structures such as 1.2c.$^{8-12}$

Figure 1.2 Proposed deprotonation of a [c]-annulated thiophene and examples of a few resonance structures.
Figure 1.3 illustrates the proposed use of the resultant diradical character in the resonance structure from the deprotonation of [c]-annulated thiophenes for the metal mediated cyclization to form a precursor for 1,2,4-ethanobridged cyclopentadienyl compounds. 1,2,4-ethanobridged cyclopentadienyl compounds have potential use as monomers for conductive polymers based on repeating ferrocene units.

Pentamethylcyclopenta[c]thiophene, 1.3, was chosen as a model ligand and target molecule because pentamethylcyclopentadienyl metal complexes are typically more stable than unmethylated analogs. Also, the proposed technique to synthesize 1.3 is novel and may be applicable for the annulation of other aromatics. The strategy of the proposed synthesis of 1.3 involved a cationic ring closure to fuse the cyclopentadienyl to the thiophene. A summary of the attempted cyclizations are illustrated in Figure 1.4.
Figure 1.4  Summary of attempted cyclizations of thiophene derivatives to 1.3 and 1.6.

1.2 Design of the Thiophene Substrate.

Figure 1.5 illustrates two retrosynthetic routes to the target molecule 1.3. Route 1 involves a cationic intramolecular cyclization initiated by the dehydration of the alcohol. Analogous dienones have undergone similar cyclizations when treated with polyphosphoric acid.\textsuperscript{13,14} Route 2 involves an anionic cyclization to form the cyclopentadienyl annulated thiophene with subsequent dehydration of the resulting cyclic alcohol to form the target molecule. Both retrosynthetic routes are broken down to simple readily available starting materials. Route 1A starts with 2,5-dimethyl thiophene and tiglic acid chloride and route 1B can be broken down to the easily synthesized 3-acetyl-2,5-dimethyl thiophene and the Grignard reagent derived from 2-bromo-2-butene. Route 2 can be broken down to easily synthesized 3,4-dibromo-2,5-dimethyl thiophene and 3-methyl-3-penten-2-one.

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1.3 Results and Discussion.

1.3.1 Attempted Synthesis of '1.3' via Retrosynthetic Routes 1A and 1B.

The attempted forward synthetic routes to 1.3 derived from retrosynthetic routes 1A and 1B are outlined in Figure 1.6. The key step in the forward synthesis of 1.3 was the carbocation ring closure of the alcohol intermediate 1.6, or in an alternate synthesis, the Narzarov cyclization\(^\text{15}\) of the intermediate 1.4. Both of these reactions failed to give 1.3. Also, the simplest synthesis of 1.3 involving a
one step acylation of 2,5-dimethylthiophene with tiglic acid to 1.4, followed by a cyclization to give 1.3 was unsuccessful.

Figure 1.6 Forward synthesis of 1.3 derived from retrosynthetic routes 1A and 1B.

The failure of 1.4 and 1.6 to undergo cyclization is believed to be due to the carbocation deactivation of thiophene towards aromatic electrophilic substitution, as shown in Figure 1.7. The attempted acid catalyzed cyclization of 1.4 failed, with starting materials recovered. Treatment of 1.6 with acid instead resulted in the two possible acyclic alkenyl thiophenes 1.7 and 1.8, evident by the presence of thiophene and vinylic protons in the $^1$H NMR.
Figure 1.7 Proposed cationic intermediates in the dehydration of 1.3.

In an effort to investigate the feasibility of any cationic ring closure similar to that proposed for 1.6, the synthesis of 3-(1-hydroxy-1-methyl-2-propenyl)-2,5-dimethylthiophene, 1.9, and subsequent acid catalyzed cyclization to 1.10 was studied as a model reaction, illustrated in Figure 1.8. The synthesis of 1.9 in an 80% yield was easily accomplished by the treatment of 3-acetyl-2,5-dimethylthiophene with vinylmagnesium bromide in tetrahydrofuran. The acid catalyzed cyclization was attempted by refluxing an ether solution of 1.9 and p-toluene sulfonic acid for two hours. Thin layer chromatography and $^1$H NMR of the crude product indicated complete consumption of the starting material but $^1$H NMR showed evidence of a major product with terminal vinylic protons at 5.0-5.5 ppm and a thiophene proton at 6.52 ppm. No cyclization products were detected.
A new strategy was developed to prevent the deactivation of the thiophene ring involved the placement of a large sterically hindering group on the thiophene that could be easily removed. This large blocking group would force the carbocation tether from planarity with the thiophene π-system, diminishing the electron withdrawing effects of the carbocation on the thiophene ring. Trimethylsilyl was the best candidate for the blocking group due to its large steric bulk and its excellent leaving aptitude in electrophilic aromatic substitution.

Attempts to trimethylsilylate ortho to substituted thiophenes or to alkylate thiophene ortho to a trimethylsilyl were unsuccessful, therefore, attempts to utilize the trimethylsilyl group as a blocker were abandoned.

1.3.2 Attempted Synthesis of '1.3' via Retrosynthetic Route 2.

The success of the forward synthetic route to 1.3 can be accomplished by either functionalizing the thiophene ring of the the allylic alcohol of 2,5
dimethylthiophene with a halogen, or by the mono alkylation of 3,4-dibromo-2,5-dimethylthiophene, followed by an anionic ring closure. Unfortunately, both strategies failed.

Using a forward synthesis derived from retrosynthetic route 2A, the attempt to alkylate the monolithio derivative of 3,4-dibromo-2,5-dimethylthiophene with 3-methyl-3-penten-2-one to form 3-bromo-4-(1-hydroxy-1,2-dimethylbutenyl)-2,5-dimethylthiophene, 1.12, was moderately successful but the subsequent deprotonation and disilylation of 1.12 produced numerous inseparable products (Figure 1.9). The model reaction between the monolithio derivative of 3,4-dibromo-2,5-dimethylthiophene and methyl vinyl ketone to produce 3-bromo-4-(1-hydroxy-1-methylpropenyl)-2,5-dimethylthiophene, 1.13, was successful, but the subsequent disilylation of the deprotonated derivative also produced numerous inseparable products. The eventual goal of these reactions was to desilylate 1.14 and 1.15 with hydrofluoric acid and cyclize them to 1.3 and 1.10 respectively.

Figure 1.10 illustrates the unsuccessful attempts at brominating the open thiophene position on 2,4,5-trisubstituted thiophenes as an alternate route to 1.13. Using a procedure designed to selectively brominate thiophene positions over the competitive acyl side-chain positions,16 attempted bromination of 3-acetyl-2,5-dimethylthiophene to 3-acetyl-4-bromo-2,5-dimethylthiophene, 1.16, in an aqueous sodium acetate solution favored bromination of the enol to form the α-bromo derivative 1.17 over thiophene ring bromination to 1.16. Also, in a procedure designed to brominate thiophene positions in the presence of competing alkenyl side chain bromination,17 the attempted bromination of 1.6 produced several products including the dibromo derivative, 1.18, as the major product instead of the desired 1.13.
Figure 1.9 Synthesis of 1.12 and 1.13 and proposed cyclizations to 1.3 and 1.10 respectively.
**Figure 1.10** Attempted bromination of 3-acetyl-2,5-dimethylthiophene and 1.13.

1.3.3 Synthesis of 3,4-Dibromo-2,5-dimethylthiophene and 3-Bromo-4-trimethylsilyl-2,5-dimethylthiophene.

The synthesis of 3,4-dibromo-2,5-dimethylthiophene and 3-bromo-4-trimethylsilyl-2,5-dimethylthiophene, 1.19, is summarized in Figure 1.11. The
synthesis of 3,4-dibromo-2,5-dimethylthiophene was very successful with an isolated yield of 91%. This is an improvement over the method by Melles and Backer because the yield is greater and the new method avoids the use of highly toxic cuprous cyanide along with toxic and extremely flammable carbondisulfide.\textsuperscript{18} The improved method requires no special handling or procedures and uses acetic acid as a solvent.

The failure of 3,4-dibromo-2,5-dimethylthiophene to undergo dilithiation with n-butyllithium is not surprising since this requires two negative charges proximate to each other. This is contrary to what is reported for various bromothiophenes.\textsuperscript{19}

\textbf{Figure 1.11} Synthesis of and summary of reactions involving 3,4-dibromo-2,5-dimethylthiophene and 1.19.
Transmetallation of 3,4-dibromo-2,5-dimethyl thiophene with 1.2 equivalents of n-butyllithium in ether at -78° C and subsequent treatment with chlorotrimethylsilane yielded 3-bromo-4-trimethylsilyl-2,5-dimethylthiophene in an 80% yield. Attempts to transmetallate 3-bromo-4-trimethylsilyl-2,5-dimethylthiophene under similar conditions failed. 3-Bromo-4-trimethylsilyl-2,5-dimethylthiophene also failed to metallate using both lithium or sodium, even with the use of ultrasound. Also, attempts to synthesize the 2,5-dimethyl-3,4-bis(trimethylsilyl)thiophene by dilithiation of 3,4-dibromo-2,5-dimethylthiophene with 2.5 equivalents of n-butyllithium and treatment with chlorotrimethylsilane resulted in the exclusive formation of 1.19 instead of the desired 2,5-dimethyl-3,4-bis(trimethylsilyl)thiophene, 1.20. The reaction of 1.19 with potassium in refluxing tetrahydrofuran is believed to cause thiophene ring opening. Treatment of 1.19 with t-butyllithium and subsequent alkylation with methyl iodide, afforded 2,3,5-trimethyl-4-trimethylsilylthiophene, 1.21 in good yield, where other electrophiles such as methyl vinyl ketone and chlorotrimethylsilane failed give 1.22 and 1.20, respectively.

X-ray quality crystals of 1.19 were obtained from hexane and a single crystal X-ray structure determination was performed. Bond lengths and bond angles for 1.19 are reported in Tables 1.1 and 1.2 respectively. Figure 1.12 shows the ORTEP drawing of 1.19. The molecule lies on a mirror plane in the crystal.
### Table 1.1 Bond Distances (Å) for '1.19'.

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Numbers in parenthesis are estimated deviations in least significant digits.

### Table 1.2 Bond Angles (°) for '1.19'.

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Numbers in parenthesis are estimated deviations in least significant digits.
Figure 1.12 ORTEP drawing of 1.19.
1.4 Conclusion.

All attempts to form methylated cyclopentadienyl[c]thiophenes failed. The accomplishments of this work include an improved method for the synthesis of 3,4-dibromo-2,5-dimethylthiophene where the yield was increased (from 82% to 91%) and the use of dangerous starting materials (cuprous cyanide and carbon disulfide) was eliminated by use of glacial acetic acid as a solvent. 3-Bromo-4-trimethylsilyl-2,5-dimethylthiophene 1.19, was synthesized in an 80% yield by the transmetallation of 3,4-dibromo-2,5-dimethylthiophene with n-butyllithium and subsequent treatment with chlorotrimethylsilane. 1.19 was fully characterized and the X-ray structure solved. 1.19 proved to be extremely unreactive towards alkylation, requiring the use of t-butyllithium for transmetallation and a sterically unhindered alkylation agent such as methyl iodide.

1.5 Experimental Section.

**General Comments:** Bromine (Baker), acetic anhydride and glacial acetic acid (Mallinckrodt); sodium, lithium, potassium, magnesium, n-butyllithium (2.5 M in hexanes), t-butyllithium (1.7 M in pentane), 2-bromo-2-butene, aluminum chloride, stannic chloride, and tiglic acid (Aldrich) were used as received. Chlorotrimethylsilane (Aldrich) was distilled from CaH₂ prior to use. 2,5-Dimethylthiophene,²⁰,²¹ 3-acetyl-2,5-dimethylthiophene,²²,²³ tiglic acid chloride,²⁴ 3-methyl-3-pentene-2-one²⁵ were prepared according to literature methods. Methyl iodide was passed through basic alumina prior to use. Ether was
distilled over Na/K (benzophenone) under argon. Tetrahydrofuran was distilled over potassium under argon. $^1$H NMR and $^{13}$C NMR spectra were measured at 200 MHz and 50 MHz, respectively, on a Bruker AC 200 spectrometer. Chemical shifts are reported in $\delta$ or ppm downfield from tetramethylsilane. IR spectra were measured on a Perkin-Elmer 1760X FTIR. Elemental analysis was performed by Oneida Research Services, Inc. (Whitesboro, NY).

1.5.1 Attempted Synthesis of '1,3' via Tandem Friedel-Crafts Reaction of 2,5-Dimethylthiophene with Tiglic Acid.

A mixture of tiglic acid (0.94 g; 9.4 mmol), 2,5-dimethylthiophene (1.13 g; 10.1 mmol) and polyphosphoric acid (7.71 g) was stirred for one hour at 80° C under argon, during which, the reaction mixture turned dark red. The reaction mixture was added to water and extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution, dried with anhydrous magnesium sulfate, and solvent removed under reduced pressure yielding a yellow solid (1.06 g). Bulb-to-bulb sublimation gave a white solid which $^1$H NMR analysis revealed to be pure tiglic anhydride.

Another procedure using a different acid involved heating a stirring mixture of tiglic acid (0.79 g; 7.9 mmol), 2,5-dimethylthiophene (0.86 g; 7.7 mmol) and polyphosphoric acid (6.26 g) under argon for 22 hours. The reaction mixture was poured into water and extracted with dichloromethane. After exhaustive washing of the combined extracts with saturated sodium bicarbonate solution, drying with anhydrous magnesium sulfate, and subsequent solvent removal under reduced pressure, a red solid (0.95 g) resulted which was subjected to column chromatography. Less than 0.1 grams eluted as a yellow solid. Analysis by $^1$H
and $^{13}$C NMR did not match what was obtained in the former procedure nor did it match what would have been expected from this reaction.

1.5.2 Attempted Synthesis of 3-(2-methyl-2-buten-1-onyl)-2,5-dimethylthiophene, '1.4'.

A mixture of tiglic acid chloride (2.17 g; 18.3 mmol) and 2,5-dimethylthiophene (2.07 g; 18.3 mmol) in anhydrous 1,2-dichloroethane (35 mL) was added via cannula to aluminum chloride (4.67; 35.0 mmol), stirred at room temperature for 1.5 hours, and refluxed for 30 minutes. The reaction mixture was poured into cold water and extracted with dichloromethane (2 x 150 mL). The combined extracts were washed with 10\% sodium hydroxide (2x) where the color changed from red to yellow. The extract was washed with water (200 mL), dried with anhydrous magnesium sulfate, and solvent removed under reduced pressure to give a yellow oil (2.88 g). Bulb-to-bulb distillation of the oil (1.15 g) gave 0.87 g of an oil (88-90° C, 0.45 mm Hg). Thin layer chromatography showed numerous inseparable products. $^1$H and $^{13}$C NMR also showed numerous products.

The attempted synthesis of 1.4 using a milder Lewis acid, stannic chloride gave similar results. Stannic chloride (2.90 g; 11.1 mmol) was added dropwise to a solution of 2,5-dimethylthiophene (4.27 g; 37.8 mmol) and tiglic acid chloride (4.48 g; 37.8 mmol) in 1,2-dichloroethane (60 mL) at 0° C. The reaction mixture was stirred at 0° C for three hours and room temperature for seven hours, poured into ice, and extracted with dichloromethane (2 x 200 mL). The combined extracts were washed with saturated sodium bicarbonate solution (3 x 200 mL) and distilled water (200 mL), dried with anhydrous magnesium sulfate, and solvent removed
under reduced pressure. Fractional distillation (108-110° C, 1 mm Hg) gave an oil (1.76 g). Gas and thin layer chromatography showed numerous inseparable products. ¹H and ¹³C NMR also showed numerous products.

1.5.3 Attempted Synthesis of 3-(1-Hydroxy-1,2-dimethyl-2-buteryl)-2,5-dimethylthiophene, '1.6'.

2-Bromo-2-butene (7.53 g, 5.7 mL; 55.8 mmol) was slowly added to freshly cut strips of lithium (0.97 g; 0.123 mmol) in anhydrous ether (5 mL), with subsequent addition of anhydrous ether (40 mL), and stirred for 2-3 hours.³⁸-³⁹ 3-Acetyl-2,5-dimethylthiophene (8.60 g; 55.8 mmol) was added slowly, with a slight rise in temperature. The mixture was stirred at room temperature for three hours, poured on to saturated ammonium chloride solution (100 mL), and extracted with ether. The combined ether layers were dried with anhydrous magnesium sulfate and the solvent removed under reduced pressure resulting in a yellow oil (2.33 g). Purification by bulb-to-bulb distillation under reduced pressure gave a yellow oil (2.28 g) which showed considerable amounts of starting material along with evidence of 1.6 according to ¹H NMR. Further purification by column chromatography was ineffective.

A similar procedure using a 50% excess of 2-bromo-2-butene with excess lithium resulted in cis and trans isomers of 1.6 (68.4% yield based on 3-acetyl-2,5-dimethylthiophene) that was at least 90% pure after bulb-to-bulb distillation according to ¹H NMR. Analysis: ¹H NMR (200 MHz, CDCl₃) δ 1.31 (m, 3 H), 1.65 (m, 3 H), 1.80 (m, 3 H), 2.32 (s, 3 H), 2.37 (s, 3 H), 5.29 (m, 1 H), 6.67 (s, 1 H); ¹³C NMR (50 MHz, CDCl₃) 14.03, 14.23, 15.10, 22.09, 29.11, 74.65, 121.12, 125.30, 132.51, 134.16, 140.63, 143.51 ppm.
An alternate method for the synthesis of 1.6 was attempted using magnesium turnings instead of lithium wire. A small portion of the total amount of 2-bromo-2-butene (4.38 g, 3.3 mL; 32.4 mmol) was added to magnesium turnings (2.02 g; 83.1 mmol) covered with anhydrous tetrahydrofuran (5 mL), initiated by a few drops of 1,2-dibromoethane. Once the reaction reached reflux temperature, the balance of 2-bromo-2-butene was added to maintain a reflux and was diluted with tetrahydrofuran (30 mL). The reflux was continued for 30 minutes and the reaction mixture was stirred for an additional two hours at room temperature. A solution of 3-acetyl-2,5-dimethylthiophene (5.0 g; 32.4 mmol) in anhydrous tetrahydrofuran (20 mL) was added slowly to the Grignard reagent, with evolution of heat. The reaction mixture was stirred for one to two hours, poured into a saturated solution of ammonium chloride, and extracted with ether. The combined ether extracts were dried with anhydrous magnesium sulfate and the solvent removed under reduced pressure to give a yellowish-brown oil (6.23 g). Bulb-to-bulb distillation (60° C, 0.5 mm Hg) gave a yellow oil which again showed considerable amounts of starting material. Further purification of the oil by column chromatography (silica gel) was ineffective.

With both lithium and magnesium metals failing to undergo exclusive carbonyl addition, a cerium (III) mediated reaction was attempted according to the literature\textsuperscript{30,31} and resulted in no reaction, with complete recovery of starting materials.
1.5.4 Attempted Cyclization of '1.6' to '1.3'.

A solution of crude 1.6 (2.12 g; 10.1 mmol) and p-toluene sulfonic acid (0.1 g) in ether (10 mL) was refluxed for two hours. After cooling to room temperature, the solution was washed with saturated sodium bicarbonate and solvent removed under reduced pressure to give a yellow oil (1.94 g). $^1$H NMR showed numerous peaks from 0.9-2.8 ppm, with a large cluster of unexpected vinyl peaks from 4.7-6.1 ppm. This evidence suggests dehydration as the major process instead of cyclization.

Similar reactions with other acids such as polyphosphoric acid and 10% aqueous sulfuric acid gave identical $^1$H NMR spectra, consistent with dehydration to acyclic thiophenes.

1.5.5 Synthesis and Attempted Acid Catalyzed Cyclization of 3-(1-Hydroxy-1-methyl-2-propenyl)-2,5-dimethylthiophene, '1.9'.

