Synthesis and Characterization of Cyclopentadienyl Transition Metal Complexes Bearing Tetrafluoropyridyl Substituents

Andrea D. Warren

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Paul A. Deck, Chairman

Alan R. Esker

Brian E. Hanson

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Three new tetrafluoropyridyl-substituted cyclopentadienes were synthesized. Reactions of pentafluoropyridine (C₅F₅N) with sodium cyclopentadienide (NaCp) in THF with excess NaH present afforded mixtures of (4-tetrafluoropyridyl)cyclopentadiene (1), 1,3-bis(tetrafluoropyridylcyclopentadiene) (2), and 1,2-bis(tetrafluoropyridylcyclopentadiene) (3). Selectivity for mono- and diarylation was controlled by varying the reaction time. Each of the three cyclopentadienes (1, 2, and 3) was converted to its corresponding substituted sodium cyclopentadienide (4, 5, and 6, respectively) by treatment with NaH in THF.

Reaction of the monoarylated sodium cyclopentadienide (4) with M(CO)₅Br in THF (M = Mn, Re) afforded the corresponding substituted CpM(CO)₃ complexes (7Mn and 7Re). The diarylated sodium cyclopentadienides (5 and 6) likewise afforded the diarylated complexes 8Mn, 8Re, 9Mn, and 9Re. Infrared spectroscopic measurements of [(C₅F₄N)ₙC₅H₅₋ₙ]M(CO)₃ (M = Mn, Re; n = 0 – 2) revealed an increase of about 6 cm⁻¹ in the A-symmetric C-O stretching mode per C₅F₄N group, which is significantly higher than the average increase (4 cm⁻¹) found earlier for C₆F₅ groups.

Reaction of 2 equiv of 4 with FeBr₂ in THF afforded the 1,1'-diarylated ferrocene (10). Analogous reactions starting with 5 and 6 afforded tetraarylated ferrocenes (11 and 12, respectively).

Reaction of 2 equiv of 4 with ZrCl₄ afforded (C₅F₄NCp)₂ZrCl₂ (13), whereas the reaction of CpZrCl₃ with 1 equiv of 4 afforded (C₅F₄NCp)CpZrCl₂ (14). Metallocene (13) was found to be moderately active for ethylene/1-hexene copolymerization (1 atm of C₂H₄, toluene solvent, methylalumoxane cocatalyst).
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Chapter 1: Introduction

Overview. The goals of the research presented in this thesis were to:

- Synthesize and characterize cyclopentadienes bearing a novel substituent, C₅F₄N.
- Synthesize and characterize transition metal cyclopentadienyl (Cp) complexes bearing the C₅F₄N substituent.
- Determine the electronic effects of C₅F₄N substituents on the physical, spectroscopic, and electrochemical properties of transition metal Cp complexes.
- Evaluate the effects of C₅F₄N substituents on the behavior of single-site metallocene olefin polymerization catalysts.

This chapter introduces the chemistry of Cp complexes and describes the effects of substituents on them. Chapter 2 presents the synthesis of three new Cp ligands bearing the tetrafluoropyridyl substituent. These ligands are used to synthesize tricarbonyl "piano stool" complexes of manganese and rhenium, which are discussed in Chapter 3. The synthesis of substituted ferrocenes is discussed in Chapter 4. Chapter 5 presents the synthesis of substituted zirconocene dichlorides and the use of these complexes as catalyst precursors for olefin polymerization. Chapter 6 reports the experimental procedures for all of the compounds that were synthesized as well as all of the spectroscopic and reactivity studies.

Cyclopentadienyl Complexes. The η⁵-cyclopentadienyl (Cp) ligand is used extensively in organometallic chemistry. Complexes containing this ligand exist for all the transition metals and many of the f-block metals.¹ There are three general categories of metal complexes containing the Cp ligand (Figure 1). One category comprises the metallocenes (Cp₂M) or "sandwich" compounds. These compounds contain two parallel Cp ligands. A second category contains the bent metallocenes (Cp₂MLₓ), or "clamshell" compounds, in which the two Cp rings are not parallel. In these compounds, the number (ₓ) of ligands (L) may vary from one to three. The third category consists of the half

metallocenes (CpML_y), sometimes referred to as "piano stool" complexes. In these complexes, the number (y) of ligands may vary from one to four.

**Figure 1: Examples of Cp complexes.**

Cp is a pentahapto ligand, meaning that the metal binds to all five carbons of the ring. Cp is an electron rich, aromatic, six-electron species that creates a stable, strong metal-Cp bond with five roughly equal metal-carbon distances. The reactive cyclopentadienyl anion is easily prepared by the reaction of cyclopentadiene with sodium hydride, as illustrated in eq 1. Other bases used to deprotonate cyclopentadiene range from amines and hydroxides to alkyl lithium compounds and Grignard reagents. The wide range of reactions that can be performed on Cp complexes illustrates the stability of the metal-Cp bond. These reactions can functionalize the ring or modify other ligands without disturbing the Cp-M bond.²

\[
cyclopentadiene + \text{NaH} \rightarrow \text{cyclopentadienyl anion}^{-} + \text{H}_2
\]

(1)

**Substituent Effects.** The attachment of substituents to Cp ligands affects metal complexes in several ways. Substituents may affect the molecular structure, physical and chemical properties, spectroscopic properties, electrochemical properties, and catalytic activity and selectivity of a complex. Both the steric bulk and the electronic quality of the substituents affect the metal complex. Steric and electronic effects must both be taken into account when determining a substituent's effect on a complex. For this reason, studies that evaluate the steric effects of different groups must use groups with similar electronic qualities. Likewise, studies that evaluate electronic effects must use groups of comparable size and shape.
Steric effects occur when the Cp substituent is bulky enough to control the orientation of reacting molecules as they approach the metal. For example, complexes that contain triisopropylcyclopentadienyl ligands \(((\text{C}_3\text{H}_7)_3\text{C}_5\text{H}_2)_2\text{M}, \text{M} = \text{Ca, Sr, Ba, Sn})\) are highly air sensitive, low-melting solids, waxes or oils. The tetraisopropylcyclopentadienyl analogues \((\text{C}_3\text{H}_7)_4\text{C}_5\text{H}_2\text{M}\), however, are less reactive toward air and nucleophiles and exist as crystalline solids. These differences are attributed to steric crowding in the tetraisopropylcyclopentadienyl complexes. In the ligand, the four isopropyl groups lie nearly perpendicular to the Cp ring. This arrangement causes the isopropyl groups to block the metal center from reactants, and restriction of the isopropyl-Cp torsional freedom leads to crystalline materials.\(^3\)

Controlling the size and position of substituents on a metallocene catalyst affects the molecular weight and tacticity of polyolefins. Marks and coworkers found that by increasing the "wingspan" of one of the \(\eta^5\) ligands of a metallocene, the average molecular weight and isospecificity could both be increased. Polymerization studies of propylene using catalyst A and catalyst B, which contains a bulkier ligand, found that \(M_w\) increased from 2,170 to 18,900 g/mol and that the isotacticity increased from 35% to 85%. The authors concluded that the catalyst with the larger "wingspan" allowed propylene to coordinate in only one direction, leading to stereoregular, isotactic polypropylene.\(^4,5\)

\(^4\) Obora, Y.; Stern, C. L.; Marks, T. J.; Nickias, P. N. *Organometallics*, 1997, 16, 2503.
The electronic character of substituents, either electron-donating or electron-withdrawing, also influences the properties and reactivities of Cp metal complexes. Electron-donating groups increase the electron density around the metal center, making the metal less electrophilic. Electron-withdrawing groups draw electron density away from the metal center, making the metal more electrophilic. Electronic effects can be measured by several techniques, including NMR spectroscopy, IR spectroscopy, X-ray photoelectron spectroscopy (XPS), electrochemistry, and gas-phase electron transfer equilibrium (ETE).

Using IR spectroscopy, Lyatifov et al. showed that the CO stretching frequencies of substituted CpRe(CO)₃ complexes decrease as methyl substitution increases. Studies conducted by Coville confirm this trend with different Cp substituents on CpFe(CO)(PPh₃)I complexes. Substituents also affect the reaction rates of metal carbonyl complexes. By studying the kinetics of the reactions between substituted CpRh(CO)₂ complexes and PPh₃, which gives substituted CpRh(CO)(PPh₃) complexes, Basolo found that electron-withdrawing substituents increase reaction rates while electron-donating substituents decrease reaction rates.

Cp substituents also affect the electrochemical properties of metal complexes. For example, Cp₂⁺M complexes are more easily oxidized and have lower oxidation potentials than the corresponding Cp₂M complexes, due to the electron-donating methyl groups on the Cp ring. Therefore, the oxidized Cp⁺ complexes are more stable than their analogs.

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unmethylated counterparts. The cationic species \( \text{Cp}_2^*\text{Ni}^{2+} \), for example, is fairly stable and well characterized, while \( \text{Cp}_2\text{Ni}^{2+} \) is very reactive.\(^1\) This stability trend illustrates the conflict between steric and electronic effects. Because both \( \text{Cp}_2^*\text{Ni}^{2+} \) and \( \text{Cp}_2\text{Ni}^{2+} \) are 18 valence electron complexes, both may be expected to be stable. Therefore, \( \text{Cp}_2^*\text{Ni}^{2+} \) may be stabilized not only by electronic effects, but also by the bulky methyl substituents blocking the coordination sphere from any nucleophiles. Electrochemistry has also been used to quantify the electronic effects of substituents on ferrocene (\( \text{Cp}_2\text{Fe} \)). Mason measured the oxidation potentials of several phenylferrocenes that contained different groups in the \textit{para}-position of the phenyl ring.\(^{16}\) He found that electron-donating groups decreased the oxidation potential while electron-withdrawing groups such as \( \text{NO}_2 \), \( \text{COMe} \), and \( \text{Br} \) raised the oxidation potential. Kuwana also studied ferrocenes bearing different substituents.\(^{17}\) Electron-donating substituents such as alkyl groups attached directly to the Cp ring lowered the oxidation potential while electron-withdrawing substituents increased the oxidation potential.

The catalytic activity of Cp complexes is also affected by the electronic abilities of substituents. For example, ethylene polymerization studies using \( (\text{CpR})_2\text{ZrCl}_2 \) (\( R = \text{H}, \text{Me}, \text{Et}, \text{i-Pr}, \text{t-Bu}, \text{SiMe}_3, \text{CMe}_2\text{Ph} \)) precatalysts show that electron-donating substituents increase catalytic activity while electron-withdrawing substituents decrease activity.\(^{18}\)

**History of Pentafluoropyridine and the Tetrafluoropyridyl Substituent.**
Pentafluoropyridine was first prepared in low yields by the defluorination of perfluoropiperidine, which is obtained by the fluorination of pyridine or piperidine (eq 2). A higher yielding process was later developed that involved the direct replacement of chlorine by fluorine (eq 3). This process is the standard reaction used for making pentafluoropyridine.\(^{19}\)

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Perutz and coworkers studied the activation of C-F bonds using pentafluoropyridine. They found that the reaction of Ni(COD)$_2$ (COD = 1,5-cyclooctadiene) with pentafluoropyridine in the presence of triethylphosphine yields the 2-pyridyl isomer of trans-Ni(PEt$_3$)$_2$(C$_5$F$_4$N)F (eq 4). This reaction is regioselective in that the nickel center attaches ortho to the nitrogen atom. Ortho-attack is unusual for pentafluoropyridine: most nucleophiles attack at the para-position. The authors also compared the rates of C-F activation using pentafluoropyridine, hexafluorobenzene, and pentafluorostyrene. The reaction represented in eq 4 was found to be much faster than the analogous reaction using hexafluorobenzene. Altering the ring slightly has dramatic effects on the reactivity. The nitrogen atom of the pentafluoropyridine is thought to be responsible for the accelerated reaction rate and the regioselectivity of the reaction. The authors suggest that the nickel center initially attacks the nitrogen atom, which leads to ortho-substitution and increased reaction rates.

In 1990, Chambers and coworkers reported the syntheses of fluorinated cyclopentadienes and cyclopentadienyl anions bearing the tetrafluoropyridyl substituent. The cyclopentadienes were produced by an electrocyclc ring closure.