A solution of 3-acetyl-2,5-dimethylthiophene (15.0 g; 97.3 mmol) in anhydrous tetrahydrofuran (20 mL) was added to a solution of vinylmagnesium bromide (132 mmol) in anhydrous tetrahydrofuran (50 mL) at 0°C, stirred for two hours, and warmed to room temperature where it was stirred for an additional hour. The reaction mixture was poured into a saturated solution of ammonium chloride and extracted with ether. The combined ether extracts were dried with anhydrous magnesium sulfate and solvent removal under reduced pressure gave a yellow oil. Fractional distillation under reduced pressure (b.p. 86-88°C; 1 mm Hg) gave a slightly yellow oil (14.2 g; 80.1% yield). $^1$H and $^{13}$C NMR strongly suggest the
structure proposed for 1.9. $^1$H NMR (200 MHz; CDCl$_3$) $\delta$ 1.60 (s, 3 H), 2.00 (s, 1 H), 2.35 (s, 3 H), 2.41 (s, 3 H), 5.13 (m, 2 H), 6.09 (m, 1 H), 6.59 (s, 1 H); $^{13}$C NMR (50 MHz; CDCl$_3$) 14.74, 14.96, 29.25, 73.87, 111.56, 125.55, 132.50, 134.21, 140.70, 143.90.

Attempted cyclization of 1.9 involved refluxing a solution of 1.9 (1.0 g) with a trace of $p$-toluene sulfonic acid in ether (20 mL) for two hours. After the solution cooled to room temperature, the reaction mixture was washed with a saturated solution of sodium bicarbonate, dried with anhydrous magnesium sulfate, and solvent removal under reduced pressure gave a yellow oil. $^1$H NMR suggested that the major product believed to be 1.11 is due to dehydration to acyclic thiophenes instead of cyclization to 1.10. The presence of unexpected major peaks at 6.52 and 6.47 ppm suggests thiophene protons and major peaks between 5.0 and 5.6 ppm indicates the presence of terminal vinylic protons.

1.5.6 Synthesis of 3,4-Dibromo-2,5-dimethylthiophene.

Bromine (46.8 g, 29.3 mmol) was added dropwise to a solution of 2,5-dimethylthiophene (15.0 g; 13.3 mmol) dissolved in glacial acetic acid (75 mL) at 0°C. After the complete addition of bromine, a gentle stream of argon was passed through the reaction mixture to facilitate the removal of hydrogen bromide gas. Within three hours, a white solid precipitated. The reaction mixture was dissolved in ether and washed with excess sodium bisulfite solution. The resulting ether solution was washed with saturated sodium bicarbonate and dried with anhydrous magnesium sulfate. Solvent removal under reduced pressure gave crude 3,4-dibromo-2,5-dimethylthiophene (34.9 g; 97.3% yield) as a yellow oil which was
essentially pure according to $^1\text{H} \text{NMR}$. Further purification by bulb-to-bulb distillation yielded 3,4-dibromo-2,5-dimethylthiophene as a white solid (32.8 g; 91.2% yield), mp: 43-45° C (lit. mp: 44-45° C).

1.5.7 Synthesis of 3-Bromo-4-(1-hydroxy-1,2-dimethylbutenyl)-2,5-dimethylthiophene, '1.12'.

A hexane solution of n-butyllithium (2.5 M, 15.0 mL; 37.5 mmol) was added slowly to a solution of 3,4-dibromo-2,5-dimethylthiophene (10.08 g; 37.7 mmol) in anhydrous ether (100 mL) at -78° C and allowed to stir for one hour. 3-Methyl-3-penten-2-one (4.14 g; 42.2 mmol) was added dropwise at -78° C, and the reaction mixture was warmed to room temperature, poured into a saturated solution of ammonium chloride, and extracted with ether. The combined ether extracts were dried with anhydrous magnesium sulfate and solvent removal under reduced pressure gave a clear oil (10.43 g; 96% crude yield). Fractional distillation under reduced pressure (115° C; 1 mm Hg) gave 1.12 as a clear oil (6.68 g; 64.2% yield) which $^1\text{H} \text{NMR}$ showed to be a mixture of cis-trans isomers. $^1\text{H} \text{NMR}$ (200 MHz; CDCl$_3$) $\delta$ 1.60 (m, 6 H), 1.70 (s, 3 H), 2.26 (s, 3 H), 2.38 (s, 1 H), 2.52 (s, 3 H), 5.54 (m, 1 H); $^{13}\text{C} \text{NMR}$ (50 MHz; CDCl$_3$) 12.57, 13.31, 15.00, 16.99, 27.61, 78.85, 109.07, 119.82, 129.99, 137.57, 139.96 ppm.

1.5.8 Attempted Deprotonation and Silylation of '1.12'.

A hexane solution of n-butyllithium (2.5 M, 8.9 mL; 22 mmol) was added dropwise to a solution of 1.12 (2.81 g; 9.72 mmol) in anhydrous ether (50 mL) at -78° C and stirred for one hour. At -78° C, chlorotrimethylsilane (2.7 g, 3.1 mL;
24 mmol) was added slowly, and the reaction mixture was warmed to room temperature and stirred for an additional hour. The reaction mixture was poured into a saturated solution of ammonium chloride and extracted with ether. The combined ether extracts were dried with anhydrous magnesium sulfate and solvent removal under reduced pressure gave an oil (2.73 g). The $^1$H NMR of the crude product and the product purified by bulb-to-bulb distillation showed numerous products with unexpected major peaks, two of which were in the thiophene region (6.49 and 6.59 ppm).

1.5.9 Synthesis of 3-Bromo-4-(1-hydroxy-1-methylpropenyl)-2,5-dimethylthiophene, '1.13'.

A hexane solution of n-butyllithium (2.5 M, 8.3 mL; 20.8 mmol) was added slowly to a solution of 3,4-dibromo-2,5-dimethylthiophene (5.10 g; 18.9 mmol) in anhydrous ether (50 mL) at -78° C and stirred for one hour. At -78° C, methyl vinyl ketone (1.59 g; 22.7 mmol) was added dropwise and the reaction mixture was warmed to room temperature, poured into a saturated solution of ammonium chloride, and extracted with ether. The combined ether extracts were dried with anhydrous magnesium sulfate and solvent removal under reduced pressure gave an oil (1.54 g; 31% crude yield). Bulb-to-bulb distillation (65 ° C; 0.3 mm Hg) gave 1.13 as an oil (1.47 g; 30% yield). $^1$H NMR (100 MHz; CDCl$_3$) δ 1.75 (s, 3 H), 2.29 (s, 3 H), 2.53 (s, 3 H), 2.61 (s, 1 H), 5.15 (m, 2 H), 6.29 (m, 1 H).
1.5.10 Attempted Silylation of '1.13' to '1.15'.

A pentane solution of t-butyllithium (1.7 M, 11.0 mL; 18.6 mmol) was added slowly to a solution of 1.13 (1.47 g; 5.65 mmol) in anhydrous ether (30 mL) at -78° C and stirred for one hour. At -78° C, chlorotrimethylsilane (2.2 mL; 17 mmol) was added dropwise and the solution was allowed to warm to room temperature. The reaction mixture was poured into a saturated solution of ammonium chloride and extracted into ether. The combined ether extracts were dried with anhydrous magnesium sulfate and solvent removed under reduced pressure to give an oil (1.76 g). ^1H NMR analysis showed numerous products, evident by at least six different trimethylsilyl protons (0.1-0.3 ppm) and unexpected thiophene protons (6.4-6.6 ppm). Purification by bulb-to-bulb distillation did not separate the products, evident by the ^1H NMR spectrum. A gas chromatograph / mass spectrum also showed at least six major peaks, none of which contained the parent ion of 1.15.

1.5.11 Attempted Bromination of 3-Acetyl-2,5-dimethylthiophene.

Bromine (11.4 g; 71.5 mmol) was added dropwise over 15-20 minutes to a solution of 3-acetyl-2,5-dimethylthiophene (9.71 g; 63.3 mmol) and sodium acetate (6.0 g; 73.3 mmol) in water (30 mL) and stirred for two hours. The reaction mixture was washed with excess thiosulfate solution, and extracted into ether. The combined ether extracts were dried with anhydrous magnesium sulfate and solvent removal under reduced pressure gave an oil (12.58 g; 85% crude yield). ^1H NMR
analysis shows at least two products with the major product partial spectrum containing a H-CBr (4.51 ppm) and a thiophene proton (6.93 ppm), indicating that the predominate reaction was the bromination of the acetyl methyl group to give 1.17 instead of 1.16.

1.5.12 Attempted Bromination of '1.6' to '1.13'.

A solution of bromine (1.93 g; 12.1 mmol) in acetic acid (15 mL) was added dropwise to a solution of 1.6 (2.0 g; 11.0 mmol) in acetic acid (25 mL) and heated for 15 minutes. Excess bisulfite solution was added and the reaction mixture was poured into cold water (100 mL) and extracted with ether. The combined ether extracts were dried with anhydrous magnesium sulfate and solvent removal under reduced pressure to give an oil (3.16 g). $^1$H NMR analysis of the crude product shows two thiophene peaks (6.46 and 6.63 ppm) and two doublets in the BrC-H region (3.80 and 4.17 ppm) suggesting that the double bond was brominated instead of the thiophene ring.

1.5.13 Synthesis of 3-Bromo-4-trimethylsilyl-2,5-dimethylthiophene, '1.19'.

A hexane solution of n-butyllithium (2.5 M, 5.2 mL; 13 mmol) was added slowly to a solution of 3,4-dibromo-2,5-dimethylthiophene (3.51 g; 13.0 mmol) in anhydrous ether (50 mL) at -78° C and stirred for one hour. Chlorotrimethylsilane (1.8 mL; 14 mmol) was added slowly to the reaction mixture at -78° C and then allowed to warm to room temperature. After stirring for an additional hour, the reaction mixture was added to a saturated solution of ammonium chloride and
extracted with ether. The combined ether layers were dried with anhydrous magnesium sulfate and solvent removal under reduced pressure gave 1.19 as a yellow oil (3.20 g; 94% crude yield). Further purification by bulb-to-bulb distillation (58-60° C. @ 0.3 mm Hg) gave a colorless oil (2.72 g; 80% yield) which solidified. Further purification by sublimation (40° C, 1 mm Hg) yielded colorless crystals, mp: 66° C. 1H NMR (200 MHz; CDCl3) δ 2.46 (s, 1H), 2.31 (s, 1H), 0.38, (s, 3H). 13C (50 MHz; CDCl3) δ 1.19, 14.53, 17.26, 115.04, 130.85, 135.05, 143.38. IR (thin film, cm⁻¹): 2953, 2921, 2898, 2858, 1520, 1444, 1250, 1180, 1138, 1038, 996, 868, 840, 819, 764, 705, 630. MS (m/z): 264, 262, 249, 247, 167, 139, 137, 125, 109, 93, 91.

Anal. Calcd. for C₉H₁₅BrSSi: C; 41.06; H, 5.74. Found: C, 41.10; H, 5.70.

1.5.14 X-ray Crystallographic Analysis of '1.19'.

Data collection was carried out on an Enraf-Nonius CAD-4 diffractometer with Mo Kα (0.71073 Å) radiation using ω-2θ scans. Data reduction included corrections for background, Lorentz, polarization, and absorption by ψ scans. The structure was solved using direct methods and refined by full-matrix least squares based upon F, with weights w=4Fo²[σ²(I) + (0.02Fo²)²]⁻¹ using the Enraf-Nonius structure determination package, scattering factors, and anomalous coefficients. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were located by ΔF and were refined isotropically. Crystal data and collection parameters are shown in Table 1.3. The atomic positional and thermal parameters for 1.19 are given in Table 1.4.
Table 1.3 Crystal Data and Collection Parameters for '1.19'.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>formula</td>
<td>C$<em>9$H$</em>{15}$BrSSi</td>
</tr>
<tr>
<td>$Mr$, g mol$^{-1}$</td>
<td>263.3</td>
</tr>
<tr>
<td>system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>$P2_1/m$</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>8.8696 (5)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>7.5478 (4)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>9.1038 (3)</td>
</tr>
<tr>
<td>$\beta$, deg</td>
<td>100.149 (4)</td>
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<tr>
<td>$V$, Å$^3$</td>
<td>599.9 (1)</td>
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<tr>
<td>$Z$</td>
<td>2</td>
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<tr>
<td>$D_c$, g/cm$^3$</td>
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<tr>
<td>cryst size, mm</td>
<td>0.11 x 0.25 x 0.30</td>
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<tr>
<td>(capillary mounted)</td>
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</tr>
<tr>
<td>radiation:</td>
<td></td>
</tr>
<tr>
<td>(graphite monochromated)</td>
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</tr>
<tr>
<td>$\mu$, cm$^{-1}$</td>
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</tr>
<tr>
<td>temp, K</td>
<td>298</td>
</tr>
<tr>
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<td>$\omega-2\theta$</td>
</tr>
<tr>
<td>collection range, deg</td>
<td>$2\theta = 1 - 35$ (first quadrant)</td>
</tr>
<tr>
<td></td>
<td>1 - 25 (second quadrant)</td>
</tr>
<tr>
<td>total data measured</td>
<td>3965</td>
</tr>
<tr>
<td>no. of unique data</td>
<td>2801</td>
</tr>
<tr>
<td>no. of observed data</td>
<td>1445 for $I &gt; 1\sigma(I)$</td>
</tr>
<tr>
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<tr>
<td>no. of variables</td>
<td>104</td>
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<tr>
<td>$R$</td>
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<tr>
<td>$R_w$</td>
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<tr>
<td>goodness of fit</td>
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<tr>
<td>extinction coefficient</td>
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<tr>
<td>residual electron density (eÅ$^{-3}$)</td>
<td></td>
</tr>
<tr>
<td>Maximum (near Br)</td>
<td>0.93</td>
</tr>
<tr>
<td>Minimum</td>
<td>-0.21</td>
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</tbody>
</table>
Table 1.4 Coordinates and Equivalent Isotropic Thermal Parameters for '1.19'.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>(B_{eq}(\text{Å}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>0.45022(4)</td>
<td>0.250</td>
<td>0.27791(5)</td>
<td>5.669(9)</td>
</tr>
<tr>
<td>S</td>
<td>0.8141(1)</td>
<td>0.250</td>
<td>0.56618(1)</td>
<td>5.24(2)</td>
</tr>
<tr>
<td>Si</td>
<td>0.8166(1)</td>
<td>0.250</td>
<td>0.1760(1)</td>
<td>3.97(2)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.6304(4)</td>
<td>0.250</td>
<td>0.5652(4)</td>
<td>4.55(8)</td>
</tr>
<tr>
<td>C2</td>
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<td>0.4184(4)</td>
<td>3.70(7)</td>
</tr>
<tr>
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<td>0.7856(3)</td>
<td>0.250</td>
<td>0.3751(3)</td>
<td>3.49(6)</td>
</tr>
<tr>
<td>C4</td>
<td>0.8934(4)</td>
<td>0.250</td>
<td>0.5025(4)</td>
<td>3.99(7)</td>
</tr>
<tr>
<td>C5</td>
<td>0.4947(5)</td>
<td>0.250</td>
<td>0.6419(5)</td>
<td>6.4(1)</td>
</tr>
<tr>
<td>C6</td>
<td>1.0222(4)</td>
<td>0.250</td>
<td>0.1583(5)</td>
<td>6.4(1)</td>
</tr>
<tr>
<td>C7</td>
<td>0.7302(3)</td>
<td>0.0471(5)</td>
<td>0.0818(3)</td>
<td>6.72(7)</td>
</tr>
<tr>
<td>C8</td>
<td>1.0660(4)</td>
<td>0.250</td>
<td>0.5233(5)</td>
<td>5.7(1)</td>
</tr>
</tbody>
</table>

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: \(B_{eq} = \frac{8\pi^2}{3} \sum \sum U_{ij} \vec{a}_i \vec{a}_j \cdot \vec{a}_i \vec{a}_j\)

1.5.15 Attempted Synthesis of 2,5-Dimethyl-3,4-bis(trimethylsilyl)thiophene, '1.20'.

A solution of 3,4-dibromo-2,5-dimethylthiophene (2.03 g; 7.52 mmol) in anhydrous ether (30 mL) was treated with a hexane solution of n-butyllithium (2.5M, 6.6 mL; 16 mmol) and allowed to stir for three hours at -78° C. Chlorotrimethylsilane (2.3 mL; 18 mmol) was added at -78° C and stirred for an additional hour. After the solution warmed to room temperature, the reaction mixture was poured into a saturated solution of ammonium chloride and extracted with ether. The combined ether extracts were dried with anhydrous magnesium
sulfate and solvent removed under reduced pressure to yield a yellow oil (1.80 g) which solidified upon standing. The $^1$H and $^{13}$C NMR spectra matched exactly with those obtained for pure 1.19. This method gave a 91% crude yield for 1.19.

1.5.16 General Procedure for the Attempted Metallation of '1.19' with Lithium, Sodium, and Potassium.

A solution of 1.19 in anhydrous ether was treated with two equivalents of metal (lithium or sodium). When it was apparent that no reaction took place, the reaction mixture was subjected to ultrasound at room temperature for two hours. The reaction mixture was then treated with one equivalent of acetic anhydride, stirred for an additional hour, poured into ice water, and then extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure with quantitative recovery of 1.19. When 1.19 was refluxed with potassium and then treated with acetic anhydride as above, a complex mixture of products resulted, none of which resembled the desired products according to $^1$H NMR analysis.

1.5.17 Attempted Synthesis of 3-(1-Hydroxy-1-methyl-2-propenyl)-4-trimethylsilyl-2,5-dimethylthiophene, '1.20'.

A pentane solution of t-butyllithium solution (1.7 M, 9.9 mL; 16.9 mmol) was added slowly to a solution of 1.19 (2.02; 7.67 mmol) in anhydrous ether (50 mL) and stirred at -78° C for two hours. Methyl vinyl ketone (0.60 g; 8.45 mmol) was added dropwise and stirred for one hour at -78° C and one hour at room
temperature. The reaction mixture was poured into a saturated solution of ammonium chloride and extracted with ether. The combined extracts were dried with anhydrous magnesium sulfate. Solvent removal at reduced pressure gave an oil (2.12 g). $^1$H NMR analysis of the crude material showed at least four silylated compounds (between 0.2 and 0.4 ppm), a thiophene proton at 6.58 ppm, and no vinyl proton peaks. $^{13}$C NMR analysis showed no [C-O] peak or vinyl carbon signals. This is not consistent with what is expected from 1.22. Gas chromatograph/mass spectrum showed at least ten different peaks of similar intensity, with only one peak where the parent ion mass resembles that of 1.22.

1.5.18 Synthesis of 2,3,5-Trime thyl-4-trimethylsil ylthiophene, '1.21'.

A pentane solution of t-butyllithium (1.7 M, 4.9 mL; 8.4 mmol) was added slowly to a solution of 1.19 (1.0 g; 3.80 mmol) in anhydrous ether (30 mL) and stirred for two hours at -78° C, followed by the addition of methyl iodide (1.2 g; 8.4 mmol). The reaction mixture was allowed to warm to room temperature where it was stirred for 18 hours, poured into a saturated solution of ammonium chloride, and extracted with ether. The combined ether extracts were dried with magnesium sulfate and solvent removal under reduced pressure gave 1.21 as a white solid (0.77 g) contaminated with a small amount of starting material. Sublimation of the crude material gave a white solid (0.74 g; 98% yield): mp 62° C. $^1$H NMR (200 MHz; CDCl$_3$) δ 0.30 (s, 9 H), 2.13 (s, 3 H), 2.26 (s, 3 H), 2.44 (s, 3 H). $^{13}$C NMR (50 MHz; CDCl$_3$) 12.50, 15.25, 16.69, 129.46, 135.85, 138.35, 142.23 ppm. MS (m/z): 198, 183, 155, 141, 129, 91. IR (thin film; cm$^{-1}$) 2968, 2921, 2861, 2361, 2341, 1255.
CHAPTER TWO
Stereoselectivity in the Synthesis of Tetramethylethano-Bridged 
3,3'-Di-tert-butyltitanocene Dichloride

2.1 Introduction.

The use of chiral cyclopentadienyl ligands as potential chiral auxiliaries in asymmetric organometallic reactions is well documented. The stereochemistry of asymmetric hydrogenation and isotactic Ziegler-Natta polymerization can be controlled using asymmetric titanocene and zirconocene dichloride precatalysts, respectively. Figure 2.1 demonstrates how a chiral metallocene controls the approach of a prochiral alkene for asymmetric hydrogenation.