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followed by elimination of fluoride ion. Loss of cyanide ion results in tetrafluoropyridyl-substituted Cp anions (Scheme 1).

**Scheme 1**

**Objective.** The synthesis of new tetrafluoropyridyl-substituted Cp ligands complexes will be presented in the following chapters. The electron-withdrawing effect of the C₅F₄N substituent will be analyzed using IR spectroscopy. The effect of this substituent on olefin polymerization will also be discussed. Several comparisons of electronic effects will be made of the C₅F₄N substituent to the C₆F₅ substituent, which is similar in size and shape but differs in electron-withdrawing ability.
Chapter 2: Ligand Synthesis and Characterization

**Introduction.** Perfluoroaryl-substituted cyclopentadienes are generally prepared by nucleophilic aromatic substitution. In this process (Scheme 2) a cyclopentadienyl anion displaces a halide from an aromatic ring by a two-step addition-elimination mechanism. In the first step, *ipso* attack by the cyclopentadienyl anion results in a "Meisenheimer" intermediate bearing a negative charge that is delocalized and/or inductively stabilized by one or more electron withdrawing groups (E). Electron-withdrawing groups, such as nitro or sulfonyl, located *ortho* or *para* to the leaving group, activate this reaction. An electron-withdrawing group such as fluorine, that stabilizes neighboring anions inductively, also activates this reaction, but several fluorines are necessary to make this process practical under reasonable reaction conditions. These electron-withdrawing substituents stabilize the intermediate anion by further dispersing the charges on carbon in the three canonical resonance forms. *Ipso* attack is fastest for fluoride (\(X = \text{F}\)) due to the polarity of the C-F bond. For this reason, the fluoride anion is the best leaving group for nucleophilic aromatic substitution. In the second step, the aromaticity of the ring is restored by the departure of the leaving group (X).\(^{23}\)

Several different perfluoroaryl-substituted cyclopentadienes can be synthesized using nucleophilic aromatic substitution. The prototypical reaction of sodium cyclopentadienide (NaCp) with hexafluorobenzene (C\(_6\)F\(_6\)) and excess NaH in THF (Scheme 3) results in a mixture of mono-, di-, and triarylated cyclopentadienes.\(^{24}\) The intermediate arylated cyclopentadienes are deprotonated by the excess NaH *in situ* and then arylated again, each time more slowly than the last. For this reason refluxing diglyme, which has a higher boiling point than THF, is needed to produce the tetra-


Scheme 2

arylated cyclopentadienes.\textsuperscript{25} All of these substituted cyclopentadienes are readily converted into their corresponding sodium salts upon treatment with NaH.

The reactions described above can be applied to other cyclopentadienes, including indenes, which are cyclopentadienes containing a fused benzene ring.\textsuperscript{26} The reaction of sodium indenide with C\textsubscript{6}F\textsubscript{6} in THF results in 3-(pentafluorophenyl)indenone or 1,3-bis(pentafluorophenyl)indenone, depending on the reaction conditions and ratios of starting materials (Scheme 4). These compounds can be converted to their corresponding sodium indenides by reaction with NaH in THF. Another example is the reaction of tetramethylcyclopentadienyl sodium with C\textsubscript{6}F\textsubscript{6} (eq 5). In this reaction the aryl group attaches to the carbon that does not contain a methyl group. A third example is the reaction of \textit{tert}-butylcyclopentadienylsodium with C\textsubscript{6}F\textsubscript{6} (eq 6), where the aryl group attacks the carbons farthest away from the \textit{tert}-butyl group due to steric effects.

Scheme 3

1. $\text{NaH}, \text{THF}$

2. $\text{aq. NH}_4\text{Cl}$

Scheme 4

1. $\text{NaH}, \text{THF}$

2. $\text{C}_6\text{F}_6$

3. $\text{aq. workup}$

4. $\text{NaH, THF}$

5. $\text{THF, 0 °C}$

6. $\text{aq. workup}$

7. $\text{NaH, THF}$

8. $\text{25 °C}$

9. $(5)$
Substituted cyclopentadienes bearing different fluoroaromatic substituents can also be made (Scheme 5). The reactivity of other perfluoroarenes, however, changes compared to C₆F₆ as one or more fluorine atoms are replaced with different groups. With these substituents the Cp nucleophile tends to replace the fluorine that is para to the differing group. One example is the reaction of pentafluorotoluene with NaCp, which is a much slower reaction than that of C₆F₆ and NaCp. The reaction of decafluorobiphenyl (C₆F₅C₆F₅) with NaCp is another example.²⁷ The para (4 and 4') positions are substituted almost as quickly as with C₆F₆, suggesting that replacing F with C₆F₅ causes little or no loss in activation. This chapter explores the reactivity of NaCp with pentafluoropyridine as the first "heterocyclic" extension of this synthetic method.

Scheme 5

Results and Discussion. As shown in Scheme 6, the reaction of NaCp with pentafluoropyridine (C₅F₅N) in refluxing THF affords either mono- or diarylated cyclopentadienes, depending on the ratio of starting materials and the reaction time. The reaction of NaCp with a limiting amount (60 mol%) of C₅F₅N in refluxing THF for 15

hours affords compound 1. The reaction of NaCp with slightly more than two equivalents of C₅F₄N in refluxing THF for 4 days affords a mixture of disubstituted isomers. NMR data shows no evidence of any monosubstituted compound in this mixture. Compounds 2a and 2b are separated from compounds 3a and 3b by silica gel chromatography and are isolated as white solids. The low yields of the diarylated compounds are likely due to the production of some black intractable tar that is always observed in the reaction mixtures.

**Scheme 6**

All of the tetrafluoropyridyl-substituted cyclopentadienes are characterized by ^1^H and ^1^9^F NMR. The chemical shift and integration data is useful in identifying 2a, 2b, 3a, and 3b. In the ^1^H NMR spectrum of 2, the allylic methylene protons of 2a and 2b are found at 4.26 and 3.96 ppm. The more downfield of these signals corresponds to the major isomer 2a, in which both of the C₅F₄N groups are adjacent to the CH₂ group. Likewise, the CH₂ signals at 3.80 and 3.62 ppm in 3 are assigned to 3a (major) and 3b, respectively. Compound 1 was further characterized by ^1^3^C NMR, but the isomer mixtures of 2 and 3 would produce spectra too complicated to be useful.

All of the tetrafluoropyridyl-substituted cyclopentadienes are efficiently converted to their corresponding sodium salts, as shown in Scheme 7. The mixture of 2a and 2b is converted to a single sodium salt (5) upon treatment with NaH. The mixture of 3a and 3b is also converted to the common salt 6 upon treatment with NaH. The sodium salts were characterized by ^1^H and ^1^9^F. The ^1^H NMR spectrum of 5 shows a peak at 7.54
ppm for the proton that is adjacent to two C₅F₄N groups. The ¹H NMR spectrum of 6 shows the signal for the hydrogens that are adjacent to only one C₅F₄N group is farther upfield at 6.49 ppm, as expected. These shifts help to confirm the structural assignments of 2 and 3.

**Scheme 7**

\[
\text{C}_5\text{F}_4\text{N} + \text{NaH} \xrightarrow{\text{THF, 25 °C, 2 h}} \text{C}_5\text{F}_4\text{NNC}_5\text{F}_4\text{NNa}^+ \quad 71\%
\]

\[
\text{NC}_5\text{F}_4\text{N} - \text{C}_5\text{F}_4\text{N} + \text{NaH} \xrightarrow{\text{THF, 25 °C, 4 h}} \text{NC}_5\text{F}_4\text{NNC}_5\text{F}_4\text{NNa}^+ \quad 75\%
\]

\[
\text{NC}_5\text{F}_4\text{N} - \text{C}_5\text{F}_4\text{N} + \text{NaH} \xrightarrow{\text{THF, 25 °C, 4 h}} \text{NC}_5\text{F}_4\text{NNC}_5\text{F}_4\text{NNa}^+ \quad 59\%
\]

**Conclusions.** Mono- and disubstituted tetrafluoropyridyl cyclopentadienes and their corresponding sodium salts were successfully synthesized. NMR spectroscopy revealed the structures of all new compounds.
Chapter 3: Piano Stool Complexes

**Introduction:** Metal carbonyl complexes are important and interesting due to their reactivity. A broad range of reactions can be performed with carbonyls, including migratory insertion, substitution of CO for other ligands, and the addition of nucleophiles to CO ligands to form Fischer carbenes (Scheme 8). By replacing one or more of the CO groups on a metal with a different ligand, the range of different CO complexes and their reactivities becomes highly diverse. Some ligands that may be used to replace carbonyls include phosphines, arenes, and cyclopentadiene (Cp). Properties of metal complexes bearing these ligands may be altered by changing one or more of their substituents, allowing those complexes to be "tuned" to possess desirable characteristics. Cp is an especially useful ligand because it is anionic, and therefore a good donor ligand. It can stabilize metals in +1 and +2 oxidation states that may normally be too electron deficient to form stable CO complexes. Examples of the change in reactivity of CpM(CO)$_n$ complexes as a function of Cp substituents were already discussed in Chapter 1.

**Scheme 8**

Cyclopentadienyl tricarbonyl complexes, commonly referred to as piano stool complexes, can be prepared with both manganese and rhenium. $\eta^5$-Cyclopentadienyltricarbonylmanganese(I), ($\eta^5$-C$_5$H$_5$)Mn(CO)$_3$, known commonly as "cymantrene," is an important compound in organomanganese chemistry, and exists as a
pale yellow, air-stable crystalline solid. This compound can be prepared by several
different methods. These traditional methods include the reaction of Mn₂(CO)₁₀ with
cyclopentadiene (eq 7), the carbonylation of (η⁵-C₅H₅)₂Mn (eq 8), and the reaction of
MnCl₂(py)₂ and CO under pressure (eq 9). Substituted cyclopentadienyltricarbonyl
complexes can also be made using similar reactions. (η⁵-Methylcyclopentadienyl)tricarbonylmanganese(I), (η⁵-C₅H₄Me)Mn(CO)₃, used as an antiknock additive in
gasoline, is prepared commercially using the method shown in eq 9, involving
MnCl₂(py)₂ and methylcyclopentadiene.²⁸ A range of structural analogues derived from
substituted Cp ligands can also be prepared using the more general anionic substitution
method shown in eq 10. This method was used by Thornberry et. al to prepare C₆F₅-
substituted piano stool complexes that are analogues to the compounds described in this
chapter.²⁴,²⁵

\[
\begin{align*}
\text{Mn}_2(\text{CO})_{10} + C_2\text{H}_6 & \rightarrow (\eta^5-\text{C}_5\text{H}_5)\text{Mn(CO)}_3 \\
(\eta^5-\text{C}_5\text{H}_5)_2\text{Mn} + 3 \text{CO} & \rightarrow (\eta^5-\text{C}_5\text{H}_5)\text{Mn(CO)}_3 \\
2 \text{MnCl}_2(\text{C}_5\text{H}_5\text{N})_2\text{Mn} + \text{Mg} + 2 \text{C}_5\text{H}_5\text{Me} + 6 \text{CO} & \xrightarrow{\text{DME}} (\eta^5-\text{C}_5\text{H}_4\text{Me})\text{Mn(CO)}_3 \\
\text{MnBr(CO)}_5 + \text{Na(C}_6\text{F}_5)_n\text{C}_5\text{H}_{5-n} & \rightarrow [\eta^5-\text{C}_5\text{H}_{5-n}(\text{C}_6\text{F}_5)_n]\text{Mn(CO)}_3
\end{align*}
\]

Piano stool complexes may also be prepared with rhenium as the metal center by
similar methods. For example, cyclopentadienyltricarbonylrhenium(I), (η⁵-
C₅H₅)Re(CO)₃, is made by the treatment of Re₂(CO)₁₀ with dicyclopentadiene (eq 11).
This compound is also prepared by reacting ReBr(CO)₅ with sodium cyclopentadienide
(eq 12). The reaction of Re₂(CO)₁₀ with pentamethylcyclopentadiene (eq 13) affords a
substituted analogue of the tricarbonyl complex, albiet under forcing conditions.³⁰
Pentafluorophenyl-substituted rhenium piano stool complexes can also be synthesized by
a method analogous to eq 12, showing that the anionic substitution method works well
for electron deficient ligands.²⁴,²⁵

This chapter describes the synthesis of tetrafluoropyridyl-substituted analogues of
CpM(CO)₃ (M = Mn, Re). Our goals were to demonstrate the synthetic utility of the

²⁸ Komiya, Sanshiro; Synthesis of Organometallic Compounds: A Practical Guide, John Wiley &
ligands described in Chapter 2 and to use the spectroscopic qualities of the tricarbonyl complexes as a tool for estimating the electronic effects of the C₅F₄N groups.