Figure 2.1 Approach of prochiral alkene to chiral titanocene dihydride intermediate.
2.2 Catalyst Design.

The design of the tetramethyl ethano bridged di t-butyl (TMEDT) metallocene is shown in Figure 2.2. The placement of identical substituents on each cyclopentadienyl of the metallocene oriented anti to each other will make the molecule chiral and give it $C_2$-symmetry. As a consequence of the $C_2$-symmetry, each reactive face of the metallocene is identical. Bridging the cyclopentadienyls together prevents free rotation of the cyclopentadienyls, thus preserving the steric integrity of the molecule.

![Figure 2.2 Design of Anti-TMEDT-Ti-Cl$_2$, 2.2.](image)

Figure 2.3 illustrates two retrosynthetic pathways to the TMEDT ligand from readily available 6,6-dimethylfulvene. Using retrosynthetic pathway B, Brintzinger and co-workers reported the synthesis of bridged titanocene dichlorides, 2.1 (meso), where the t-butyl groups have a syn geometry with respect to each other, and 2.2 (racemic), where the t-butyl groups are anti to each other. These
complexes were prepared by reaction of TMEDT-cyclopentadienyl magnesium chloride with TiCl$_3$·3THF and resulted in a 2.5:1 selectivity favoring the desired racemic (anti) isomer over the meso (syn) isomer, as shown in Figure 2.4. The goal of this work was to devise an alternate synthesis to produce 2.2 exclusively.

Figure 2.3 Retrosynthetic analysis of the TMEDT ligand.
Figure 2.4 Synthetic route for titanocene dichlorides 2.1 and 2.2 developed by H.H. Brintzinger and co-workers using retrosynthetic route B.

2.3 Results and Discussion.

2.3.1 Synthesis of Difulvene '2.3'.

2.3 was synthesized *via* a modification of a procedure by Stone and Little\(^5\) by treating proton shift isomers of 2,3-bis(cyclopenta-1,4-diene-2,3-dimethylbutane) with pyrrolidine and excess acetone at room temperature in
methanol to give 2.3 in a 82% yield. 2.3 is highly crystalline and the X-ray structure has been determined.\textsuperscript{52} Tables 2.1 and 2.2 list bond distances, bond angles, and selected torsion angles of 2.3. Figure 2.5 is a perspective drawing of 2.3.

\begin{table}[h]
\centering
\caption{Bond Distances (Å) of '2.3'.}
\begin{tabular}{llllllllllll}
\textbf{C1} & \textbf{C1'} & 1.583(3) & \textbf{C1} & \textbf{C2} & 1.513(2) & \textbf{C1} & \textbf{C8} & 1.537(2) \\
\textbf{C1} & \textbf{C9} & 1.542(3) & \textbf{C2} & \textbf{C3} & 1.344(2) & \textbf{C2} & \textbf{C6} & 1.479(2) \\
\textbf{C3} & \textbf{C4} & 1.459(2) & \textbf{C4} & \textbf{C5} & 1.462(2) & \textbf{C4} & \textbf{C7} & 1.346(2) \\
\textbf{C5} & \textbf{C6} & 1.336(3) & \textbf{C7} & \textbf{C10} & 1.496(3) & \textbf{C7} & \textbf{C11} & 1.501(3) \\
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Bond Angles (°) and Selected Torsion Angles (°) of '2.3'.}
\begin{tabular}{llllllllllll}
\textbf{C1'} & \textbf{C1} & \textbf{C2} & 111.4(2) & \textbf{C1'} & \textbf{C1} & \textbf{C8} & 110.6(2) & \textbf{C1'} & \textbf{C1} & \textbf{C9} & 111.1(2) \\
\textbf{C2} & \textbf{C1} & \textbf{C8} & 108.8(1) & \textbf{C2} & \textbf{C1} & \textbf{C9} & 108.3(2) & \textbf{C8} & \textbf{C1} & \textbf{C9} & 106.7(2) \\
\textbf{C1} & \textbf{C2} & \textbf{C3} & 129.2(2) & \textbf{C1} & \textbf{C2} & \textbf{C6} & 124.3(2) & \textbf{C3} & \textbf{C2} & \textbf{C6} & 106.5(2) \\
\textbf{C2} & \textbf{C3} & \textbf{C4} & 110.5(2) & \textbf{C3} & \textbf{C4} & \textbf{C5} & 104.6(2) & \textbf{C3} & \textbf{C4} & \textbf{C7} & 128.7(2) \\
\textbf{C5} & \textbf{C4} & \textbf{C7} & 126.6(2) & \textbf{C4} & \textbf{C5} & \textbf{C6} & 108.7(2) & \textbf{C2} & \textbf{C6} & \textbf{C5} & 109.8(2) \\
\textbf{C4} & \textbf{C7} & \textbf{C10} & 121.5(2) & \textbf{C4} & \textbf{C7} & \textbf{C11} & 123.7(2) & \textbf{C10} & \textbf{C7} & \textbf{C11} & 114.8(2) \\
\textbf{C5} & \textbf{C1} & \textbf{C6} & \textbf{C7} & -0.3(4) & \textbf{C2} & \textbf{C1} & \textbf{C6} & \textbf{C11} & 0.5(4) \\
\end{tabular}
\end{table}

The cyclopentadienylidene ring exhibits the expected localized valence bond alternation within the five-membered ring. The bond angle exo to the exocyclic double bond is 114.8(2)°. The pentafulvenes are anti and the methyl groups are all gauche to the pentafulvene rings. The cyclopentadienylidene ring is planar with
maximum deviation of 0.002(2) Å. Dimethylfulvene at 248 K\textsuperscript{53} and the dipentafulvenes, 1,4-(2,4-cyclopentadien-1-ylidene)cyclohexane\textsuperscript{54}, 1,5-bis(cyclopenta-2,4-dien-1-ylidene)cyclooctane,\textsuperscript{55} 9-(2,4-cyclopentadien-1-ylidene)bicyclo[3.3.1]nonane,\textsuperscript{56} and cis-3,7-bis(cyclopenta-2,4-dien-1-ylidene)bicyclo[3.3.0]-octane\textsuperscript{57} exhibit a similar localized valence bond alternation within the five-membered rings. The bond angle exo to the pentafulvene ring exocyclic double bond, C10-C7-C11=114.8(2)° is similar to the analogous bond angles of dimethylfulvene, 114.0(6)°, and 1,4-(2,4-cyclopentadien-1-ylidene)cyclohexane, 112.71(9)°.
Figure 2.5 ORTEP drawing of 2.3 representing C atoms as 40% probability ellipsoids and H atoms as circles of arbitrary radius.
2.3.2 Synthesis of Dilithio Salt, '2.4'.

Reaction of 2.3 with excess methyllithium in anhydrous ether followed by washing the dilithio salt with fresh anhydrous ether gave 2.4 which was dissolved in anhydrous tetrahydrofuran. This solution was then treated with various titanium sources as outlined below.

2.3.3 Synthesis of Meso and Racemic TMEDT-Ti-Cl₂, '2.1' and '2.2'.

Attempts to synthesize 2.2 using the lithium reagent, 2.4, with TiCl₃·3THF, TiCl₄, and titanocene dichloride resulted in a 1:4 to a 1:1 racemic : meso mixture in a combined yield of 20% to 44%, is demonstrated in Figure 2.6. Collins and co-workers reported similar racemic : meso selectivities of 1:1.3 to 1:2.0 for the synthesis of the unmethylated ethano bridged substituted titanocene dichlorides when lithium bis(cyclopentadienide) is used. It is surprising that the magnesium and lithium bis(cyclopentadienides) should prefer opposite isomers, but the relative energy difference between a 2.5:1 and 1:2 racemic : meso ratio is small (approximately 1-2 kcal / mole).
Figure 2.6 Synthetic route to 2.1 and 2.2 using retrosynthetic route A.

The results for the synthesis of 2.1 and 2.2 using various titanium sources are summarized in Table 2.3. Although many different titanium sources were used in attempts to favor the racemic isomer, only the use of a directing ligand on the titanium to control the stereoselectivity of titanium complexation of 2.4 was successful in producing the racemic isomer exclusively. Others have used 1,1-bi-2-naphtholate to concomitantly separate and resolve racemic bridged titanocene
derivatives, but this method of directing the approach of the incoming substituted bridged bis(cyclopentadienide) is novel.

**Table 2.3: Selectivity for the Reaction of '2.4' with Various Titanium Sources.**

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<th>Ti SOURCE</th>
<th>TEMP (°C)</th>
<th>YIELD</th>
<th>RAC : MESO</th>
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<td>TiCl₄</td>
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<td>20%</td>
<td>1 : 4</td>
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<tr>
<td>TiCl₃ · 3THF</td>
<td>-78</td>
<td>44%</td>
<td>1 : 4</td>
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<td></td>
<td>24</td>
<td>36%</td>
<td>1 : 2</td>
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<tr>
<td>TiCp₂Cl₂</td>
<td>24</td>
<td>30%</td>
<td>1 : 1</td>
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**2.3.3.1 Via TiCl₃·3THF and TiCl₄.**

Solutions of 2.4 were treated with TiCl₃·3THF or TiCl₄ in anhydrous tetrahydrofuran at -78° C. After refluxing for 18-24 hours and standard work up, solvent removal gave titanocene dichloride isomers 2.2 and 2.1 in a 1:4 ratio as determined by ¹H NMR analysis. When TiCl₃·3THF was added at room temperature, the ratio of 2.2 to 2.1 increased to 1:2 in a similar yield. Recrystallization of the 1:4 mixture from refluxing toluene yielded the pure meso isomer in two forms: red hexagonal plates (solvate), which lost solvent readily and orange rectangular plates. Single crystal X-ray analysis of the red and orange plates confirmed a syn geometry for the major isomer, 2.1. Unresolved disorder in the solvent led to slightly lower precision for this structure, therefore it will not be discussed in detail.
Selected bond lengths, bond angles, and torsion angles for unsolvated 2.1 are presented in Table 2.4 and 2.5. The chloride atoms in 2.1 lie in different environments; Ti-Cl(1) and Ti-Cl(2) bond distances are 2.3276 (6) and 2.3597 (6) Å, respectively. The Cl(1)-Ti-Cl(2) bond angle, 96.35 (3)°, is 1 to 2° wider than the analogous bond angles in titanocene dichloride and the ethano-bridged titanocene dichloride derivative. This appears to better accommodate the crowded Cl(1) in the groove of the t-butyl groups. The t-butyl groups are displaced out from the Cp1 and Cp2 plane by 10.9° and 11.0°, respectively and the cyclopentadienyl ring carbons attached to the tetramethylethano-bridge exhibit a torsion angle, Cl-C6-C7-C8, of 36.0(3)°. The Cp1 centroid-Ti and Cp2 centroid-Ti distances are 2.092 and 2.014 Å, respectively and the Cp1 centroid-Ti-Cp2 centroid angle is 128.8°, which are within the expected values for titanocenes. Figure 2.7 shows a perspective drawing of the unsolvated form of 2.1.

Table 2.4 Bond Lengths (Å) for '2.1' (unsolvated).

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| C2    | C1   | C6   | C14  | -161.7(2)| C5   | C1   | C6   | C7   | -108.0(3) |
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| C1    | C2   | C3   | C4   | 2.5(3)   | C1   | C2   | C3   | C17  | -166.0(2) |
| C2    | C3   | C4   | C5   | -1.4(3)  | C17  | C3   | C4   | C5   | 167.6(2)  |
| C2    | C3   | C17  | C18  | -141.2(3)| C2   | C3   | C17  | C19  | -16.9(4)  |
| C2    | C3   | C17  | C20  | 100.3(3) | C4   | C3   | C17  | C18  | 52.3(3)   |
| C4    | C3   | C17  | C19  | 176.6(2) | C4   | C3   | C17  | C20  | -66.2(2)  |
| C1    | C6   | C7   | C8   | 36.0(3)  | C1   | C6   | C7   | C15  | -83.9(3)  |
| C1    | C6   | C7   | C16  | 155.6(2) | C13  | C6   | C7   | C8   | 155.6(2)  |
Table 2.5 (cont.) Bond Angles (*) and Selected Torsion Angles (*)
for '2.1' (unsolvated).

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Figure 2.7 ORTEP drawing of 2.1 (unsolvated).
2.3.3.2 Via Titanocene Dichloride.

2.4 was added to titanocene dichloride in anhydrous tetrahydrofuran at room temperature and was refluxed for 19 hours. Although titanocene dichloride may be an odd titanium(IV), this procedure has been used previously in the synthesis of bridged titanocene dichlorides. After oxidation with carbon tetrachloride and purification by flash chromatography on silica gel, the product ratio of 2.2 and 2.1 was 1:1 in a combined 30% yield.

The meso isomer, 2.1, is photochemically inert unlike titanocene dichloride and resists conversion to the racemic isomer 2.2, contrary to other examples of titanocene dichlorides of this type. Therefore, an alternate synthesis was devised using a C$_2$ symmetric directing ligand at the titanium center to guide the incoming lithium TMEDT bis(cyclopentadienyl) anion t-butyl groups in the anti geometry.

2.3.4 Synthesis of Racemic-TMEDT-Ti-Binaphtholate '2.6' by Using a C$_2$ Symmetric Directing Group.

Titanocene alkoxide and aryloxide complexes are common, and are typically synthesized via the action of an alkoxide or aryloxide on titanocene dichloride. Our synthesis differs in that the bridged cyclopentadienyls react with a titanium dichloride-binaphtholate adduct, thus replacing the two chlorides with η$^5$-cyclopentadienyl ligands. The binaphtholate rings create a C$_2$ symmetric "groove" that directs the t-butyl groups to a conformation of minimum steric interaction as shown in the proposed intermediates in Figure 2.8. The syn η$^1$ complex is far less
stable because of steric interaction between t-butyl groups and binaphtholate rings. The anti $\eta^1$ complex formation is favorable and leads to the anti $\eta^5$ complex, 2.6.

![Diagram of complexes](image)

**Figure 2.8** $\eta^1$ intermediates formed in the reaction between 2.4 and 2.5.

Treatment of 2.4 with the freshly generated 1:1 adduct of racemic 1,1'-bi-2-naphtholate, 2.5, and TiCl$_4$ gave the anti titanocene 1,1'-bi-2-naphtholate derivative, 2.6, in a 15% yield as shown in Figure 2.9. Flash chromatography on silica gel, eluting with a hexane-dichloromethane gradient, followed by recrystallization of 2.6 from refluxing toluene gave X-ray quality red rectangular plates. The 1,1'-bi-2-naphtholate adduct 2.5 quickly oligomerizes so it must be treated with 2.4 promptly or the yield of any titanocene product is diminished. The yield of 2.6 was reduced to 8% and to 5% with longer reaction times at -78°C for the TiCl$_4$ and 1,1'-bi-2-naphtholate reaction. Also, the isolated adduct of 1,1'-bi-2-naphtholate and TiCl$_4$ gave no significant yield of 2.6 when reacted with 2.4.
Figure 2.9 Reaction scheme for the synthesis of 2.2 via 2.6.

Compound 2.6 is not formed by reaction of unreacted TiCl$_4$ with 2.4 followed by a derivatization of only the anti titanocene isomer and a selective destruction of the meso isomer. The isolated 1:4 ratio of 2.2 and 2.1 when treated with 1,1'-bi-2-naphtholate under similar reaction conditions did not give an appreciable yield of the racemic titanocene product 2.6, but the predominate product is a meso TMEDT-Ti-binaphtholate-chloride derivative. This compound was not formed as an appreciable co-product with 2.6.
Figure 2.10 shows the ORTEP drawing of 2.6. Inspection of the X-ray crystal structure of 2.6 shows that the desired anti geometry is probably controlled by the steric interactions between t-butyl groups and the binaphtholate rings. The t-butyl groups in 2.6 are displaced outwards from the plane defined by their respective cyclopentadienyls (10.2° and 9.2°). The crystal structure of the meso titanocene dichloride showed a similar t-butyl-group outward displacement of about 11° from the cyclopentadienyl plane. This is not much different than the t-butyl displacement observed in the unbridged dichlorobis(η⁵-t-butyl cyclopentadienyl) titanium (IV) (10.5°)⁶⁹ and the methyl displacement in the permethylated titanocene dichloride (approximately 8°).⁷⁰ However, steric interactions between binaphtholate and syn oriented t-butyls would have been prohibitive.

Bond lengths and bond angles are included in Tables 2.6 and 2.7. Other structural features of note for 2.6 include O1-Ti-O2 bond angle of 94.09(6)° which is similar to the Cl-Ti-Cl bond found in titanocene dichlorides and the unequal Ti-O bond lengths: Ti-O1=1.908(2) Å and Ti-O2=1.923(2) Å. The centroid-Ti bond lengths are Ci1-Ti=2.118 Å and Ti-Ci2=2.112 Å and the centroid-Ti-centroid bond angle is 128.5° which are similar to those found in 2.1 at 2.092 Å, 2.014 Å, and 128.8°, respectively. The torsion angle about the central C-C bond of the binaphtholate ligand is -60.84(4)°.
Figure 2.10 ORTEP drawing of 2.6.
The solvate form of 2.6 crystallizes from 25:75 toluene:hexane as orange plates with composition $2.6 \cdot \frac{1}{2} C_6H_{14}$. We have also determined the structure of this solvate by X-ray crystallography. The molecular structure of 2.6 in the solvate crystal is nearly identical to that in the unsolvated crystal, including the unequal Ti-O bond distances (1.904(3) and 1.926(3) Å). Unresolved disorder in the solvent led to lower precision for this structure, therefore it will not be discussed in detail.

**Table 2.6 Bond Distances (Å) for '2.6'**

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2.3.5 Use of Other C₂ Symmetric Directing Groups.

Experiments using other dialkoxy and diaryloxy anti-directors at the titanium center were investigated. The study centered on the use of vicinal diols that could form five membered rings with titanium, however, 1,2-catechol, 2,3-dimethyl-2,3-butanediol, and hydrobenzoin titanium alkoxide-dichloride derivatives prepared according to the 1,1'-bi-2-binaphtholate titanium dichloride method failed to react with 2.4.

2.3.6 Synthesis of Racemic-TMEDT-Ti-Cl₂,'2.2'.

Treatment of 2.6 with excess HCl gas in hexane, solvent removal, and silica gel flash column chromatography with hexane/ether, as with the mixture of 2.1 and 2.2, gave exclusively the racemic titanocene dichloride derivative, 2.2, which matches the ¹H NMR assigned to the minor isomer produced by reaction of 2.3 with the various titanium sources. The crystal structure of 2.2, could not be solved with satisfactory resolution because of the presence of two independent molecules that are not related by symmetry and unresolved disorder in the tetramethylethano bridge, although the crystallographic data strongly suggest the expected anti conformation.⁷¹

Titanocene derivatives 2.1, 2.2, and 2.6 are inert toward silica gel. Other titanocene dichlorides and even bridged titanocene dichlorides are sensitive to purification on silica gel chromatography, requiring at least silanized silica gel and sometimes low temperatures.⁶⁰,⁶⁷ An initial wash with hexane left 2.1 and 2.2 at the origin and eluted the hydrocarbon impurities. Hexane slowly eluted 2.6. A
hexane/dichloromethane gradient moved 2.1, 2.2, and 2.6 quickly, but eluted binaphthol very slowly. A hexane/ether gradient moved them equally as fast. These properties allow for easy purification and are important when precatalyst separation/recovery are considered.