**Results and Discussion.** Substitution reactions of sodium tetrafluoropyridyl-cyclopentadienyl ligands with Mn(CO)₅Br or Re(CO)₅Br in refluxing THF for 24 hours yield the corresponding piano stool complexes (Scheme 9). The monoarylated piano stool complexes 7Mn and 7Re were separated from impurities using silica gel chromatography. The diarylated complexes (8Mn, 8Re, 9Mn, and 9Re) were purified by recrystallization from mixtures of hexane and toluene. All of the manganese complexes were isolated as yellow or orange solids, and the rhenium complexes as colorless solids. The yields of these compounds are low to moderate, most likely due to incomplete substitution reactions or partial hydrolysis of the ligands. ¹H and ¹⁹F NMR analysis of the crude products show evidence of unreacted hydrolyzed ligands. One way to avoid this problem in the future and possibly improve the yield would be to include NaH in the reaction mixture as a scavenger for adventitious moisture.

**Scheme 9**

\[
\text{Re}_2(\text{CO})_{10} + \quad \text{Na}^+ \quad \text{C}_5\text{F}_4\text{N}^- \quad \longrightarrow \quad (\eta^5-\text{C}_5\text{H}_5)\text{Re(CO)}_3 \quad (11)
\]

\[
\text{ReBr(\text{CO})}_5 + \quad \text{Na}^+ \quad \longrightarrow \quad (\eta^5-\text{C}_5\text{H}_5)\text{Re(CO)}_3 \quad (12)
\]

\[
\text{Re}_2(\text{CO})_{10} + \quad \text{C}_5\text{Me}_3\text{H} \quad \xrightarrow{150-210^\circ\text{C}} \quad (\eta^5-\text{C}_5\text{Me}_3)\text{Re(CO)}_3 \quad (13)
\]

The anionic substitution method was chosen for these syntheses due to the ease of the synthetic process and the ability of these reaction conditions to work well for a series...
of different ligands. The method shown by eqs 7 and 11 is undesirable because it involves oxidation and reduction of the metal, which may not work well with electron deficient Cp ligands. The synthetic routes shown in eqs 8 and 9 are not used because they require high pressures of CO, which is an inconvenience in the laboratory.

Infrared spectra of the tricarbonyl species shows the expected pattern of strong bonds for the symmetric and asymmetric carbonyl stretching modes (Table 1). Although the complexes are only sparingly soluble in hydrocarbons, n-decane was used to record the infrared spectra to minimize solvent interactions and to enable direct comparisons with other compounds in the literature. The asymmetric bands are split for the disubstituted complexes due to perturbed C$_3$v symmetry. Inspection of the symmetric stretches shows that the frequencies increase as substitution of the ring increases. This trend reveals that the tetrafluoropyridyl substituent is electron-withdrawing. As electron-withdrawing groups are added to a Cp ligand, electron donation by the ring decreases. With less electron density at the metal center, backbonding to the carbon of the carbonyl group is slightly diminished. With decreased backbonding, the C-O bond is strengthened and vibrates at a higher frequency.

Table 1. Carbonyl Stretching Wavenumbers of Piano Stool Complexes

\[
((C_5F_4N)_nCp)M(CO)_3
\]

\[(n = 1,2; M = Mn, Re)^a\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Wavenumbers (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\nu_{CO}$ (A)</td>
</tr>
<tr>
<td>1.</td>
<td>(C$_5$F$_4$NCp)Mn(CO)$_3$ (7Mn)</td>
<td>2035</td>
</tr>
<tr>
<td>2.</td>
<td>(1,2-(C$_5$F$_4$N)$_2$Cp)Mn(CO)$_3$ (8Mn)</td>
<td>2041</td>
</tr>
<tr>
<td>3.</td>
<td>(1,3-(C$_5$F$_4$N)$_2$Cp)Mn(CO)$_3$ (9Mn)</td>
<td>2041</td>
</tr>
<tr>
<td>4.</td>
<td>(C$_5$F$_4$NCp)Re(CO)$_3$ (7Re)</td>
<td>2037</td>
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<tr>
<td>5.</td>
<td>(1,2-(C$_5$F$_4$N)$_2$Cp)Re(CO)$_3$ (8Re)</td>
<td>2043</td>
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<td>6.</td>
<td>(1,3-(C$_5$F$_4$N)$_2$Cp)Re(CO)$_3$ (9Re)</td>
<td>2043</td>
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</tbody>
</table>

$^a$ Recorded in decane solvent

The tetrafluoropyridyl substituent can be quantitatively compared to the pentafluorophenyl substituent by comparing the shifts in their respective symmetric IR wavenumbers.$^{25}$ A plot of the wavenumbers for the manganese tricarbonyl complexes (Figure 2) shows that the slope of the tetrafluoropyridyl line (Ar = C$_5$F$_4$N) is approximately 50% greater than the slope of the pentafluorophenyl line (Ar = C$_6$F$_5$). The slope of the line represents the average effect of that substituent. For the rhenium
tricarbonyl complexes (Figure 3), the slope of the tetrafluoropyridyl line is about 60%
greater than the slope of the pentafluorophenyl line. From these data it can be concluded
that the tetrafluoropyridyl substituent is about 50-60% more electron-withdrawing than
the pentafluorophenyl group.