### 2.3.7 Proton NMR Analysis of Titanocenes '2.1', '2.2' and '2.6'.

The $^1$H NMR spectra of 2.1, 2.2, and especially 2.6 have interesting features. The peak positions of the bridge methyl protons on 2.1 and 2.2 shift upfield by almost 0.5 ppm when the NMR solvent was changed from CDCl$_3$ (1.34 and 1.46 ppm for 2.1; 1.37 and 1.43 ppm for 2.2) to benzene-$d_6$ (0.92 and 0.99 ppm for 2.1; 0.93 and 0.99 ppm for 2.2) the solvent used by Brintzinger and co-workers. The $^1$H NMR spectrum of 2.6 in CDCl$_3$ showed a relatively small shift in the bridge methyl protons (1.30, 1.41, 1.57, 1.81 ppm) from the values observed for 2.1 and 2.2, however, the t-butyl group protons shift upfield (at 0.63 ppm) by almost 0.8 ppm from the tert-butyl resonances of 2.1 and 2.2. This upfield t-butyl shift due to shielding by the aromatic ring has precedent.$^{60}$

### 2.3.8 Attempted Hydrogenation of $\alpha$-Ethylstyrene Using '2.2' as a Precatalyst.

The prochiral alkene, $\alpha$-ethylstyrene, was used as a substrate to test the effectiveness of 2.2 as an asymmetric hydrogenation precatalyst. When 2.2 and a solution of Red-Al (3.4 $M$, sodium bis(2-methoxyethoxy)aluminum hydride in toluene) was subjected to hydrogen at atmospheric pressure, the green color that is
associated with the titanocene hydride intermediate was observed, but no hydrogenation product was detected.

2.4 Conclusion.

Although there is no significant difference in yield of titanocene dichlorides from the reaction of the TMEDT dianion with TiCl$_4$, the synthetic route developed by H.H. Brintzinger gave the highest amount of the desired stereoisomer 2.2. Neither method produced 2.2 exclusively. The use of a chiral C$_2$ symmetric director on titanium forced the t-butyl groups anti to each other. This was accomplished by reacting the TMEDT dianion with the freshly generated adduct of dilithiobinaphtholate and TiCl$_4$ to give a 9-15% yield of anti-TMEDT-Ti-Binaphtholate, 2.6. Treatment of 2.6 with HCl gas in hexane generated 2.2 in a quantitative yield. The utility of 2.5 as an effective director for the t-butyl groups is limited because it quickly oligomerizes to an unreactive substrate, leading to low yields of 2.6.

The low overall yield in the synthesis of 2.2 and its failure to act as an effective hydrogenation precatalyst precluded further work on this type of catalyst. Future work that may be warranted for this type of compound involves the replacement of the t-butyl groups with isopropyl groups. This can easily be accomplished by treating the difulvene precursor 2.3 with lithium aluminum hydride instead of methyllithium, with subsequent reaction with TiCl$_3$·3THF. The ratio of racemic to meso isomer in the proposed reaction is uncertain as with the TMEDT dianion.
2.5 Experimental Section.

General Procedures: All reactions were carried out under argon atmosphere using Schlenk techniques. NMR spectra were recorded on the IBM AF100, Bruker AC/WP200, and Bruker AM400 multiprobe spectrometers. Chemical shifts are reported in δ or ppm downfield from tetramethylsilane. Infrared spectra were recorded on a Beckman IR4230. Elemental analysis were performed by Oneida Research Services Inc, Whitesboro, NY. Mass spectra were measured on a Hewlett Packard 5985A mass spectrometer and high resolution mass spectrometry was performed by the Midwest Center for Mass Spectrometry, Lincoln, NE. Melting points are uncorrected.

Materials and Methods: 1,1'-Bi-2-naphthol, methyllithium (1.4 M in ether), titanocene dichloride, carbon tetrachloride, pyrrolidine (Aldrich), acetone, ethyl acetate, hexanes, dichloromethane, and methanol (Mallinckrodt) were used as received. TiCl₃·3THF was prepared according to the literature method. Tetrahydrofuran was distilled from potassium under argon. Ether was distilled from liquid Na/K under argon. Titanium tetrachloride (Aldrich) was degassed and distilled prior to use.

2.5.1 Preparation of 2,3-Bis[3-(1-methylethylidene)cyclopenta-1,4-diene]-2,3-dimethylbutane, '2.3'.

A suspension containing the proton shift isomers of 2,3-bis[3-cyclopenta-1,4-diene]-2,3-dimethylbutane (1.9 g, 8.9 mmol) in 8.0 mL of reagent grade methanol was treated with reagent grade acetone (3.2 mL, 44 mmol) and
pyrrolidine (2.5 mL, 30 mmol) at room temperature. The suspension immediately disappeared, forming a deep-red solution. A yellow precipitate formed after 30 minutes and three hours later, 2.3 was isolated by vacuum filtration as a yellow powder (1.69 g, 65% yield) after washing with copious amounts of distilled water. An additional 0.45 g (17% yield) was recovered from the filtrate for an 82% overall yield. Further purification of 2.3 was accomplished by recrystallization from ethyl acetate; yellow crystals: mp 144° C; IR (CDCl$_3$) 3100, 2995, 2980, 2900, 2860, 1640, 1435, 1370, 1349, 1300, 1230, 1130 cm$^{-1}$; $^1$H NMR (200 MHz; CDCl$_3$) δ 1.19 (s, 12 H), 2.15 (s, 12 H), 6.15 (m, 2 H), 6.38 (m, 4 H); $^{13}$C NMR (100 MHz; CDCl$_3$) 22.69, 24.66, 41.31, 116.57, 118.77, 133.66, 141.83, 146.28, 153.42 ppm; MS, m/z (relative intensity) 294 (M$^+$, 1.9), 147 (100), 119 (17.6), 105 (30.2), 91 (14.6), 77 (18.1).

Anal. Calcd for C$_{22}$H$_{30}$: C, 89.73; H, 10.27. Found: C, 89.67; H, 10.32.

2.5.2 Preparation of 2,3-Bis[3-(1,1-dimethylethyl)cyclopent-1,3-diene-5-yl]-2,3-dimethylbutanediolithium, '2.4'.

A solution of 2.3 (2.38 g; 8.09 mmol) in anhydrous diethylether (30 mL) was treated with excess 1.4 M methylolithium (18.0 mL; 24.3 mmol) to give 2,3-bis[3-(1,1-dimethylethyl)-1,3-cyclopentadien-5-yl]-2,3-dimethylbutanediolithium, 2.4, as an insoluble gel (not isolated), which was washed with anhydrous ether (3 x 20 mL).
2.5.3 Preparation of Racemic and Meso Ansa-(2,3-dimethyl-2,3-butanono)-3,3'-bis(1,1'-dimethylethyl)cyclopenta-1,3-diene-5-yl)titanium dichloride '2.1' and '2.2' by Reaction of '2.4' with TiCl₃·3THF.

2.4 was diluted with anhydrous tetrahydrofuran (250 mL) and treated with TiCl₃·3THF (3.0 g; 8.09 mmol) at -78°C. The reaction mixture was warmed to room temperature and then refluxed for 18-24 hours. After addition of 6 M hydrochloric acid (5.0 mL) and stirring for four to five hours, solvent removal under reduced pressure gave a residue which was redissolved in chloroform, separating it from the insolubles. The deep red solution was dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (60-200 mesh) by eluting first with hexane, then with 50/50 (v/v) hexane/ether. Solvent removal gave a red powder (1.58 g; 44% yield). ¹H NMR of the red powder showed evidence of a mixture of isomers. Recrystallization from refluxing toluene gave red hexagonal plates and orange rectangular plates, which when dried was identified as the meso isomer. Compound 2.1, mp 193-194°C, IR (CDCl₃) 3120, 2990, 2960, 2920, 2900, 2865, 1500, 1460, 1380, 1370, 1360, 1250, 1175 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) 6 1.34 (s, 6 H), 1.36 (s, 18 H), 1.46 (s, 6 H), 6.05 (t, 2 H), 6.48 (t, 2 H), 6.61 (t, 2 H); ¹³C NMR (50 MHz, CDCl₃) 27.40, 28.89, 30.84, 34.30, 45.70, 111.23, 114.98, 127.62, 142.09, 147.20 ppm; MS, m/z (relative intensity) 442 (M⁺, 6.7), 282 (53.0), 280 (76.3), 246 (33.0), 244 (100), 228 (30.0)

Anal. Calcd. for C₂₄H₃₆Cl₂Ti: C, 65.02; H, 8.18. Found: C, 64.89; H, 8.23.
2.5.4 Preparation of Racemic and Meso Ansa-(2,3-dimethyl-2,3-butano)-3,3'-bis(1,1'-dimethylethyl)cyclopenta-1,3-diene-5-yl)titanium dichloride '2.1' and '2.2' by Reaction of '2.4' with Titanocene Dichloride.

A solution of 2.4 (4.04 mmol) in anhydrous tetrahydrofuran (60 mL) was added slowly over 10 minutes to a solution of titanocene dichloride (1.00 g; 4.04 mmol) in tetrahydrofuran (65 mL) at room temperature, stirred for 45 minutes, and refluxed for 19 hours. The resulting dark colored solution was cooled to 0° C and was treated with dry degassed CCl₄ (8.5 mL; 35 mmol) and left stirring at 0° C for one hour and for another two hours at room temperature. The solvent was removed under reduced pressure and the red residue purified by flash chromatography as previously described for 2.1 and 2.2. A microcrystalline red solid (0.53 g; 30% yield) was recovered which was a 1:1 mixture of 2.2 and 2.1 as determined by ¹H NMR.

2.5.5 Preparation of Ansa-(2,3-dimethyl-2,3-butano)-anti-3,3'-bis(1,1-dimethylethyl)cyclopenta-1,3-dien-5-yl)titanium-1,1'-bi-2-naphtholate, '2.6'.

A solution of 1,1'-bi-2-naphthol (2.32 g; 8.09 mmol) in anhydrous tetrahydrofuran (75 mL) was deprotonated with an ether solution of methyllithium (1.4 M, 11.6 mL; 16.2 mmol) at -78° C. A solution of titanium tetrachloride (1.53 g; 8.09 mmol) in anhydrous tetrahydrofuran (75 mL) was prepared at -78° C. The dilithiobinaphtolate solution was added slowly to the TiCl₄ solution forming the TiCl₂(1,1'-bi-2-naphtholate) adduct 2.5₁³ After stirring for two hours at -78° C (stirring for longer time periods decreases the yield), the red suspension was added
to a solution of 2.4 (8.09 mmol) in anhydrous tetrahydrofuran (75 mL) at -78° C and then refluxed for 18 hours. Column chromatography on silica gel (60-200 mesh) by eluting first with hexane, then with 50/50 (v/v) hexane/methylene chloride and solvent removal gave red microcrystals of the racemic titanocene 1,1'-bi-2-naphtholate derivative (0.80 g; 15% yield), mp 268-269 °C; IR (CDCl₃) 3079, 3060, 3045, 2990, 2970, 2960, 2935, 2920, 2910, 2900, 2860, 1611, 1590, 1500, 1460, 1421, 1380, 1272, 1228, 1195, 1138, 1069 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 0.63 (s, 18 H), 1.32 (s, 6 H), 1.76 (s, 6 H), 5.25 (t, 2 H), 5.73 (t, 2 H), 6.13 (t, 2 H), 6.9-7.3 (m, 8 H), 7.77 (t, 4 H); ¹³C NMR (50 MHz, CDCl₃) 26.54, 28.99, 29.78, 33.31, 44.73, 105.52, 108.60, 112.70, 117.39, 121.22, 121.78, 125.04, 126.99, 127.44, 128.57, 135.04, 143.48, 155.91, 165.54 ppm; MS, m/z (relative intensity) 656 (M⁺, 25.6), 494 (100), 476 (23.8), 437 (55.3), 333 (66.3), 314 (18.2), 252 (19.1), 147 (18.8).


2.5.6 Preparation of Racemic Ansa-(2,3-dimethyl-2,3-butano)anti-3,3'-bis(1,1'-dimethylethyl)cyclopenta-1,3-dien-5-yl) titanium dichloride, '2.2'.

2.2 was prepared in a quantitative yield by treating a hexane solution of 2.6 with hydrogen chloride gas with subsequent purification by flash chromatography. Elution with a hexane/dichloromethane gradient to separate the product from binaphthol and recrystallization from refluxing toluene yielded pure ansa-(2,3-dimethyl-2,3-butano)-anti-3,3'-bis(1,1'-dimethylethyl)cyclopenta-1,3-dien-5-yl)titanium dichloride (red rectangular plates, mp 248° C), IR (CDCl₃) 3160, 2960, 2925, 2900, 2880, 1800, 1500, 1462, 1385, 1372, 1264, 1251, cm⁻¹.
1H NMR (200 MHz, CDCl₃) δ 1.33 (s, 18 H), 1.37 (s, 6 H), 1.43 (s, 6 H), 6.21 (t, 2 H), 6.34 (t, 2 H), 6.5 (m, 2 H); 13C NMR (50 MHz, CDCl₃) 27.94, 28.38, 30.60, 34.51, 45.68, 111.47, 115.79, 123.15, 143.02, 151.27 ppm. MS, m/z (relative intensity) 442 (M⁺, 5.4), 407 (16.38) 282 (64.2), 280 (94.8), 246 (33.2), 244 (100), 147 (35.6); HRMS m/z Calcd. for C₂₄H₃₈Ti₃⁵Cl₂ 442.1655 Found 442.1688 and Calcd. for C₂₄H₃₈Ti₃⁵Cl₃⁷Cl 444.1643 Found 444.1648.

2.5.7 Reaction of a 1:4 Mixture of '2.2' and '2.1' with Dilithiobinaphtholate.

A solution of dilithio-1,1'-bi-2-naphtholate (1.62 mmol) in anhydrous tetrahydrofuran (20 mL) was added to a solution of a 1:4 mixture of 2.2 and 2.1 (0.720 g; 1.62 mmol in 20 mL tetrahydrofuran) at -78° C. The solution was then refluxed for 19 hours. After solvent removal, the residue was purified by flash chromatography on silica. The hexane fraction contained pure 2.6 (0.06 g; 28% of the total 2.2 to be derivatized) according to 1H NMR. The dichloromethane/hexane fraction contained traces of 2.1 and 2.2. The major portion of this fraction appeared to be a binaphtholate-chloride derivative which is believed to be compound 2.7, characterized by 1H NMR (400 MHz, CDCl₃) δ 0.78 (s, 9 H), 1.27 (s, 9 H), 1.30 (s, 3 H) 1.41 (s, 3 H), 1.57 (s, 3 H), 1.81 (s, 3 H), 4.04 (m, 1 H), 5.62 (m, 1 H), 5.66 (m, 1 H), 5.97 (m, 1 H), 6.28 (m, 1 H), 6.70 (m, 1 H), 6.81 (m, 1 H), 6.93-6.96 (m, 2 H), 7.08-7.18 (m, 4 H), 7.63-7.70 (m, 2 H), 7.75-7.81 (m, 2 H). LRMS, m/z (no M⁺) 656, 494, 437, 333, 287, 147, 107 HRMS m/z Calcd. for C₄₄H₄₈O₂⁴⁷Ti 655.3179 Found 655.3185.

This binaphtholate derivative was not present in the synthesis of 2.6. A second purification of this fraction by flash chromatography and treatment with
hydrogen chloride gas yielded pure \textbf{2.1} according to $^1$H and $^{13}$C.NMR, and melting point.

\textbf{2.5.8 Photolysis of 2.1.}

Recrystallized \textbf{2.1} was photolyzed in quartz NMR tubes with UV radiation (450 W high pressure Hg lamp). The samples were photolyzed in four different solvents: CDCl$_3$, THF-$d_8$, acetonitrile-$d_3$-CDCl$_3$ (6:1), and MeOH-$d_4$-CDCl$_3$ (4:1). The reaction progress was followed by $^1$H NMR by monitoring the changes in the characteristic cyclopentadienyl proton resonances. After six hours of photolysis, no changes in the $^1$H NMR spectra were observed. In a separate experiment, \textbf{2.1} was photolyzed in CDCl$_3$ and in benzene-$d_6$ for 24 hours at 300 nm with no change in the $^1$H NMR spectra of the cyclopentadienyl protons.

\textbf{2.5.9 Crystal Structure Determinations.}

\textbf{General Experimental Procedures:} Intensity data were obtained from crystals mounted in a random orientation on an Enraf-Nonius CAD-4 diffractometer. The structures were solved by direct methods for \textbf{2.3} and \textbf{2.6}, and heavy atom methods for \textbf{2.1}, and refined by full-matrix least squares based upon $F$, with weights $w=4F_0^2[\sigma^2(I) + (0.02F_0^2)^2]^{-1}$ using the Enraf-Nonius structure determination package,$^{32}$ scattering factors,$^{33}$ and anomalous coefficients.$^{34}$ All data reductions included corrections for background, Lorentz, and polarization.
2.5.9.1 Crystal Structure Data for 2,3-Bis[3-(1-methylethylidene)cyclopenta-1,4-diene]-2,3-dimethylbutane, '2.3'.

A summary of the key crystal data and parameters for the data collection for 2.3 (solvated and unsolvated forms) are given in Table 2.8. Cell dimensions were determined at 297 K by a least-squares fit to setting angles of 25 reflections having 22° > θ > 18°. The theta values were derived from measurements at ±2θ. One quadrant of data having 2° < θ < 55°, 0 ≤ h ≤ 9, 0 ≤ k ≤ 25, -9 ≤ l ≤ 9 were measured using graphite monochromated MoKα radiation. The ω-2θ scans were made at speeds ranging from 0.45 to 4.0 deg. min⁻¹ to measure all significant data with approximately equal precision. Absorption was negligible.

The space group was determined by systematic absences h0l with l odd and 0k0 with k odd. Non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located in a ΔF map and were refined isotropically. Final R=0.063 (R=0.169 for all 2128 data), Rw=0.046, S=1.760 for 160 variables. The largest shift was 0.02σ in the final cycle, maximum residual density 0.15 e Å⁻³, minimum -0.14 e Å⁻³. The atomic positional and thermal parameters for 2.3 are given in Table 2.9.
Table 2.8 Crystal Data and Collection Parameters for '2.3'.

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Table 2.9  Atomic Coordinates and Equivalent Isotropic Thermal Parameters for '2.3'.

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<td>C7</td>
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<td>0.3674(3)</td>
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</tr>
<tr>
<td>C8</td>
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<td>0.0298(1)</td>
<td>0.3450(3)</td>
<td>6.28(6)</td>
</tr>
<tr>
<td>C9</td>
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<td>-0.0316(1)</td>
<td>0.2248(3)</td>
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</tr>
<tr>
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<td>0.4171(4)</td>
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<tr>
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<td>0.3084(1)</td>
<td>0.3222(4)</td>
<td>8.28(8)</td>
</tr>
</tbody>
</table>

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: \( B_{eq} = \frac{8\pi^2}{3} \sum a_i a_j a_i^* a_j^* \).

2.5.9.2  Crystal Structure Data For Syn-TMEDT-Ti-Cl₂, '2.1'.

A summary of the key crystal data and parameters for the data collection for 2.1 (solvated and unsolvated forms) are given in Table 2.10. Cell dimensions were determined at 296 K by a least-squares fit to setting angles of 25 reflections having 24°<2θ<20°. The theta values were derived from measurements at ±2θ. One hemisphere of data having 2°<θ<55°, 0≤h≤12, -13≤k≤13, -17≤l≤17 were measured using graphite monochromated MoKα radiation. Absorption.
corrections were based on $\psi$ scans, with minimum relative transmission 0.945. Of 5352 unique data, 3617 had $I > 3\sigma(I)$, and were used in the refinement.

The space group was determined by successful refinement of a centrosymmetric model. Non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located in a $\Delta F$ map and were refined isotropically. Final $R=0.040$ ($R=0.075$ for all 5352 data), $R_w=0.045$, $S=1.727$ for 389 variables. The largest shift was $0.02\sigma$ in the final cycle, maximum residual density $0.34$ e Å$^{-3}$, minimum $-0.30$ e Å$^{-3}$. The atomic positional and thermal parameters for 2.1 (unsolvated) are given in Table 2.11.
Table 2.10 Crystal Data and Collection Parameters for '2.1'
(unsolvated).

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<th>Parameter</th>
<th>Value</th>
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</tr>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>c, Å</td>
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</tr>
<tr>
<td>$\alpha$, deg</td>
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<td>$\beta$, deg</td>
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</tr>
<tr>
<td>$\gamma$, deg</td>
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</tr>
<tr>
<td>V, Å$^3$</td>
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</tr>
<tr>
<td>Z</td>
<td>2</td>
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<td>$D_c$, g/cm$^{-3}$</td>
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</tr>
<tr>
<td>(graphite monochromated)</td>
<td>Mo K$\alpha$ ($\lambda = 0.71073$ Å)</td>
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<td>$\mu$, cm$^{-1}$</td>
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</tr>
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<td>goodness of fit</td>
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Table 2.11 Atomic Positional and Thermal Parameters for '2.1' (unsolvated).

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<th>y</th>
<th>z</th>
<th>B(eq)(Å²)</th>
</tr>
</thead>
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<tr>
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<tr>
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<tr>
<td>C2</td>
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<td>C4</td>
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<td>0.7133(3)</td>
<td>0.9224(2)</td>
<td>3.12(6)</td>
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<tr>
<td>C5</td>
<td>0.2382(3)</td>
<td>0.7975(3)</td>
<td>0.9210(2)</td>
<td>3.25(6)</td>
</tr>
<tr>
<td>C6</td>
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<td>0.8752(3)</td>
<td>0.7928(2)</td>
<td>3.51(6)</td>
</tr>
<tr>
<td>C7</td>
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<td>1.0214(3)</td>
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<td>3.12(6)</td>
</tr>
<tr>
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<td>2.64(5)</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
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<tr>
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<td>0.8208(2)</td>
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<tr>
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<td>0.7575(3)</td>
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<td>5.18(9)</td>
</tr>
</tbody>
</table>

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: \( B_{eq} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j \)
2.5.9.3 Crystal Structure Data For Anti-TMEDT-Binaphtholate, '2.6'.

A summary of the key crystal data and parameters for the data collection for 2.6 (solvated and unsolvated forms) are given in Table 2.12. X-ray quality crystals of 2.6 were obtained as red plates (unsolvated) from refluxing toluene and orange plates (solvate) from a refluxing 25:75 hexane:toluene mixture. Cell dimensions of the unsolvated form were determined by a least squares fit to setting angles of 25 reflections having $22 > 2\theta > 20^\circ$. The $\theta$ values were derived from measurements from at $\pm 2\theta$. One quadrant of data having $2 < 2\theta < 50$, $0 \leq h \leq 12$, $0 \leq k \leq 34$, $-14 \leq l \leq 14$ was measured using graphite monochromated MoKα radiation. Absorption corrections were based on $\psi$ scans, with minimum relative transmission coefficient 96.5%. Of 6237 unique data, 4153 had $I > 2\sigma(I)$, and were used in the refinement.

The space group was determined by systematic absences. Non-H atoms were refined anisotropically; the H atoms were located by difference maps and are not refined. The largest shift was less than 0.01σ in the final cycle, maximum residual density 0.21, minimum -0.30 eÅ⁻³. A secondary extinction coefficient refined to a value of 1.71(11) x 10⁻⁷. The atomic positional and thermal Parameters for 2.6 (unsolvated) are given in Table 2.13.

Analogous structure refinement of $2.6\cdot1/2C_6H_{14}$ was performed. The hydrogens were not refined and the hexane H’s ignored. The largest shift was less than 0.01σ in the final cycle, maximum residual density 0.34, minimum -0.29 eÅ⁻³. A secondary extinction coefficient refined to a value of 3.2(3) x 10⁻⁷.
Table 2.12 Crystal Data and Collection Parameters for '2.6'.

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<th>Unsolvated</th>
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</thead>
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<td>TiC₄₄H₄₈O₂</td>
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<td>P2₁/c</td>
</tr>
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</tr>
<tr>
<td>c, Å</td>
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<td>-</td>
</tr>
<tr>
<td>β, deg</td>
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<td>99.37(2)</td>
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<td>γ, deg</td>
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<td>-</td>
</tr>
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<td>3555(2)</td>
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<tr>
<td>Z</td>
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<td>4</td>
</tr>
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Table 2.13 Atomic Positional and Thermal Parameters for '2.6' (unsolvated).

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</tr>
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<tr>
<td>C28</td>
<td>0.6874(3)</td>
<td>0.88006(9)</td>
<td>1.0932(2)</td>
<td>4.33(7)</td>
</tr>
<tr>
<td>C29</td>
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<td>1.1705(3)</td>
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<tr>
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<td>0.8869(1)</td>
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<td>5.59(9)</td>
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</tbody>
</table>
Table 2.13 (cont.) Atomic Positional and Thermal Parameters for '2,6' (unsolvated)

<table>
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<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Beq(Å²)</th>
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<tr>
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<td>0.9024(2)</td>
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<td>C35</td>
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<td>0.91304(9)</td>
<td>0.7870(2)</td>
<td>3.17(6)</td>
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</table>

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: \( B_{eq} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} \mathbf{a}_i \cdot \mathbf{a}_j \).
CHAPTER THREE.
Attempted Synthesis of Conductive Polymer Precursors: From Diethano-Bridged Bis(cyclopentadieny) to Ferrocenophenes

3.1 Introduction.

The omnipresent goal of this dissertation research was to synthesize conductive polymers based on repeating ferrocene units. The original idea was to synthesize one dimensional conductive polymers based on 1,2,4-ansa bridged cyclopentadienides joined by iron(II) and iron(III) atoms, thus forming ferrocene and ferrocenium links. Eventually, another idea followed where ferrocenes could be linked in conjugation by double bonds.

Presently, a number of organic and inorganic conductive polymers exist. The list includes the common conductive polymers polythiazyl, polyacetylene, polyphenylene, polypyrrole, and polythiophene (Figure 3.1). All have the conjugated \( \pi \)-system in common. Also, all doped conductive polymers are air-sensitive except for polypyrrole. Table 3.1 compares conductivities of common conductive polymers with those of metals and semi-conductors. Except for doped polythiazyl and polyacetylene, most conductive polymers have conductivities of semi-conductors.
Figure 3.1 Common conductive polymers.

Table 3.1 Conductivities of Metals, Conductive Polymers, and Semiconductors.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductance ( \Omega^{-1} \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. Metals</strong></td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>( 7.0 \times 10^5 )</td>
</tr>
<tr>
<td>Copper</td>
<td>( 6.0 \times 10^5 )</td>
</tr>
<tr>
<td>Tungsten</td>
<td>( 2.0 \times 10^5 )</td>
</tr>
<tr>
<td>Nichrome</td>
<td>( 6.0 \times 10^4 )</td>
</tr>
<tr>
<td><strong>B. Conductive Polymers</strong></td>
<td></td>
</tr>
<tr>
<td>Polythiazyl</td>
<td>( 10^3 - 10^4 )</td>
</tr>
<tr>
<td>Polyacetylene</td>
<td>( 10^{-9} - 10^3 )</td>
</tr>
<tr>
<td>Polypyrrole</td>
<td>( 1 - 10^2 )</td>
</tr>
<tr>
<td>Polyphenylene</td>
<td>( 10^{-14} - 10^2 )</td>
</tr>
<tr>
<td>Polythiophene</td>
<td>( 10^{-4} - 10^{-3} )</td>
</tr>
<tr>
<td><strong>C. Semiconductors</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>( 3.0 \times 10^2 )</td>
</tr>
<tr>
<td>Germanium</td>
<td>( 2.0 \times 10^{-2} )</td>
</tr>
<tr>
<td>Silicon</td>
<td>( 4.0 \times 10^{-6} )</td>
</tr>
</tbody>
</table>
The electrical conductance of conductive polymers can be explained through band theory. In any material, there exists two bands created by the mixing of bonding and antibonding orbitals. These bands are separated on a potential energy diagram by the band gap. The width of the band gap is determined by the nature of the orbitals being mixed. If enough energy is present, electrons can be promoted past the band gap to the antibonding energy level, which is the conduction band (Figure 3.2). The amount of energy required to promote an electron into the conductance band for insulators is too high, and will usually decompose the material before conduction occurs. In semiconductors, thermal energy is enough to promote electrons to the conduction band. In metals, the band gap is infinitesimally small thus electrons readily move from the filled bonding levels to the conducting band. Conduction will also take place when an electron is taken away from the filled bonding level or when an electron is added to the conductance band by chemical means. This is referred to as doping.

Figure 3.2 Band Theory.
When a large number of $\pi$-orbitals interact in conjugation, the band gap (difference in energy between bonding and antibonding orbitals) decreases. It is believed this band gap lowering will occur in the ferrocene polymers when a large number of $\pi$-orbitals are placed in conjugation.

The two models that these ferrocene polymers are based on is illustrated in Figure 3.3. Polymer 3.1 (Type I) was first target molecule proposed to be a potential conductive polymer based on bridged cyclopentadienyls linked by iron(II), making ferrocene links. The 1,2,4-ethano bridges hold $\pi$-orbitals of the cyclopentadienyls within the Van der Waals distances of the $\pi$-orbitals to facilitate electron transfer. The second of the two models involves a polyferrocene-ene, 3.2, a string of ferrocene units linked by a $\pi$-system defined by a backbone of double bonds in conjugation (Type II). Other possible conductive polymers considered in this study were those of Type II, where 3.4 can form a three dimensionally conductive polymer (Figure 3.4).

**Figure 3.3** Target molecules for proposed conductive polymers.
The immediate goal for this work was to design convenient synthetic methods for the bulk synthesis of the monomers for conductive polymers, with their subsequent polymerization. All of these methods must involve inexpensive starting materials with promise of scaling up to industrial scale.

3.2 Designing the Synthesis of Conductive Polymers Based on Ferrocene.

The drawbacks of most existing conductive polymers are their air sensitivity, brittleness, and lack of solubility. Most of these problems are due to the doping process that makes them electrically conductive. In the design of a new generation of conductive polymers, these limitations must be solved. The proposed conductive polymers 3.1, 3.2, 3.3, and 3.4 all have the ferrocene linkage in common. Ferrocene is air stable and thermally stable to 350° C. Like most conductive polymers, the ferrocene polymers must be doped to create an electron
hole which facilitates electron movement. This could simply be accomplished by oxidizing some of the iron atoms from iron(II) to iron(III). Ferrocenium, Cp₂Fe⁺, is also air and thermally stable. Therefore, the doping process should pose no stability problems to the ferrocene polymers.

The design idea behind 3.1 is to create a bifunctional stack linked by iron(II) forming a ferrocene link, which is stable. Partial oxidation of the irons will create electron holes giving rise to a conductive polymer. The design of the Type II conductive polymers 3.2, 3.3, and 3.4 involves a hybrid between two known conductive polymers, polyferrocene and polyacetylene (Figure 3.5). Polyferrocene is semiconductive but suffers from the inability to form high polymer. Polyacetylene is a good conductor, but suffers from brittleness and air sensitivity as a consequence of the doping process.

\[
\begin{align*}
&\left( \text{C} = \text{C} \right)_n \\
&\text{Polyacetylene}
\end{align*}
\]

\[
\begin{align*}
&\left[ \text{\(\text{Fe}\)} \right]_n \\
&\text{Polyferrocene}
\end{align*}
\]

\[
\begin{align*}
&\left[ \text{\(\text{Fe}\)} \right]_n \\
&\text{3.2}
\end{align*}
\]

**Figure 3.5** Design components of the Type II conductive polymers.

The two conductive polymers 3.1 and 3.2 are very different and therefore, their syntheses are different and pose unique synthetic challenges. The proposed synthesis of each polymer, illustrated in Figure 3.6, is quite simple. The synthetic challenge lies in the monomers. The same is true for the synthesis of the proposed
monomers 3.3 and 3.4 where the synthesis involves the fusion of a
cyclobutadiene to ferrocene, annihilating aromatic and antiaromatic rings. This
would pose a problem in the synthesis of the monomer, but would make 3.8 and
3.9 very interesting target molecules. Ring Opening Metathesis Polymerization
(ROMP) of monomers 3.6, 3.7, 3.8, and 3.9 would lead to the respective
copolymers shown in Figures 3.6 and 3.7.

Figure 3.6 Proposed synthesis of conductive polymers 3.1 and 3.2.
ROMP is an effective way to polymerize monomers possessing strained alkene rings. The mechanism involves the insertion of a transition metal alkylidene through a [2+2] cycloaddition into the alkene ring (Figure 3.8). A [2+2] ring opening leads to oligomerization, then with subsequent steps, polymerization to high polymer. ROMP is considered a "living polymerization" because it will continue polymerization with added monomer and will terminate only when an aldehyde or ketone is added.

**Figure 3.7** ROMP of monomers 3.8 and 3.9.

**Figure 3.8** Mechanism for the ROMP of monomer 3.6 to polymer 3.2.
3.2.1 Retrosynthetic Analysis of '3.5'.

The retrosynthetic analysis of monomer 3.5 is illustrated in Figure 3.9. Although the complexity of 3.5 affords numerous potential retrosynthetic routes, only those relevant to this study will be illustrated. The synthetic challenge of 3.5 is the 1,2-ethano bridge joining the cyclopentadienyls, as proposed in 3.10. Retrosynthetic route A involves constructing each ethano bridge in succession until all three bridges are in place. Because of steric effects, the initial placement of the bridges is easier with 1,3 substitution rather than the desired 1,2 substitution pattern. Therefore, a large blocking group such as trimethylsilyl could be employed to force the bridge placement to the desired 1,2 substitution pattern.

Retrosynthetic route B to 3.10 involves a [4+4] cycloaddition of 1,2-bis(methylene)cyclopentane followed by halogenation, dehydro-dehalogentaion, and subsequent isomerization of the resulting double bonds to form the 1,2-ethanobridged cyclopentadienyl rings. The challenge of this pathway is the [4+4] cycloaddition because very few synthetic procedures are known to be successful for intermolecular [4+4] cycloaddition reactions involving 2,3 substituted butadienes.

Retrosynthetic pathway C to 3.10 involves a ketene addition to the inexpensive starting material 1,5-cyclooctadiene with subsequent ring expansion of the four-membered rings to five-membered rings. The carbonyl can be reduced to an alcohol and then dehydrated to a cyclopentene. 3.10 can be formed by tandem-tandem dehydro-dehalogenation of the tetrahalide.
Figure 3.9 Retrosynthetic analysis of monomer 3.5.
The addition of the third bridge in the 4-position would involve a simple dialkylation of the dicyclopentadienyl 3.10. Another possibility would be the formation of the dipentafulvene of 3.10 with subsequent reductive coupling to form the tetramethylethano bridge.

3.2.2 Retrosynthetic Analysis of '3.6'.

The retrosynthetic route to 3.6 is illustrated in Figure 3.10. The retrosynthesis of 3.6 is very simple. Dehydration of the ferrocene diol, 3.11, gives 3.6. 3.11 can be obtained from the known 1,4-(1,1'-ferrocenediy1)-1,4-butanedione, 3.12, synthesized by the intramolecular oxidative coupling of 1,1'-diacetylferrocene, which is commercially available.

Figure 3.10 Retrosynthetic analysis of 3.6.
3.2.3 Retrosynthetic Analysis of '3.8' and '3.9'.

The retrosynthetic analysis of 3.8 and 3.9 are shown in Figures 3.11 and 3.12. As mentioned previously, the synthesis of 3.8 and 3.9 poses a uniquely difficult task because they involve the fusion of an antiaromatic four membered ring to an aromatic five-membered ring. Also, four membered rings are difficult to synthesize. 3.8 can be derived from a deprotonation, ring closure, and displacement of two trimethylamines from the 1,2-bis(trimethylammoniummethyl)ferrocene salt, which can easily be synthesized from 1,2-bis(dimethylaminomethyl)ferrocene. 1,2-bis(dimethylaminomethyl)ferrocene can be synthesized by the reduction of dimethyliminium ferrocene salt from the (dimethylaminomethyl)ferrocene aldehyde, which is derived from orthometallation of (dimethylaminomethyl)ferrocene and treatment with N,N-dimethylformamide to form the (dimethylaminomethyl)ferrocene aldehyde.

\[
\begin{align*}
\text{Fe} & \quad \text{Fe} \\
\text{3.8} & \quad \text{Fe} \\
X & \quad Y \\
\rightarrow & \quad \rightarrow \\
X = Y = \text{NMe}_2 & \quad \text{O} & \quad \text{NMe}_2 \\
X = Y = +\text{NMe}_3 & \quad \text{Fe} & \quad \text{NMe}_2
\end{align*}
\]

Figure 3.11 Retrosynthetic analysis of 3.8.

The retrosynthetic strategy for 3.8 can also be applied to the retrosynthetic analysis of 3.9 when dealing with the construction of the fused four-membered
ring on ferrocene. The other retrosynthetic pathway is to break 3.9 into iron(II) and a [3.2.0] bicyclic cyclopentadienyl ligand, building the bicyclic framework early in the synthesis. This retrosynthetic route is illustrated in Figure 3.12. The construction of the [3.2.0] bicyclic framework is accomplished by an easy ketene addition to cyclopentadiene. Next, a free radical addition of a halogen, followed by a dehydro-dehalogenation and deprotonation to form the bicyclo-cyclopentadienide, which serves as a ligand for iron forming the ferrocene derivative. The cyclobutadiene portion is the last to be built because its formation would be more favored after the iron is bound to the adjacent cyclopentadienyl, forcing the cyclobutadiene to act less like an antiaromatic system and more like an isolated double bond by the electron withdrawing action of the iron.

Figure 3.12 Retrosynthetic analysis of 3.9.
3.3 Results and Discussion

3.3.1 Attempted Synthesis of '3.10' via Retrosynthetic Pathway A.

Retrosynthetic route A in Figure 3.9 involves bridging two cyclopentadienyls with the successive placement of three ethano bridges. The initial goal to synthesize 1,2-bis(3-trimethylsilylcyclopentadienyl)ethane, 3.13, the first synthon to 3.10 failed. The proposed forward synthesis of 3.10 from cyclopentadiene and 1,2-dibromoethane is illustrated in Figure 3.13. The attempted synthesis of 3.13 followed two routes, the first by alkylating trimethylsilylcyclopentadiene with 1,2-dibromoethane via a modification of an existing procedure.\(^{75}\) The original procedure involved the alkylation of bis(cyclopentadienyl)magnesium and ethylenediamine with 1,2-dibromoethane. The synthesis of bis(cyclopentadienyl)magnesium involves passing cyclopentadiene onto a bed of magnesium in a tube furnace,\(^{76}\) which is impractical according to the goals of this project. Using bis(cyclopentadienyl)magnesium instead of the usual lithium or sodium cyclopentadienides prevents the formation of the kinetically favored spiro[2,4]hepta-4,6-diene derivatives.\(^{77}\) Attempts to alkylate cyclopentadienyl magnesium halides with 1,2-dibromoethane failed to achieve the same results as bis(cyclopentadienyl)magnesium.

The second method involved silylating 1,2-bis-(cyclopentadienyl)ethane with trimethylchlorosilane. In both attempts, both gas chromatography and \(^1\)H NMR analysis showed numerous products beyond the expected cyclopentadienyl proton shift isomers. Also, the trimethylsilyl group thermodynamically favors geminal
substitution on a cyclopentadienyl ring and will undergo [1,5] sigmatropic trimethylsilyl shifts to attain geminal substitution.

\[
\begin{align*}
\text{SiMe}_3 & \quad 1. \text{MeMgCl} \\
& \quad 2. \text{EDA/-78°C} \\
& \quad 3. \text{BrCH}_2\text{CH}_2\text{Br}
\end{align*}
\]

\[
\begin{align*}
1. \text{MeMgCl} & \quad \text{EDA/-78°C} \\
& \quad 3. \text{BrCH}_2\text{CH}_2\text{Br}
\end{align*}
\]

Figure 3.13 Proposed synthesis of 3.13, a synthon for 3.10.