Crystal structures for $^{7}\text{Re}$ and $^{8}\text{Mn}$ were obtained, as shown in Figures 4 and 5,
respectively. Crystallographic data is presented in Table 2, and selected bond lengths and
angles are shown in Table 4. Inspection of the metric parameters shows that there are no
significant structural aberrations. All of the M-CO bonds are equidistant, and the Cp-M-
CO angles are all approximately 90°. The distances from the metal to each of the Cp
carbons are approximately equal in each crystal structure, indicating that there is no
"slipped" or "folded" character to the Cp rings. Structures $^{7}\text{Re}$ and $^{8}\text{Mn}$ can be compared to crystal structures for the
pentafluorophenyl-substituted piano stool complexes $^{C}$, $^{D}$, and $^{E}$. The Cp-Re distance in
$^{7}\text{Re}$ is within experimental error of the Cp-Re distances in $^{C}$ and $^{D}$. In addition, the Cp-
Mn distance in $^{8}\text{Mn}$ is within experimental error of the Cp-Mn distance in $^{E}$. These data
show that the electron-withdrawing character of the Cp substitutents is not strong enough
to have a large influence on the Cp-M bond distances.

Conclusions. A range of manganese and rhenium piano stool complexes bearing
the tetrafluoropyridyl substituent were successfully synthesized and characterized.
Crystal structures of two of the compounds showed that this substituent does not distort
their "piano stool" structures. The carbonyl stretching frequencies of these complexes
were compared to known values in order to show that the electron-withdrawing effect of
this substituent is about 50 - 60% more than that of the $^{C}_{6}F_{5}$ substituent.

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30 Blanchard, M. D.; Hughes, R. P.; Concolino, T. E.; Rheingold, A. L. Chem. Mater., 2000, 12,
1604.
31 Deck, P. A.; Lane, M. J.; Montgomery, J. L.; Slebodnick, C.; Fronczek, F. R. Organometallics,
2000, 19, 1013.
$\text{Re-Cp} = 1.955(8)$ Å

$\text{Re-Cp} = 1.968(6)$ Å

$\text{Mn-Cp} = 1.780(4)$ Å
Table 3. Crystallographic Data.

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<th>compound</th>
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<td>C_{18}H_{3}F_{8}N_{2}O_{5}Mn</td>
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<tr>
<td>fw</td>
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<td>7.1125(8)</td>
</tr>
<tr>
<td>b (Å)</td>
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<td>c (Å)</td>
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<td>γ (deg)</td>
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<td>Z</td>
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<td>F_{000}</td>
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<td>3111</td>
</tr>
<tr>
<td>no. of indep reflns</td>
<td>2837</td>
<td>3111</td>
</tr>
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<td>abs corr method</td>
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<td>Empirical</td>
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<td>peak, hole (e Å⁻³)</td>
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<td>0.126, -0.321</td>
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<td>compound</td>
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<td>8Mn</td>
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<td>---------</td>
<td>---------</td>
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<tr>
<td>Cp-M</td>
<td>1.962(9)</td>
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<tr>
<td>C1-M</td>
<td>2.295(7)</td>
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<td>C2-M</td>
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<td>C3-M</td>
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<td>C5-M</td>
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<td>C6-M</td>
<td>1.917(9)</td>
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<tr>
<td>C7-M</td>
<td>1.924(9)</td>
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<td>C8-M</td>
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<td>C7-M-C8</td>
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<td>91.7(3)</td>
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<td>C8-M-C6</td>
<td>87.3(3)</td>
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<td>Cp-C5F4N</td>
<td>23.6(12)</td>
<td>4.4(8), 29.0(6)</td>
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*aInterplanar torsion angle*
Figure 2. Carbonyl Stretching Wavenumbers for (Ar$_n$Cp)Mn(CO)$_3$ Complexes.

(*) Ar = C$_5$F$_4$N; (o) Ar = C$_6$F$_5$. 
Figure 3: Carbonyl Stretching Wavenumbers for (ArₙC₅p)Re(CO)₃ Complexes.

- Solid circle (●) Ar = C₅F₄N
- Open circle (○) Ar = C₆F₅

Slope = 6.0
Ar = C₅F₄N

Slope = 4.0
Ar = C₆F₅
Figure 4: Thermal ellipsoid plot of 7Re shown at 50% probability.
Figure 4: Thermal ellipsoid plot of 8Mn shown at 50% probability.
Chapter 4: Ferrocenes

Introduction: Dicyclopentadienyliron complexes, commonly known as ferrocenes, consist of an iron atom that is bonded in an $\eta^5$ fashion to two cyclopentadienyl ligands. The discovery in 1951 of ferrocene, the first known compound to contain $\eta^5$-bonded Cp ligands, transformed the field of organometallic chemistry. Ferrocene may be synthesized by several routes, including the reaction of cyclopentadiene with anhydrous iron dichloride in the presence of diethylamine\textsuperscript{32} (eq 14) and the anionic substitution reaction of sodium or lithium cyclopentadienide with anhydrous FeCl\textsubscript{2} in THF (eq 15).\textsuperscript{33}

\begin{equation}
\begin{array}{c}
\text{FeCl}_2 + \text{C}_5\text{H}_6 \xrightarrow{\text{Et}_2\text{NH}} \text{Fe(C}_5\text{H}_5)_2 \\
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
2\text{NaC}_5\text{H}_5 + \text{FeCl}_2 \xrightarrow{\text{THF-reflux}} \text{Fe(C}_5\text{H}_5)_2 + 2\text{NaCl} \\
\end{array}
\end{equation}

Ferrocene is an important compound in organometallic chemistry. Due to its stability and its ability to maintain the iron-Cp bond under harsh reaction conditions, many organic reactions may be performed on the Cp ring. Some examples of these reactions include Friedel-Crafts acylation (eq 16), the Mannich reaction (aminomethylation) (eq 17), and mettallation, in which a ring hydrogen atom is replaced by a metal atom such as lithium (eq 18).\textsuperscript{34}

\begin{equation}
\begin{array}{c}
\text{Fe} + \text{CH}_3\text{COCl} \xrightarrow{\text{AlCl}_3} \text{Fe} + \text{CH}_3\text{COFe} \text{CH}_3 \\
\end{array}
\end{equation}

Altering the substituents on the Cp ring affects the reactivity of ferrocene complexes. Ferrocene itself is readily oxidized to dicyclopentadienyliron(III), also known as ferrocenium. This cation can be obtained electrochemically, photochemically, or by using various oxidizing agents such as benzoquinone, FeCl₃, and N-bromosuccinimide. The oxidation of ferrocene (eq 19) is electrochemically and chemically reversible and the potential is sensitive to the nature of the substituents. When alkyl groups, which are electron donating, are added to ferrocene, the complex is more easily oxidized. E₁/₂ decreases by about 0.05 V for each alkyl group attached. Electron withdrawing groups have the opposite effect. Phenyl and CO₂H substituents decrease ferrocene's ability to be oxidized, and increase E₁/₂ by 0.023 and 0.280 V, respectively, when compared to unsubstituted ferrocene. ⁳⁴ A pentafluorophenyl group on each of the Cp rings increases E₁/₂ by about 0.16 V. ²⁶

This chapter describes the synthesis of tetrafluoropyridyl substituted analogues of Cp₂Fe. Our goals were to demonstrate the synthetic utility of the ligands described in chapter 2 by making a range of substituted ferrocene complexes, and to examine the effects of the substituents electrochemically.