3.3.2 Attempted Synthesis of '3.10' via Retrosynthetic Pathway B.

Retrosynthetic pathway B involves bisecting the molecule through the eight-membered ring. The forward synthetic strategy involved building the eight-membered ring via a [4+4] cycloaddition using Ni(0). Intramolecular [4+4] ring closures using Ni(COD)_2 has been used by Wender in the synthesis of various natural products.\(^7\) The attempted forward synthesis of 3.10 is illustrated in Figure 3.14.
Figure 3.14 Synthesis of 3.14 and attempted synthesis of 3.10.
The attempted synthesis of 3.10 fell short early after the successful synthesis of (E,E)-1,2-bis[(trimethylsilyl)methylene cyclopentane, 3.14. Several attempts at the intermolecular coupling of 3.14 with Ni(COD)$_2$ failed, recovering only starting material. The inability of 3.14 to undergo intermolecular coupling is probably due to the steric bulk of the four trimethylsilyl groups.

1,2-bis(methylene)cyclopentane has been synthesized previously using methods involving numerous steps.\textsuperscript{79,80} The goal was to desilylate 3.14 to find a shorter synthesis to 1,2-bis(methylene)cyclopentane. Typical reagents for the desilylation of vinyl silanes, such as hydroiodic acid (in pentane or benzene), cesium fluoride (in tetrahydrofuran, acetonitrile, and dimethylsulfoxide),\textsuperscript{81} tetrabutylammonium fluoride (TBAF) in tetrahydrofuran, and concentrated sulfuric acid in pentane,\textsuperscript{82} were ineffective in the desilylation of 3.14.

After all attempts to develop a convenient synthesis of 1,2-bis(methylene)cyclopentane failed, a new precursor for 3.10 was tested. 1-Vinylcyclopentene is easily synthesized from cyclopentanone and vinylmagnesium bromide.\textsuperscript{83,84} Nickel catalyzed [4+4] coupling of 1-vinylcyclopentene also failed to form the eight-membered ring in a reasonable yield.

### 3.3.3 Attempted Synthesis of '3.10' via Retrosynthetic Pathway C.

The proposed forward synthesis of 3.10 derived from retrosynthetic route C is illustrated in Figure 3.15. The first step of this synthesis involved the addition of two equivalents of dichloroketene to 1,5-cyclooctadiene. Integration of the vinylic protons present against the methylene protons in the $^1$H NMR spectrum suggested
that only one dichloroketene added to the 1,5-cyclooctadiene. Even when the reaction was carried out in a 5.0 M solution of lithium perchlorate in ether, the mono-addition product was favored. Reactions run in saturated solutions of lithium perchlorate are known to increase the rates of Diels-Alder reactions and it was hoped that it would aid in the addition of dichloroketene to 1,5-cyclooctadiene. Mono-addition was also favored in the dibromocarbene addition to 1,5-cyclooctadiene, even after adding excess dibromocarbene.\textsuperscript{85}

Figure 3.15 Proposed synthesis of 3.10 via attempted addition of dichloroketene to 1,5-cyclooctadiene.
3.3.4 Improved Synthesis of 1,2-Bis(dimethylaminomethyl)ferrocene and Attempted Synthesis of '3.8'.

The formation of the cyclobutene ring fused to the ferrocene cyclopentadienyl was the synthetic challenge of 3.8. As mentioned previously, not only are four-membered rings difficult to synthesize, but the ring fusion to ferrocene creates an analog of cyclobutadiene, which is likely to show antiaromatic behavior. The synthetic strategy is to build the cyclobutadiene onto the ferrocene, which is outlined in Figure 3.16.

![Figure 3.16 Improved synthesis of 3.16 and attempted synthesis of 3.8.](image-url)
Ortholithiation of (dimethylaminomethyl)ferrocene\textsuperscript{86,87} and subsequent treatment with anhydrous N,N-dimethylformamide gave 1-(dimethylaminomethyl)-2-formyl-ferrocene, \textit{3.15}, as an orange oil in a quantitative yield. After modification of an existing method,\textsuperscript{88} treatment of crude \textit{3.15} with dimethylammonium chloride and sodium borohydride in methanol gave bis(dimethylaminomethyl)ferrocene, \textit{3.16}, as an orange solid. Further purification of \textit{3.16} by recrystallization from ethanol gave orange crystals in an 85\% yield, which were used to determine the X-ray structure. Treatment of an ether solution of \textit{3.16} with methyl iodide resulted in the bis(trimethylammoniumiodide) salt, \textit{3.17}, as a yellow powder in an 85\% yield. Attempts to form the four-membered ring \textit{via} cyclization failed when the deprotonation of \textit{3.17} with 50\% aqueous potassium hydroxide gave an inseparable mixture of products showing no vinylic protons in the $^1\text{H}$ NMR. Deprotonation of \textit{3.17} with lithium diisopropylamide resulted in a small amount of an inseparable mixture of products, with $^1\text{H}$ NMR showing both vinylic protons and unexplained aromatic protons around 7.1 ppm. No reaction resulted with the attempted deprotonation by refluxing \textit{3.17} with sodium methoxide in a methanol-tetrahydrofuran mixture. Because of the failure of 1,2-bis[(dimethylamino)methyl]ferrocenes to undergo cyclizations to four-membered rings, synthesis of \textit{3.9} \textit{via} similar pathways would be useless.

Figure 3.17 is an ORTEP drawing of \textit{3.16}. Bond lengths are listed in Table 3.2 and bond angles and selected torsion angles are listed in Table 3.3. Both cyclopentadienyls are planar and parallel as expected for ferrocenes.
<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
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<td>Fe Cl</td>
<td>2.040(7)</td>
<td>N1 C11</td>
<td>1.456(9)</td>
<td>C3 C4</td>
<td>1.43(1)</td>
<td></td>
</tr>
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<td>C4 C5</td>
<td>1.39(1)</td>
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</tr>
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<td>C6 C7</td>
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<td>1.473(7)</td>
<td>C6 C10</td>
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<tr>
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<td>N2 C15</td>
<td>1.451(9)</td>
<td>C6 C11</td>
<td>1.504(8)</td>
<td></td>
</tr>
<tr>
<td>Fe C6</td>
<td>2.021(6)</td>
<td>N2 C16</td>
<td>1.468(9)</td>
<td>C7 C8</td>
<td>1.407(8)</td>
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</tr>
<tr>
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<td>1.958(8)</td>
<td>C1 C2</td>
<td>1.38(1)</td>
<td>C8 C9</td>
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</tr>
<tr>
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<td>2.006(6)</td>
<td>C1 C5</td>
<td>1.41(1)</td>
<td>C9 C10</td>
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<td>C10 C14</td>
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</tr>
<tr>
<td>Fe C10</td>
<td>2.033(5)</td>
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</tr>
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Table 3.2 Bond Distances (Å) for '3.16'.

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Numbers in parentheses are estimated standard deviations in the least significant digits.
Figure 3.17 ORTEP drawing of 1,2-bis(dimethylaminomethyl)ferrocene.
3.3.5 Attempted Synthesis of '3.9' via 4-Bromo-7,7-dichlorobicyclo[3.2.0]heptan-2-en-6-one.

The failure to fuse a four-membered ring to ferrocene inspired an alternate route. The second strategy for the fusion of a cyclobutadiene to ferrocene was developed using the retrosynthetic analysis outlined in Figure 3.12, where the bicyclic framework was constructed before iron(II) was complexed to the cyclopentadienyl anion. The attempted and anticipated steps in the synthesis of 3.9 are outlined in Figure 3.18.

Figure 3.18 Synthesis of 3.18 and the proposed synthesis of 3.9.

The [3.2.0] bicyclic skeleton was formed by the reaction of dichloroketene with cyclopentadiene to form 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one in 83% yield. Formation of the cyclopentadienyl anion requires further functionalization of the cyclopentene ring. 7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one was brominated
with N-bromosuccinimide in the presence of light and benzoyl peroxide in refluxing carbon tetrachloride to give 4-bromo-7,7-dichlorobicyclo[3.2.0]heptane-2-en-6-one, \textit{3.18}, in an 85\% yield. Recrystallization from refluxing hexane gave X-ray quality crystals from which the structure was determined and verified. Attempted dehydro-debromination of \textit{3.18} with the hindered bases lithium diisopropylamide and sodium bis(trimethylsilyl)amide and subsequent iron complexation of the proposed cyclopentadienyl using ferrous chloride were unsuccessful in producing \textit{3.9}. The failure of \textit{3.18} to undergo dehydro-debromination is not surprising due to absence of an anti conformation between the \(\alpha\)-hydrogens and the bromide leaving group, evident in the x-ray structure. Anticipating the interference of the carbonyl on \textit{3.18} on the dehydro-debromination step, attempts to protect the ketone as a ketal failed, as \textit{3.18} proved to be too unreactive towards ketalization. Also, the attempt to brominate the ethylene glycol ketal of dechlorinated \textit{3.18}, bicyclo[3.2.0]hept-2-ene-6-one, was unsuccessful.

Bromination of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one can take place at two allylic sites, at the ring junction carbon or at the 3-position. X-ray crystallography of \textit{3.18} confirmed that the major site of bromination is the 3-position. No other isomers were isolated or detected. An ORTEP drawing of \textit{3.18} is illustrated in Figure 3.19. A list of bond distances is contained in Table 3.4 and a list of bond angles is included in Table 3.5 for \textit{3.18}. As expected, \textit{3.18} is non planar with the dihedral angle between the planes defined by atoms \([\text{C1,C2,C5,C6, C7}]\) and atoms \([\text{C2,C3,C4,C5}]\) is 66.8°.
Figure 3.19 ORTEP drawing of 3.18.
**Table 3.4 Bond Distances (Å) for '3.18'.**

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Numbers in parentheses are estimated standard deviations in the least significant digits.

**Table 3.5 Bond Angles (°) and Selected Torsion Angles for '3.18'.**

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Numbers in parentheses are estimated standard deviations in the least significant digits.
3.3.6 **Synthesis of 1,4-(1,1'-Ferrocenediyl)-1,3-butadiene, '3.6'.**

The ferroceneophane 1,4-(1,1'-ferrocenediyl)-1,3-butadiene, 3.6, showed the most promise as a potential monomer for ROMP to the polyferrocene-ene 3.2. The key step in the synthesis of 3.6 is the early formation of the four carbon bridge, starting with the synthesis of 3.12, which is accomplished in moderate yields by oxidatively coupling the enolate of 1,1-diacetylferrocene with anhydrous cupric chloride. Attempts to form 3.6 via the Shapiro Reaction\(^{89-91}\) on 3.12 failed.

Reduction of 3.12 to 1,4-(1,1'-ferrocenediyl)-1,4-butandiol, 3.11, opens up new routes to 3.6. Dehydration of alcohols is one of the most commonly used methods for the synthesis of alkenes. Consequently, a number of dehydrating agents were applied to 3.11 in the attempts to synthesize 3.6. Simplicity and the ability to scale up the synthesis was the criteria used in the choice of prospective dehydrating agents. Simply refluxing 3.11 in dilute aqueous acids failed to produce 3.6. The Burgess reagent,\(^{92}\) a facile dehydration method, failed to react with 3.11. The most successful techniques used to dehydrate 3.11 to 3.6 involved solid state dehydrations using both silica gel and alumina (basic and neutral) and acid catalyzed dehydration in a non-aqueous solvent.
3.4.7 Synthesis of '3.6' via Solid State Dehydration of '3.11'.

The synthesis of 3.6 begins with the reduction of 3.12, with sodium borohydride in methanol or analogously, with lithium aluminum hydride in tetrahydrofuran to give a diastereomeric mixture of 3.11 in a quantitative yield. The final step in the synthesis of 3.6 involves the dehydration of 3.11.

Metal oxides are commonly used for solid state dehydrations, where the dehydration rates increase with the increasing covalent character of the metal-oxygen bond in the catalyst. Therefore, the catalysts can be placed in the following order of dehydrating ability:

\[ \text{WO}_3 > \text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{Cr}_2\text{O}_3 > \text{FeO} > \text{ZnO} > \text{MgO} > \text{CaO} \]

The technique used for the solid state dehydration of 3.11 involved heating a 10% (by weight) mixture of 3.11 with four different solid supports: tungsten(VI) oxide, silica gel, alumina (neutral), or alumina (basic) under vacuum in a sublimation apparatus. Between 180-260° C, a red powder sublimed on the cold finger, which \(^1\text{H} \text{NMR}, \^{13}\text{C} \text{NMR}, \text{and mass spectroscopy revealed to be a mixture of 3.6 and 1,4-(1,1'}-\text{ferrocenediyl)-1-butene, 3.20, for all of the solid supports used. If silica gel was used, 2,5-(1,1'}-\text{ferrocenediyl})\text{tetrahydrofuran, 3.21, also formed as an impurity. All yields are based on moles of material converted to dehydration products and were between 20-60%. When tungsten (VI) oxide was used, less than a 10% yield of 3.6 resulted with numerous unidentified products as contaminates.}
The presence of 3.21 in the solid state dehydration is not surprising because it is a partial dehydration product, but 3.20 must be due to an inter or intramolecular reduction. Mass spectroscopy of the dehydration products from the crossover experiments involving the solid state dehydration of equimolar quantities of 3.11 and (1,4-\textit{d}_{2})-1,4-(1,1'-ferrocenediyl)-1,4-butadiol, \textit{d}_{2}-3.11, produced isotopic isomers of 3.6 and 3.20 that would be consistent with intermolecular reduction, as illustrated in Figure 3.20. If intramolecular reduction was the sole process, structures 3.6, 3.20, 3.6a, and 3.20a would be the only species present. Instead, parent ions with molecular weights resembling structures of 3.6b and 3.20b were also observed in the mass spectrum, which is consistent with an intermolecular reduction. A possible mechanism for the intermolecular reduction to produce 3.20 from 3.11 is proposed on Figure 3.21. This hypothesis led to attempts to dehydrate 3.11 in more dilute mixtures of the solid phase medium. The results are reported on Table 3.6. Diluting 3.11 from 10\% to 1\% mixtures in alumina was ineffective, but the amount of 3.20 and 3.21 was substantially reduced when analogous dilutions in silica gel were attempted. This was the major breakthrough because 3.6 and 3.20 are inseparable by conventional means. With reduced amounts of 3.20 in the product, 3.6 could now be successfully purified by recrystallization.
Figure 3.20 Crossover study of the solid state dehydration of a 1:1 mixture of 3.11 and 3.11-d2.
Figure 3.21 Proposed mechanism for formation of 3.20.
Table 3.6 Solid Support Dehydration of '3.11' and Resulting Product Ratios.

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3.4.8 Synthesis of '3.6' via Solution Dehydration of '3.11'.

Dehydrations of 3.11 to 3.6 were also attempted in solution. Various concentrations of sulfuric and phosphoric acids failed to yield any significant amounts of 3.6. Dehydration of 3.11 by refluxing in benzene with p-toluenesulfonic acid gave results similar to those obtained from heating 3.11 in silica gel at 10% by weight. The drawback of the dilute solid state methods were the low yields. With the results from the crossover experiment, moving to more dilute conditions was the logical choice.

The most successful synthesis of 3.6 involved refluxing a dilute solution of 3.11 in benzene and p-toluene sulfonic acid (10% by mole, based on moles of hydroxyl) yielding 3.6 with the smallest amounts of 3.20 and 3.21, compared to
more concentrated solutions and solid state techniques. Purification by silica gel column chromatography eluting with hexane yielded 3.6 in a 61% yield, contaminated with a minute amount 3.20. Elution with a hexane/ethyl acetate gradient eluted a small amount of 3.21. Recrystallization of 3.6 by slow cooling from refluxing ethanol, aided by a seed crystal gave X-ray quality crystals.

X-ray structure determination of both 3.6 and 3.12 revealed interesting features. Most striking are the strain induced distortions in the bridge sp² carbon bond angles in 3.6 where C1-C11-C12, C11-C12-C13, C12-C13-C14, and C13-C14-C6 are 128.5°, 130.9°, 130.7°, and 129.0° respectively where the bridge sp² carbon bond angles impose about 10° of bond angle strain. This strain will prove useful in driving the ROMP of 3.6. The bridge imposes a nearly equal twist angle of 43.6° and 44.0° in 3.6 and 3.12 respectively, while the tilt angle between cyclopentadienyl planes show a greater distortion in 3.6 at 10.2° compared to 6.7° for 3.12. Table 3.7 lists bond distances and Table 3.8 lists bond angles with selected torsion angles for 3.6. Table 3.9 lists bond distances and Table 3.10 lists bond angles with selected torsion angles for 3.12. Figures 3.22 and 3.23 give the side view ORTEP's of 3.6 and 3.12 respectively. Figure 3.24 gives the top view ORTEP's of 3.6 and 3.12.
Table 3.7 Bond Distances in (Å) of '3.6'.

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Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3.10 Bond Angles (°) for '3.12'.

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Numbers in parentheses are estimated standard deviations in the least significant digits.
Figure 3.22 Side ORTEP view of 3.6.
Figure 3.23 Side ORTEP view of 3.12.
Figure 3.24 Top ORTEP views of 3.6 and 3.12.
3.5 Conclusion.

In the search for potential monomers for conductive polymers based on repeating ferrocene units, only one ferrocene, 1,4-(1,1'-ferrocenediyl)-1,3-butanediene, 3.6, shows promise. It was synthesized from the known 1,4-(1,1'-ferrocenediyl)-1,4-butanedione, 3.12, in a 61% overall yield. The strain in the butadiene bridge induced by the 10° distortions in the bridge sp² carbon bond angles and cyclopentadienyl tilt angle of 10.2° provide evidence that 3.6 will be an excellent candidate for ROMP to the first polyferrocene-ene conductive polymer.

Future directions planned for this research include testing various ROMP catalysts on 3.6 in ROMP feasibility studies. Also, it has been proposed that 3.6 may make an oligomer too crystalline to polymerize further to high polymer. The solution to this drawback would be to synthesize ferroceneophane monomers analogous to 1,4-(1,1'-ferrocenediyl)-1,3-butanediene, involving long alkyl chains emanating from the cyclopentadienyls to break up potential crystallinity. Other anticipated advantages of this modification would be a polymer with increased solubility in organic solvents and greater flexibility.
3.6 Experimental Section.

General Comments: n-Butyllithium (1.6 M and 2.5 M in hexanes), methylithium (1.4 M in ether), methylmagnesium bromide (3.0 M in ether), methylmagnesium chloride (3.0 M in tetrahydrofuran), dimethyamine hydrochloride, (dimethylaminomethyl)ferrocene, N,N-dimethylformamide (anhydrous), 1,5-cyclooctadiene, and dichloroacetylchloride were used as received from Aldrich. Ethylenediamine (Aldrich) was distilled over calcium oxide prior to use. Methyl iodide and 1,2-dibromoethane (Aldrich) were passed through a column of basic alumina prior to use. Triphenylphosphine (Aldrich) was recrystallized from ethanol and dried under high vacuum. Tetramethylethlenediamine (TMEDA) (Aldrich) was distilled under reduced pressure from n-butyllithium prior to use. Triethylamine was distilled from CaH$_2$ prior to use. Chlorotrimethylsilane (Aldrich) was distilled from CaH$_2$ prior to use. Lithium perchlorate (anhydrous) was heated and dried under high vacuum in the presence of phosphorous pentoxide. Cyclopentadiene was distilled directly from cracked dicyclopentadiene (Aldrich), collected in dry ice, and used immediately. Ether was distilled over Na/K (benzophenone) under argon. Tetrahydrofuran was distilled from potassium under argon. Toluene was distilled from sodium under argon and degassed by freeze-thaw method. Hexane was distilled from CaH$_2$ under argon. Trimethylsilylcylopentadiene$^{94}$ was prepared according to a literature method. 1,1'-Diacetylferrocene$^{95}$ was prepared according to a literature method or purchased from Sigma and used as received. 7,7-Dichlorobicyclo[3.2.0]hept-2-ene-6-one and bicyclo[3.2.0]hept-2-ene-6-one were synthesized according to literature methods.$^{96}$
**General Methods:** All reactions and manipulations were performed under argon except where noted. $^1$H NMR and $^{13}$C NMR spectra were measured at 200 MHz and 50 MHz, respectively, on a Bruker AC 200 spectrometer. Chemical shifts are reported in $\delta$ or ppm downfield from tetramethylsilane. IR spectra were measured on a Perkin-Elmer 1760X FTIR. Elemental analysis for new compounds was obtained from Oneida Research Services, Inc. (Whitesboro, NY) and Desert Analytics (Tucson, AZ). GC/MS were performed on a Hewlett Packard HP5995. High Resolution Mass Spectra were performed by Midwest Mass Spectroscopy Services (Lincoln, NE).

3.6.1 Attempted Synthesis of 1,2-Bis-(3-trimethylsilylcyclopentadienyl)ethane, ‘3.13’.

3.6.1.1 Via Trimethylsilylcyclopentadiene and 1,2-Dibromoethane.

Methylmagnesium chloride (3.0 M, 18.8 mL; 47.3 mmol) was added dropwise to a solution of trimethylsilylcyclopentadiene in anhydrous tetrahydrofuran (50 mL) at -78° C, allowed to warm to room temperature, and stirred for two hours. The solution was then cooled to -78° C and ethylenediamine (3.2 mL; 47 mmol) was added slowly to the reaction mixture and stirred for 30 minutes. 1,2-Dibromoethane (1.9 mL; 23 mmol) was added slowly to the reaction mixture at -78° C, warmed to 0° C, and stirred overnight. The reaction mixture was poured into a 7 N HCl / ether mixture, and extracted with ether. The combined ether extracts were dried with calcium chloride and solvent removal under reduced pressure gave a yellow oil. Bulb-to-bulb distillation under reduced pressure gave a yellow oil.
(1.5 g, b.p. 55-60° C @ 0.5 mm Hg). \(^1\)H NMR showed numerous multiplets from 6.9-6.0 ppm, broad triplets at 3.59 and 3.05 ppm, and numerous singlets between 0 and 0.3 ppm. There was no conclusive evidence that 3.13 was synthesized. In an effort to trap the possible 3.13 in an easily characterized metallocene form using a standard procedure to make metallocenes,\(^97\) the above fraction was subjected to deprotonation and then treated with TiCl\(_3\)-3THF. No titanocene was recovered. 3.13 is unlikely to have been synthesized if no titanocene was produced.

3.6.1.2 Via 1,2-Bis(cyclopentadienyl)ethane and trimethylchlorosilane.

Methylmagnesium bromide (3.0 M; 91.3 mL; 0.274 mol) was added slowly to cyclopentadiene (22.5 mL; 0.274 mol) in anhydrous ether (500 mL) at 0° C. Ethylenediamine (18.5 mL; 0.274 mol) was then slowly added with the evolution of gas and the formation of a white precipitation. The reaction mixture was stirred for two hours. The suspension was then cooled to -78° C and 1,2-dibromoethane (11.8 mL; 0.137 mol) was added slowly to the reaction mixture and stirred at 0° C for 3.5 hours. The reaction mixture was treated with a 7 M HCl / ether mixture (150 mL), warmed to room temperature, and extracted with ether. The combined ether extracts were dried with calcium chloride and solvent removal under reduced pressure gave an oil, which was immediately was passed through a short chromatography column (25 g silica gel), eluting with hexane. Removal of solvent under reduced pressure at 0° C yielded only 1,2-dibromoethane. The reaction was repeated as above replacing TMEDA for EDA, which also resulted in recovery of starting material.
3.6.3 Synthesis of (E,E)-1,2-Bis[(trimethylsilyl)methylene]-cyclopentane '3.14'.

Using a modification of a known procedure, a solution of 1,7-bis(trimethylsilyl)-1,6-heptadiyne (6.00 g; 25.4 mmol) and zirconocene dichloride (8.93 g; 30.5 mmol) in anhydrous tetrahydrofuran (250 mL) was quickly added to a suspension (stirred for 15 minutes prior to addition) of magnesium turnings (4.03 g; 166 mmol) and mercury(II) chloride (4.55 g; 16.8 mmol) in anhydrous tetrahydrofuran (250 mL). The reaction mixture was allowed to stir at room temperature for 18-24 hours. The solution was decanted from the unreacted magnesium into a separatory funnel filled with 10% sulfuric acid (250 mL) and hexane (250 mL). The aqueous layer was washed with hexanes (2x). The combined hexane extracts were washed with saturated sodium bicarbonate solution (200 mL) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and bulb-to-bulb distillation of the residue under reduced pressure afforded 3.14 as a yellow oil (5.67 g; 94% yield). Further purification by vacuum fractional distillation yielded a clear oil (4.3 g; 71% yield), (b.p. 73-75°C @ 0.7 mm Hg). \(^1\)H NMR (100 MHz; CDCl\(_3\)) \(\delta\) 0.2 (s, 18 H), 1.7 (m, 2 H), 2.4 (m, 4 H), 6.0 (s, 2 H); IR (neat; cm\(^{-1}\)): 2960, 1619, 1253, 1138; MS (m/z): 135, 121, 109, 95, 83, 73, 59.


Toluene solutions (50 mL of toluene in each) of 3.14 (4.0 g; 16.8 mmol), triphenylphosphine (0.221 g; 0.84 mmol), Ni(COD)$_2$ (0.116 g; 0.42 mmol) were prepared under argon. The triphenylphosphine solution was transferred to the solution of 3.14 with gentle stirring. The Ni(COD)$_2$ solution was added to the mixture, turning a deep red color. The reaction mixture was heated at 80° C, stirred for 24 hours, and cooled to room temperature where it was air oxidized for one hour where it turned a dark green. The solution was filtered through a short silica gel column, eluting with ether to remove the nickel waste and solvent removal under reduced pressure gave a golden colored oil (3.86 g) which $^1$H NMR and GC analysis showed to be starting materials.

3.6.5 Attempted [4+4] Coupling of 1-Vinylcyclopentene with Ni(COD)$_2$.

Using similar techniques used in the [4+4] coupling of 3.14, solutions of 1-vinylcyclopentene (3.16 g; 33.6 mmol) in toluene (40 mL), triphenylphosphine (0.442 g; 1.68 mmol) and Ni(COD)$_2$ (0.232; 0.84 mmol) in toluene (25 mL each) were prepared. The solution of 1-vinylcyclopentene was transferred to solution of triphenylphosphine and Ni(COD)$_2$, where the reaction mixture turned a deep red color. The reaction mixture was heated at 80° C and stirred for 24 hours, cooled to room temperature, and air oxidized for one hour where it turned dark green. The solution was filtered through a short silica gel column, eluting with ether to remove the nickel waste, solvent was removal under reduced pressure gave a trace of
residue. The reactants were very volatile, therefore, it was concluded that no reaction took place and the unreacted starting materials were lost in the solvent removal.

3.6.6 Attempted Addition of Dichloroketene to 1,5-Cyclooctadiene.

A solution of triethylamine (3.8 mL; 40 mmol) in hexane (16 mL) was added slowly over 1.5 hours to a solution of 1,5-cyclooctadiene (1.9 mL; 16 mmol) and dichloroacetyl chloride (3.8 mL; 40 mmol) in hexane (32 mL). The resulting suspension was stirred for 24 hours. The dark colored suspension was filtered by vacuum filtration and the solid was washed with a small amount of hexane. The solvent was removed from the filtrate under reduced pressure. 1H NMR showed numerous high intensity peaks between 5.6 and 6.0 ppm. It was concluded that the product was the result of monoaddition of the dichloroketene and it was not further characterized. A similar reaction was run as above except hexane was replaced with 5.0 M lithium perchlorate in ether. 1H NMR also showed numerous high intensity peaks between 5.6 and 6.0 ppm, as in the first reaction.

3.6.7 Improved Synthesis of 1-Formyl-2-(dimethylaminomethyl)ferrocene, '3.15' and 1,2-Bis[(dimethylamino)methyl]ferrocene, '3.16'.

n-Butyllithium (21.0 mL; 51.4 mmol) was added dropwise over five minutes to a solution of (dimethylaminomethyl)ferrocene (8.1 mL; 41 mmol) in anhydrous ether (50 mL) turning solution from orange to a deep red color. The solution was stirred for five hours and then cooled to 0° C. Dimethylformamide (4.8 mL; 62
mmol) was added dropwise, turning the reaction mixture orange. The reaction mixture was stirred at room temperature overnight, forming an orange precipitate. Distilled water (16 mL) was added and the organic layer was separated and combined with the ether extracts from the aqueous layer. The combined ether layers were dried over anhydrous sodium sulfate and solvent removal under reduced pressure gave a red-orange oil (11.2 g; 100% yield). $^1$H NMR confirmed the identity of the oil as 1-formyl-2-(dimethylaminomethyl)ferrocene, 3.15. A solution of crude 3.15 (2.15 g; 7.56 mmol) and dimethylamine hydrochloride (1.9 g; 23 mmol) in methanol (25 mL) was cooled to 0° C, where sodium borohydride (3.7 g; 98 mmol) was added slowly, resulting in vigorous effervescence and color change from deep red to light orange. The reaction mixture was warmed to room temperature after one hour, poured onto ice, and extracted into ether (3 x 150 mL). The combined ether extracts were dried with anhydrous magnesium sulfate and solvent removal under reduced pressure gave an orange solid (1.93 g; 85% yield), with $^1$H and $^{13}$C NMR spectra consistent with those reported for 1,2-bis[(dimethylamino)methyl]ferrocene. Recrystallization of 3.16 from refluxing absolute ethanol yielded X-ray quality crystals (mp. 84-85° C), from which the structure was determined.

3.6.8 Synthesis of 4-Bromo-7,7-dichlorobicyclo[3.2.0]heptane-2-en-6-one '3.18'.

A refluxing solution of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one (6.06 g; 34.2 mmol), N-bromosuccinimide (6.73 g; 37.8 mmol), and benzoyl peroxide (0.4 g) in carbon tetrachloride (60 mL) was irradiated with a sun lamp for 3.5 hours. After cooling to room temperature, the solution was filtered through a Florisil pad,
rinsing with carbon tetrachloride. Solvent removal under reduced pressure gave an oil. The crude material (8.48 g) was redissolved in ether and washed with water (5 x 70 mL). The ether was removed under reduced pressure, resulting in a yellow-brown solid that distilled (bulb-to-bulb) from 60-75° C / 0.5 mm Hg) to give 3.18 as white solid (7.26 g; 83% yield) that was free of contaminants according to ¹H and ¹³C NMR. Further recrystallization by slow cooling from refluxing hexane gave X-ray quality crystals as colorless diamond plates. ¹H NMR (200 MHz; CDCl₃) δ 4.30 (m, 1H), 4.54 (m, 1H), 5.14 (d, 1H), 6.02 (m, 1H), 6.27 (m, 1H); ¹³C NMR (50 MHz; CDCl₃) δ 49.62, 58.41, 68.32, 131.89, 139.03, 119.174 ppm.

3.6.9 Attempted Synthesis of '3.9'.

3.6.9.1 Deprotonation of '3.18' with Lithium Diisopropylamidine and Subsequent Complexation with Ferrous Chloride.

A cyclohexane solution of lithium diisopropylamidine (1.5 M; 17.2 mmol) was added slowly to a solution of 3.18 (2.0 g; 7.82 mmol) in anhydrous ether (30 mL) at -78° C, with the solution immediately turning to a dark color. After stirring the solution for 30 minutes, it was warmed to room temperature and stirred for 45 minutes. Using air-free transfers, anhydrous ferrous chloride was slowly added to the reaction mixture at -78° C with no significant color change. The solution was warmed to room temperature and stirred for 20 hours, where the reaction mixture consisting of a dark solution with a fine brown precipitate, was poured into a dilute hydrochloric acid solution. The ether layer was removed and the aqueous layer was washed with additional dichloromethane. The combined organic layers were dried
with anhydrous magnesium sulfate and solvent was removal gave a dark colored residue (1.7 g). The $^1$H NMR spectrum consisted of numerous very broad peaks, none of which resembled those expected for a metallocene.

### 3.6.9.2 Deprotonation of '3.18' with Sodium Bis(trimethylsilylamide) and Subsequent Complexation with Ferrous Chloride.

A solution of 3.18 (1.0 g; 3.9 mmol) in anhydrous tetrahydrofuran (50 mL) was added over 15 minutes to a solution of sodium bis(trimethylsilylamide) (1.0 M; 8.2 mL, 8.2 mmol) at -78° C, where the reaction mixture immediately turned purple. The reaction mixture was allowed to warm to room temperature and stirred for one hour. Anhydrous ferrous chloride (0.25 g; 1.95 mmol) was added over five minutes, using an air-free transfer, with no immediate change in color. After stirring at room temperature for 14 hours, the solvent was removed under reduced pressure and the residue was redissolved in dichloromethane and passed through fluted filter paper. The dichloromethane from the filtrate was removed under reduced pressure, the residue was redissolved in CDCl$_3$, and passed through glass wool to remove the insolubles. Attempts to perform a $^1$H NMR failed due to the presence of paramagnetic species.

### 3.6.10 Synthesis of Bicyclo[3.2.0]hept-2-en-6-one Ethylene Glycol Ketal.

A solution of bicyclo[3.2.0]hept-2-en-6-one (13.8 g; 133 mmol), ethylene glycol (7.8 mL; 140 mmol), and p-toluenesulfonic acid (0.07 g; 0.37 mmol) in benzene (250 mL) was refluxed for approximately four hours or until no more...
water was collected in a Dean-Stark trap. The solution was cooled to room temperature and washed with 10% sodium hydroxide solution (20 mL). The mixture was extracted with ether (30 mL), and resulting organic layer was washed with distilled water (3 x 25 mL). The organic layer was dried overnight with potassium carbonate and the ether was removed from the organic layer under reduced pressure. The resulting oil was distilled under reduced pressure (1-5 mm Hg) to give a colorless oil (11.33 g; 57% yield). $^1$H NMR (200 MHz; CDCl$_3$) $\delta$ 2.05 (m, 1H), 2.35 (m, 1H), 2.60 (m, 2H), 3.13 (m, 2H), 3.82 (m, 4H), 5.75 (m, 2H); $^{13}$C NMR (50 MHz; CDCl$_3$) $\delta$ 32.78, 36.54, 42.04, 48.66, 63.03, 64.57, 108.28, 131.36, 132.86 ppm. NMR showed slight contamination from starting material.

3.6.11 Attempts to Brominate Bicyclo[3.2.0]hept-2-en-6-one Ethylene Glycol Ketal.

A refluxing solution of bicyclo[3.2.0]hept-2-en-6-one ethylene glycol ketal (2.70 g; 17.7 mmol), N-bromosuccinimide (3.44 g; 19.3 mmol), and benzoyl peroxide (0.15 g) in carbon tetrachloride (30 mL) was irradiated with a sun lamp for 5.5 hours, after which a tarry residue was present on the side of the flask. The reaction mixture was allowed to stir for 24 hours at room temperature, filtered through a Florisil pad rinsing with dichloromethane, washed with water (5x), dried with anhydrous magnesium sulfate, and solvent removed under reduced pressure to give a dark oil (3.44 g). $^1$H NMR analysis showed mostly starting material.
3.6.12 Attempted Ketalization of '3.18'.

A solution of 3.18 (1.00 g; 3.91 mmol), ethylene glycol (7.6 g; 122 mmol), 
$p$-toluenesulfonic acid (53.2 mg), and trimethylorthoformate (1.7 g; 15.7 mmol) 
in dichloromethane (25 mL) was stirred at room temperature for 72 hours,\textsuperscript{102} and 
turned to a light yellow. The reaction mixture was washed with saturated sodium 
bicarbonate solution (4x), the organic layer dried with anhydrous magnesium 
sulfate, and solvent removal under reduced pressure gave a yellow oil (0.77 g). 
The resulting oil was distilled (bulb-to-bulb) and sublimed as diamond shaped 
crystals, which were identified as 3.18 by \textsuperscript{1}H NMR.

3.6.13 Synthesis of 1,4-(1,1'-Ferrocenediy1)-1,4-butanediol, 
'3.11' via Reduction of 1,4-(1,1'-Ferrocenediy1)-1,4- 
butanedione with Sodium Borohydride in Methanol.

3.12 (1.19 g, 4.44 mmol)\textsuperscript{103} was suspended in methanol (20 mL) while 
sodium borohydride (0.14 g, 3.70 mmol) was added gradually, accompanied by a 
mild effervescence. The reaction mixture was stirred for one hour, after which all 
the dione dissolved and the solution turned a bright yellow. It was then poured into 
water and extracted with ethyl acetate (3 x 50 mL). The combined organic layers 
were dried with magnesium sulfate and solvent removal under reduced pressure 
gave a diastereomeric mixture of 3.11 as a yellow powder (1.21 g, 100% yield) 
mp. dec>165° C. \textsuperscript{1}H NMR (200 MHz, DMSO-d\textsubscript{6}) \textdelta 1.68 (m), 2.17 (m), 4.03 
(m), 4.31 (m), 4.68 (m); \textsuperscript{13}C NMR (50 MHz, DMSO-d\textsubscript{6}) 31.44, 66.66, 67.38, 
67.91, 91.53 ppm; IR (thin film, cm\textsuperscript{-1}) 3331, 3086, 2940, 2858. Note: 3.11 was 
not stable in GC/MS conditions and split into three molecules of molecular weights
(M⁺) 236, 238, and 254. The MS of the fractions matched those of 3.6, 3.20, 3.21.

3.6.14 Synthesis of 1,4-(1,1'-Ferrocenediyl)-1,4-butanediol, '3.11' via Reduction of 1,4-(1,1'-Ferrocenediyl)-1,4-butanedione with Lithium Aluminum Hydride in Tetrahydrofuran.

3.12 (4.19 g, 15.6 mmol) was suspended in anhydrous tetrahydrofuran (150 mL) while lithium aluminum hydride (0.60 g, 15 mmol) was added gradually. The reaction mixture was stirred for three hours, after which all the dione dissolved and the solution turned a bright yellow. The excess lithium aluminum hydride was destroyed by the dropwise addition of ethyl acetate. The reaction mixture was poured into water and extracted with ethyl acetate until the aqueous layer was colorless. The combined ethyl acetate extracts were dried with magnesium sulfate and solvent removal under reduced pressure gave a diastereomeric mixture of 3.11 as a yellow powder (4.25 g, 100% yield). ¹H and ¹³C NMR, GC/MS, and IR match those obtained from NaBH₄ / MeOH synthetic method.

Synthesis of 3.11-d₂ follows a similar procedure except instead of using lithium aluminum hydride to reduce 3.12, lithium aluminum deuteride is used as the reducing agent. Reducing 3.12 (0.88 g; 3.28 mmol) with lithium aluminum deuteride (0.14 g; 3.3 mmol) in tetrahydrofuran (40 mL) gave 0.90 g; 100% yield) of 3.11-d₂ as a yellow powder.
3.6.15 Synthesis of 1,4-(1,1'-Ferrocenediyl)-1,3-butadiene, '3.6' via Solid State Dehydration of '3.11'.

3.6.15.1 Synthesis of '3.6' via Heating '3.11' in Basic Alumina.

A mixture of 3.11 (0.50 g) in basic alumina (10.6 g) was heated in a sublimator to 180° C at reduced pressure (0.2 mm Hg). After one hour, a red-orange solid (0.27 g) sublimed on the cold finger. Analysis using ¹H and ¹³C NMR along with GC/MS showed that the solid was a 1.5:1 mixture of 3.6 and 3.20.

3.6.15.2 Synthesis of '3.6' via Heating '3.11' in Neutral Alumina.

A mixture of 3.11 (1.22 g) in neutral alumina (10.0 g) was heated in a sublimator to 180° C at a reduced pressure (0.2 mm Hg). After one hour, a red-orange solid (0.46 g) sublimed on the cold finger. Analysis using NMR along with GC/MS showed that the solid was a 1:1 mixture of 3.6 and 3.20. Analysis for 3.20 matched that reported in the literature.¹⁰⁴ Heating a 1% mixture of 3.11 in neutral alumina had no effect on the product ratio of 3.6 : 3.20, but decreased the yield considerably.