**Results and Discussion.** Substitution reactions of C₅F₄N-substituted cyclopentadienyl ligands 4, 5, and 6 with FeBr₂ in THF at room temperature for 15 hours yield the corresponding ferrocenes (Scheme 10). These compounds are synthesized using the anionic substitution method because the synthetic process is straightforward and this
method has been shown to work well for other ferrocenes made in our laboratory. All of the ferrocenes were purified by recrystallization from mixtures of hexane and toluene and isolated as dark red or orange solids. The low yields using the diarylated ligands are attributed to incomplete reactions or partial hydrolysis of the ligands, which is common when reactions are done on a small scale. NMR analysis of the crude products shows evidence of some unreacted, hydrolyzed ligands. Including NaH in the reaction mixture could help improve future yields by scavenging adventitious moisture and keeping the ligand in its anionic form.

Electrochemical studies performed on 10 and 11 showed that the reduction of these complexes are reversible (Figure 6). As tetrafluoropyridyl groups are added to each ring, the oxidation potential increases, showing that this substituent is electron-withdrawing (Table 5). A comparison of the oxidation potentials of tetrafluoropyridyl-substituted ferrocenes to pentafluorophenyl-substituted ferrocenes was made to quantify the electron-withdrawing ability of the tetrafluoropyridyl substituent. A plot of these potentials shows that the slope of the tetrafluoropyridyl line (Ar = C₅F₄N) is 55% greater than the slope of the pentafluorophenyl line (Ar = C₆F₅), which reveals that the tetrafluoropyridyl substituent is about 55% more electron-withdrawing than the pentafluorophenyl group (Figure 7). These results are in agreement with the results of the IR studies discussed in Chapter 3.

Table 5. Electrochemical Data for Aryl-substituted Ferrocenes.

<table>
<thead>
<tr>
<th>No. of substituents</th>
<th>E°(ox)</th>
<th>C₅F₄N</th>
<th>C₆F₅</th>
<th>(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>520</td>
<td>350</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>985</td>
<td>680</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>945</td>
<td></td>
</tr>
</tbody>
</table>

(a) Data from Ref. 24

Conclusions. Several tetrafluoropyridyl-substituted ferrocenes were successfully synthesized and characterized, showing that the tetrafluoropyridyl Cp ligand is useful for the synthesis of substituted ferrocenes.
Scheme 10

10, 66%

11, 70%

12, 33%
Figure 6. Cyclic and Square Wave Voltammograms for Ferrocenes 10 and 11.
Figure 7. Oxidation Potentials for (Ar_nCp)_2Fe Complexes.
(o) Ar = C_5F_4N; (●) Ar = C_6F_5.
Chapter 5: Zirconocene Dichlorides

Introduction. Metallocenes of the group 4 metals, especially zirconium, are useful as polymerization catalysts. Unlike conventional Ziegler-Natta catalysts, metallocenes tend to form homogeneous solutions of the catalytically active species. Solubility is advantageous because an active site is formed from every molecule in solution, resulting in high activities per mole. Metallocenes also have the potential to yield stereospecific polymers. For example, catalysts may be designed to give isotactic, syndiotactic, or hemitactic polypropylene. Group 4 metallocene catalysts function as "single site" catalysts, producing polyolefins with narrow molecular weight distributions ($M_w/M_n = 2$) and regularly distributed short or long chain branches. Finally, these catalysts are versatile in that they can be attached to a solid support, which alters the activity and the properties of the resulting polymer.35

Metallocene dichlorides, the focus of this chapter, are not catalysts themselves, but catalyst precursors. These catalyst precursors are typically made by the reaction of a cyclopentadienyl-metal complex with the metal tetrachloride (Scheme 11).

Scheme 11

\[
\text{C}_5\text{H}_6\text{MgBr} + \text{MCl}_4 \rightarrow (\text{C}_5\text{H}_5)_2\text{MCl}_2 \\
\text{NaC}_5\text{H}_5 + \text{MCl}_4 \rightarrow (\text{C}_5\text{H}_5)_2\text{MCl}_2 \quad (\text{M} = \text{Li, Na})
\]

The catalyst precursor must then be activated with a cocatalyst before polymerization can occur (Scheme 12). The most commonly used cocatalyst is methylalumoxane (MAO). MAO performs several functions in a polymerization, including alkylation of the dichloride, abstraction of a methyl anion, stabilization of the activated catalyst, and elimination of impurities such as oxygen and water from the reaction.36 The activation reaction occurs in two steps. First, MAO replaces the chlorides with methyl groups. Second, MAO abstracts one methyl group to produce a monomethyl metallocene cation containing a "free coordination site." This cationic species is the active catalytic species. For best catalyst performance, large molar excesses of MAO are needed, typically about 2000 times as much MAO as catalyst.35

Chain propagation occurs by the insertion of an olefin molecule, usually ethylene, into the metal-Me bond of the catalyst. The chain grows by the repeated insertion of monomer into the metal-carbon bond. Scheme 13 shows the polymerization of ethylene. Chain termination occurs mainly by β-hydride elimination (Scheme 14), but may also be caused by the addition of molecular hydrogen, which can compete with the olefin for the free coordination sites. Other termination routes include chain transfers to aluminum and to the monomer and decomposition of the catalyst.\textsuperscript{35}