3.6.15.3 Synthesis of '3.6' via Heating '3.11' in Silica Gel.

A mixture of 3.11 (0.96 g) in silica gel (10.0 g) was heated in a sublimator to 300° C at a reduced pressure (0.2 mm Hg). After one hour, a red-orange solid (0.38 g) sublimed on the cold finger. Analysis using NMR along with GC/MS
showed that the solid was a mixture of 3.6 and 3.21 with a small amount of 3.20. Column chromatography on silica gel eluting with hexane gave a red powder (0.21 g) which $^1$H NMR revealed to be a 4.5:1 mixture of 3.6 and 3.20. Subsequent elution with ethyl acetate yielded a yellow solid (0.17 g) which NMR and GC/MS spectra fit what would be expected for 3.21. Analysis for 3.21: $^1$H NMR (200 MHz, CDCl$_3$) δ 2.03 (m, 2 H), 4.05 (m, 1 H), 4.16 (m, 2 H), 4.86 (m, 1 H); $^{13}$C NMR (50 MHz, CDCl$_3$) 27.02, 68.43, 68.82, 70.43, 70.82 ppm. MS, m/z 254 (M$^+$), 225, 158, 121, 56.

For the dehydration of 3.11-$d_2$ on silica gel, a dilute mixture of 3.11-$d_2$ (0.1 g) in silica gel (10.0 g) was heated in a sublimator to 300°C at reduced pressure (0.2 mm Hg). After one hour, a red-orange solid (0.06 g) sublimed on the cold finger. Analysis using NMR along with GC/MS showed that the solid was almost exclusively 3.6-$d_2$: $^1$H NMR (200 MHz, CDCl$_3$) δ 2.03 (s), 4.16 (m), 4.46 (m), 5.54 (s).

3.6.15.4 Synthesis of '3.6' via Heating '3.21' in Neutral Alumina.

A mixture of 3.21 (0.10 g) in neutral alumina (2.0 g) was heated in a sublimator to 180°C at a reduced pressure of 0.2 mm Hg. After one hour, a red-orange solid (0.07 g) sublimed on the cold finger. Analysis using $^1$H NMR confirmed that the solid was 3.6 and a trace of 3.20.
3.6.15.5 Crossover Study of the Solid State Dehydration of '3.11' and '3.11'-d₂ in Basic Alumina.

A mixture of 3.11 (0.10 g) and 3.11-d₂ (0.10 g) in basic alumina (2 g) was heated in a sublimator to 200° C at reduced pressure (0.2 mm Hg). After one hour, a red-orange solid (0.08 g) sublimed on the cold finger. Analysis of the solid using GC/MS showed molecular weights for high abundance parent ions from the dehydration of 3.11 (3.6 [M⁺=236] and 3.20 [M⁺=238]), and 3.11-d₂ (3.6a [M⁺=238] and 3.20a [M⁺=241]) along with molecular weights for the parent ions expected for intermolecular reduction (3.6b [M⁺=240] and 3.20b [M⁺=239]).

3.6.16 Synthesis of 1,4-(1,1'-Ferrocenediyl)-1,3-butadiene, '3.6' via Solution Acid Catalyzed Dehydration.

A dilute solution of 3.11 (0.57 g; 2.09 mmol) was refluxed in benzene (400 mL) with p-toluenesulfonic acid (20 mole %) for 12 hours. After cooling to room temperature, the solution was washed with saturated aqueous sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Solvent removal under reduced pressure gave an orange-red solid (0.41 g; 84% yield). The reaction mixture was purified by column chromatography with silica gel, eluting with hexane to give 3.6 (0.30 g, 61 % yield) as a red solid, with traces of 3.20. Elution with a 1:1 hexane-ethyl acetate gave a trace of 3.21. Recrystallization of 3.6 by slow cooling from refluxing ethanol, aided by a seed crystal, gave X-ray quality crystals of 3.6: mp: 65° C, ¹H NMR (200 MHz, CDCl₃) δ 4.16 (m, 2 H), 4.45 (m, 2 H), 5.54 (m, 1 H), 6.27 (m, 1 H); ¹³C NMR (50 MHz, CDCl₃) 67.85, 69.90, 78.10, 126.84, 129.78 ppm. IR (thin film, cm⁻¹) 3111, 3086, 3013; MS,
m/z 236 (M+), 178, 152, 121, 56; HRMS, calc. for $^{12}\text{C}_{13}\text{H}_{12}\text{Fe}$ \(237.0322\), found 237.0320, calc. for $^{12}\text{C}_{14}\text{H}_{12}\text{Fe}$ \(236.0288\), found 236.0296.


3.5.17 Crystal Structure Determinations.

**General Experimental Procedures:** Intensity data were obtained from crystals mounted in a random orientation on an Enraf-Nonius CAD-4 diffractometer. The structures were solved by direct and heavy atom methods, and refined by full-matrix least squares based upon F, with weights $w=4F_0^2[\sigma^2(I) + (0.02F_0^2)^2]^{-1}$ using the Enraf-Nonius structure determination package, scattering factors, and anomalous coefficients. All data reductions included corrections for background, Lorentz, and polarization.

3.5.17.1 Crystal Structure Data for 1,2-Bis[(dimethylamino)methyl]ferrocene, '3.16'.

A summary of the key crystal data and parameters for the data collection for 3.16 are given in Table 3.11. Cell dimensions were determined at 296 K. One octant of data was measured using graphite monochromated MoKα radiation. Absorption was corrected using $\psi$-scans with a minimum transmission of 90.98%. Of 2422 unique data, 1387 had $I > 3\sigma(I)$, and were used in the refinement. The space group was determined by systematic absences. Non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located in a ΔF map and were not refined. Final $R=0.047$ ($R=0.124$ for all 2422 data), $R_w=0.049$, $S=1.884$ for 171 variables. The largest shift was 0.01σ in the final cycle, maximum residual density
0.81 e Å⁻³, minimum -0.36 e Å⁻³. The atomic positional and thermal parameters for 3.16 are given in Table 3.12.

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<tr>
<th>Table 3.11 Crystal Data and Collection Parameters for '3.16'.</th>
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<tbody>
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<tr>
<td><strong>Mr, g mol⁻¹</strong></td>
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### Table 3.12 Atomic Coordinates and Equivalent Isotropic Thermal Parameters for '3.16'.

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<tr>
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<tr>
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<tr>
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Starred atoms were refined isotropically. The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation:

$$B_{eq} = \frac{8\pi^2}{3} \sum \sum U_{ij} \alpha_i^* \alpha_j^* \alpha_i \cdot \alpha_j$$
3.6.17.2 Crystal Structure Data for 4-Bromo-7,7-
dichlorobicyclo[3.2.0]heptan-2-en-6-one, '3.18'.

A summary of the key crystal data and parameters for the data collection for 3.18 are given in Table 3.13. The colorless crystal fragment was mounted inside a capillary to prevent sublimation and turned slightly brown after collection time. One quadrant of data was measured using graphite monochromated MoKα radiation. Absorption corrections were based on ψ scans, with minimum relative transmission of 69.86%. Of 1552 unique data, 992 had I > 3σ(I), and were used in the refinement.

The space group was determined by systematic absences. Non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located in a ΔF map and were not refined. Final R=0.088 (R=0.133 for all 1552 data), Rw=0.105, S=4.872 for 101 variables. The largest shift was 0.02σ in the final cycle, maximum residual density 1.54 e Å⁻³, minimum -2.06 e Å⁻³. The atomic positional and thermal parameters for 3.18 are given in Table 3.14.
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<th>Crystal Data and Collection Parameters for '3.18'</th>
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<tr>
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<td>c, Å</td>
</tr>
<tr>
<td>β, deg</td>
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<tr>
<td>V, Å^3</td>
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<tr>
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<td>D_c, g/cm^{-3}</td>
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<td>no. of variables</td>
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Table 3.14 Atomic Coordinates and Equivalent Isotropic Thermal Parameters for '3.18'.

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<th>y</th>
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<th>Beq(Å²)</th>
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The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation: 

\[ B_{eq} = \frac{8\pi^2}{3} \sum \sum a_i^* a_j^* \]
3.6.17.3 Crystal Structure Data for 1,4-(1,1'-Ferrocenediyl)-1,4-butanedione, '3.12'.

A summary of the key crystal data and parameters for the data collection for 3.12 are given in Table 3.15. One hemisphere of data were measured using graphite monochromated MoKα radiation. Absorption corrections were based on ψ scans, with minimum relative transmission of 93.43%. Of 5451 unique data, 4886 had I > 3σ(I), and were used in the refinement.

The space group was determined by systematic absences. Non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located in a ΔF map and were refined. Final R=0.025 (R=0.030 for all 5451 data), Rw=0.036, S=2.013 for 203 variables. The largest shift was 0.01σ in the final cycle, maximum residual density 0.42 e Å⁻³, minimum -0.20 e Å⁻³. The extinction coefficient was 3.73(12) x 10⁻⁶. The atomic positional and thermal parameters for 3.12 are given in Table 3.16.
Table 3.15 Crystal Data and Collection Parameters for '3.12'.

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Table 3.16 Positional Parameters and Equivalent Isotropic Thermal Parameters for '3.12'.

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<td>2.60(2)</td>
</tr>
<tr>
<td>C6</td>
<td>0.3163(2)</td>
<td>0.3902(1)</td>
<td>0.37105(8)</td>
<td>2.34(1)</td>
</tr>
<tr>
<td>C7</td>
<td>0.1668(2)</td>
<td>0.3077(1)</td>
<td>0.44862(8)</td>
<td>2.67(2)</td>
</tr>
<tr>
<td>C8</td>
<td>0.2705(2)</td>
<td>0.1922(1)</td>
<td>0.48678(9)</td>
<td>3.18(2)</td>
</tr>
<tr>
<td>C9</td>
<td>0.4849(2)</td>
<td>0.2023(1)</td>
<td>0.4347(1)</td>
<td>3.10(2)</td>
</tr>
<tr>
<td>C10</td>
<td>0.5152(2)</td>
<td>0.3243(1)</td>
<td>0.36332(9)</td>
<td>2.65(2)</td>
</tr>
<tr>
<td>C11</td>
<td>0.2940(2)</td>
<td>0.2486(1)</td>
<td>0.07197(8)</td>
<td>2.49(1)</td>
</tr>
<tr>
<td>C12</td>
<td>0.2281(2)</td>
<td>0.4067(1)</td>
<td>0.07719(9)</td>
<td>3.07(2)</td>
</tr>
<tr>
<td>C13</td>
<td>0.3648(2)</td>
<td>0.5351(1)</td>
<td>0.1904(1)</td>
<td>3.34(2)</td>
</tr>
<tr>
<td>C14</td>
<td>0.2451(2)</td>
<td>0.5002(1)</td>
<td>0.29920(9)</td>
<td>2.78(2)</td>
</tr>
</tbody>
</table>

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{eq} = \frac{8\pi^2}{3} \Sigma_i \Sigma_j U_{ij} a_i^* a_j \cdot a_i \cdot a_j$
3.5.17.4 Crystal Structure Data for 1,4-(1,1'-Ferrocenediyl)-1,3-butanediene, '3.6'.

A summary of the key crystal data and parameters for the data collection for 3.6 are given in Table 3.17. One quadrant of data were measured using graphite monochromated MoKα radiation. Absorption corrections were based on ψ scans, with minimum relative transmission of 95.05%. Of 7291 unique data, 3380 had I > 3σ(I), and were used in the refinement.

The space group was determined by systematic absences. The unit cell contained three independent molecules. Non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located in a ΔF map and were not refined. Final R=0.042 (R=0.140 for all 7291 data), Rw=0.041, S=1.506 for 406 variables. The largest shift was 0.01σ in the final cycle, maximum residual density 0.76 e Å⁻³ near Fe1c, minimum -0.14 e Å⁻³. The atomic positional and thermal parameters for 3.12 are given in Table 3.18.
Table 3.17 Crystal Data and Collection Parameters for '3.6'.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
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<tbody>
<tr>
<td>** formula **</td>
<td>FeC₁₄H₁₂</td>
</tr>
<tr>
<td>** Mr, g mol⁻¹ **</td>
<td>236.1</td>
</tr>
<tr>
<td>** system **</td>
<td>monoclinic</td>
</tr>
<tr>
<td>** space group **</td>
<td>P2₁/n</td>
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<tr>
<td>** a, Å **</td>
<td>10.4137 (4)</td>
</tr>
<tr>
<td>** b, Å **</td>
<td>21.8611 (9)</td>
</tr>
<tr>
<td>** c, Å **</td>
<td>13.9521 (13)</td>
</tr>
<tr>
<td>** β, deg **</td>
<td>90.488 (5)</td>
</tr>
<tr>
<td>** V, Å³ **</td>
<td>3176.1 (6)</td>
</tr>
<tr>
<td>** Z **</td>
<td>12</td>
</tr>
<tr>
<td>** D₀, g/cm⁻³ **</td>
<td>1.481</td>
</tr>
<tr>
<td>** cryst size, mm **</td>
<td>0.12 x 0.17 x 0.30</td>
</tr>
<tr>
<td>** radiation- **</td>
<td>Mo Kα (λ = 0.71073 Å)</td>
</tr>
<tr>
<td>** μ, cm⁻¹ **</td>
<td>13.8</td>
</tr>
<tr>
<td>** temp, K **</td>
<td>299</td>
</tr>
<tr>
<td>** scan type **</td>
<td>ω-2θ</td>
</tr>
<tr>
<td>** collection range, deg **</td>
<td>2θ = 2 - 55</td>
</tr>
<tr>
<td>** no. of unique data **</td>
<td>7291</td>
</tr>
<tr>
<td>** no. of data **</td>
<td>3389 for I&gt;3σ(I)</td>
</tr>
<tr>
<td>** p **</td>
<td>0.02</td>
</tr>
<tr>
<td>** no. of variables **</td>
<td>406</td>
</tr>
<tr>
<td>** R **</td>
<td>0.042</td>
</tr>
<tr>
<td>** Rw **</td>
<td>0.041</td>
</tr>
<tr>
<td>** goodness of fit **</td>
<td>1.506</td>
</tr>
<tr>
<td>Atom</td>
<td>x</td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>Fe1a</td>
<td>0.99754(6)</td>
</tr>
<tr>
<td>C1a</td>
<td>1.1254(4)</td>
</tr>
<tr>
<td>C2a</td>
<td>1.1871(4)</td>
</tr>
<tr>
<td>C3a</td>
<td>1.1264(5)</td>
</tr>
<tr>
<td>C4a</td>
<td>1.0281(5)</td>
</tr>
<tr>
<td>C5a</td>
<td>1.0260(5)</td>
</tr>
<tr>
<td>C6a</td>
<td>0.8761(4)</td>
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<tr>
<td>C7a</td>
<td>0.9738(5)</td>
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<tr>
<td>C8a</td>
<td>0.9685(5)</td>
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<tr>
<td>C9a</td>
<td>0.8694(5)</td>
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<tr>
<td>C10a</td>
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<tr>
<td>C11a</td>
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<td>C12a</td>
<td>1.0767(7)</td>
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<tr>
<td>C13a</td>
<td>0.9374(7)</td>
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<tr>
<td>C14a</td>
<td>0.8531(6)</td>
</tr>
<tr>
<td>Fe1b</td>
<td>0.50133(6)</td>
</tr>
<tr>
<td>C1b</td>
<td>0.3780(4)</td>
</tr>
<tr>
<td>C2b</td>
<td>0.3133(4)</td>
</tr>
<tr>
<td>C3b</td>
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</tr>
<tr>
<td>C4b</td>
<td>0.4772(5)</td>
</tr>
<tr>
<td>C5b</td>
<td>0.4790(5)</td>
</tr>
<tr>
<td>C6b</td>
<td>0.6247(4)</td>
</tr>
<tr>
<td>C7b</td>
<td>0.5250(4)</td>
</tr>
<tr>
<td>C8b</td>
<td>0.5294(4)</td>
</tr>
<tr>
<td>C9b</td>
<td>0.6294(4)</td>
</tr>
<tr>
<td>C10b</td>
<td>0.6898(4)</td>
</tr>
<tr>
<td>C11b</td>
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</tr>
<tr>
<td>C12b</td>
<td>0.4290(6)</td>
</tr>
<tr>
<td>C13b</td>
<td>0.5699(6)</td>
</tr>
<tr>
<td>C14b</td>
<td>0.6513(5)</td>
</tr>
<tr>
<td>Fe1c</td>
<td>0.49805(6)</td>
</tr>
<tr>
<td>C1c</td>
<td>0.3783(4)</td>
</tr>
<tr>
<td>C2c</td>
<td>0.3099(4)</td>
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Table 3.18 (cont.) Coordinates and Equivalent Isotropic Thermal Parameters for '3.6'.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B_{eq}(E^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3c</td>
<td>0.3662(5)</td>
<td>0.6848(3)</td>
<td>0.5953(4)</td>
<td>5.4(1)</td>
</tr>
<tr>
<td>C4c</td>
<td>0.4685(5)</td>
<td>0.6468(2)</td>
<td>0.6254(4)</td>
<td>5.0(1)</td>
</tr>
<tr>
<td>C5c</td>
<td>0.4757(4)</td>
<td>0.6482(2)</td>
<td>0.7253(3)</td>
<td>4.0(1)</td>
</tr>
<tr>
<td>C6c</td>
<td>0.6261(5)</td>
<td>0.7730(2)</td>
<td>0.7618(4)</td>
<td>5.3(1)</td>
</tr>
<tr>
<td>C7c</td>
<td>0.5265(5)</td>
<td>0.8145(2)</td>
<td>0.7405(4)</td>
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</tr>
<tr>
<td>C8c</td>
<td>0.5244(6)</td>
<td>0.8239(3)</td>
<td>0.6392(5)</td>
<td>6.8(2)</td>
</tr>
<tr>
<td>C9c</td>
<td>0.6234(5)</td>
<td>0.7884(3)</td>
<td>0.5999(4)</td>
<td>6.6(1)</td>
</tr>
<tr>
<td>C10c</td>
<td>0.6866(4)</td>
<td>0.7575(3)</td>
<td>0.6749(5)</td>
<td>6.0(1)</td>
</tr>
<tr>
<td>C11c</td>
<td>0.3560(5)</td>
<td>0.7065(3)</td>
<td>0.8584(4)</td>
<td>6.3(2)</td>
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<td>C12c</td>
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<td>0.9254(4)</td>
<td>7.0(2)</td>
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<tr>
<td>C13c</td>
<td>0.5782(6)</td>
<td>0.7262(3)</td>
<td>0.9223(4)</td>
<td>7.8(2)</td>
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<tr>
<td>C14c</td>
<td>0.6567(6)</td>
<td>0.7459(3)</td>
<td>0.8566(5)</td>
<td>7.7(2)</td>
</tr>
</tbody>
</table>

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{eq} = \frac{8\pi^2}{3} \sum_j U_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.


71. Fronczek, F.R. LSU Crystallographic Facility, private communication.


85. Erickson, M.S.; McLaughlin, M.L. Unpublished results.


VITA

Mark Steven Erickson was born on July 2, 1962 in Rockford, Illinois. He received his B.A. degree (American Chemical Society certified) in Chemistry from Hamline University in Saint Paul, Minnesota in May 1984. After a brief employment with Medtronic's Energy and Technology Division in Brooklyn Center, Minnesota as a summer intern working on the synthesis of biodegradable polymers, he began his graduate studies in polymers and coatings at North Dakota State University in Fargo, North Dakota from September 1984 to September 1985 under the direction of S. Peter Pappas. In the middle of his graduate studies, Mark took time off to work for IBM in Endicott, New York from September 1985 through June 1986 to learn photoresist technology for North Dakota State University as a substrate engineer. After a brief return to North Dakota State University in August 1986 to November 1986, he decided to leave the field of polymer and coatings chemistry and follow his true interests in organic and organometallic synthesis by pursuing a doctorate degree in organic chemistry at Louisiana State University from January 1987 to the present, where he studied under the direction of Dr. Mark McLaughlin. Currently, he is a candidate for the degree of Doctor of Philosophy in the Department of Chemistry and has accepted an Office of Naval Technology Postdoctoral Fellowship with the Naval Research Laboratory in Washington, D.C.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate:  Mark Steven Erickson

Major Field: Chemistry (Organic)

Title of Dissertation: Synthesis of Novel Metallocenes: Asymmetric Hydrogenation Catalysts to Conductive Polymers

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

October 21, 1992