Scheme 13. Chain Propagation

Scheme 14. Chain Termination

The metallocene dichloride complex can be altered to control polymer properties by introducing substituents to the Cp ligand or by altering the metal center (M = Ti, Zr, Hf). The introduction of substituents affects the steric and electronic properties of the complex as well as the symmetry of the catalyst, which is important in producing stereospecific polyolefins. Adding steric bulk to Cp ligands tends to increase catalyst
activity (up to a point) and molecular weight of the resulting polymer. These increases may be due to the substituents partially blocking the free coordination site on the catalyst, inhibiting the $\beta$-hydride elimination and other chain termination reactions. In the area of electronic effects, most of the literature has focused on electron donating substituents, because these groups tend to increase catalyst activity. Electron donating groups increase the electron density around the metal, weakening the bonds between the metal and the other ligands. The unstable M-R bond is especially weakened, causing that bond to become more reactive to olefin insertion. Conversely, electron withdrawing groups on Cp increase the positive charge on the metal, strengthening the bonds between the metal and the other ligands and causing the M-R bond to be less reactive.\(^35\)

The ability to "tune" the electronic character of Cp ligands is important in designing catalysts that produce polyolefins with desirable activities and physical properties. Polymerization studies in our laboratories with pentafluorophenyl-substituted zirconocene dichlorides show that as the electron withdrawing character of the ligand increases, the catalytic activity decreases, the average molecular weight of the polymer decreases, and the amount of 1-hexene incorporation in a copolymerization increases.

This chapter focuses on the synthesis of two tetrafluoropyridyl-substituted zirconium dichlorides and explores the effect of the tetrafluoropyridyl substituent on the polymerization of ethylene and the copolymerization of ethylene and 1-hexene.

**Results and Discussion.** Substitution reactions of sodium tetrafluoropyridyl-cyclopentadienyl ligands with $\text{ZrCl}_4(\text{THF})_2$ or $\text{CpZrCl}_3(\text{DME})$ in toluene at 110 °C for 15 hours yield the corresponding zirconocene dichlorides 13 and 14 (Scheme 15). Both metallocenes were obtained in good yield (around 65%), which indicates that the tetrafluoropyridyl substituent does not impede the formation of a group 4 metallocene. Other (as yet unpublished) results in our laboratories suggest that some pentafluorophenyl-substituted and indenyl ligands do not readily form complexes with titanium or zirconium via ligand substitution reactions such as those shown in Scheme 15. The white solid products were purified by washing with hexanes to remove any unreacted hydrolyzed ligand. These compounds slowly decompose when exposed to air and must be stored in a glovebox.
**Scheme 15**

\[
\begin{align*}
\text{ZrCl}_4(\text{THF})_2 & + 2 \text{Na}^+ \text{C}_5\text{F}_4\text{N}^- \rightarrow \text{C}_5\text{F}_4\text{N} \text{ZrCl}_3(\text{THF}) + 2 \text{NaCl} + 2 \text{THF} \\
\text{CpZrCl}_3(\text{DME}) & + \text{Na}^+ \text{C}_5\text{F}_4\text{N}^- \rightarrow \text{C}_5\text{F}_4\text{N} \text{ZrCl}_3(\text{DME}) + \text{NaCl} + \text{DME}
\end{align*}
\]

13 and 14 are characterized using $^1$H and $^{19}$F NMR spectroscopy. The $^1$H NMR spectra of both complexes show two peaks around 7 ppm in a 1:1 ratio that corresponds to the hydrogens on the substituted Cp ring. The structures may be differentiated, however, by the peak representing the 5 unsubstituted Cp ring hydrogens in 14 that occurs farther upfield. $^{19}$F NMR spectra of each complex show two peaks in a 1:1 ratio, as is expected.

The new arylated metallocenes (13 and 14) were used as catalyst precursors in several olefin polymerization reactions. The resulting polymerization data was compared to results already obtained in our laboratories using precatalysts F, G and H. All polymerizations were conducted using the same reaction conditions so that accurate comparisons could be made.

Ethylene homopolymerization was conducted with precatalyst 13, with MAO as the cocatalyst. The polyethylene produced was a white, brittle solid. Table 5 shows the resulting average catalytic activity and molecular weight distribution ($M_w/M_n$) for polymerizations using 13, F, and G. The activities reported below represent the average rates of reaction over the entire duration of the polymerization. Activities of at least $10^7$ at 50 °C are needed to be industrially viable. $M_w/M_n$, also called the polydispersity index (PDI), is a measure of the breadth of the molecular weight distribution. $M_w/M_n$ values of around 2.0 are typical for a metallocene-catalyzed ethylene polymerization, and $M_w/M_n$
values of below 1.1 are typical for some of the newer "living" single-site catalysts. Importantly, precatalyst 13 does not behave as expected. Although a slightly lower activity is expected, the activity observed for 13 is lower than that of F and G by a factor of 100. The polydispersity of the polyethylene made using 13 is very broad, due to a bimodal molecular weight distribution (Figure 8). This bimodal molecular weight distribution suggests that more than one different kind of catalyst is active in the polymerization process, and that 13 may be decomposing during activation or polymerization to produce these unexpected results.

**Table 5: Ethylene Homopolymerization Results.**

<table>
<thead>
<tr>
<th>Precatalyst</th>
<th>Activity$^a$</th>
<th>$M_W/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>$6.6 \times 10^4$</td>
<td>63</td>
</tr>
<tr>
<td>F</td>
<td>$5.3 \times 10^6$</td>
<td>2.5</td>
</tr>
<tr>
<td>G</td>
<td>$1.4 \times 10^6$</td>
<td>2.6</td>
</tr>
</tbody>
</table>

$^a(g\text{ of polymer})/[(\text{mol Zr})*p(\text{C}_2\text{H}_4)*h]$  

Ethylene/1-hexene copolymerizations were performed using precatalysts 13 and 14. The resulting copolymers were colorless, rubbery solids. The activities, polydispersities, and comonomer incorporations (mole %) found using these complexes were compared to precatalysts F, G, and H (Table 2). Precatalyst 14 follows the expected trends, giving a slightly lower activity and higher 1-hexene incorporation. Precatalyst 13, however, has an activity that is dramatically lower than that of F or G, and the polydispersity of the copolymer is large, due again to a bimodal molecular weight distribution (Figure 9). The 1-hexene incorporation is also lower than expected. Again, these data reveal that the precatalyst 13 may be decomposing under the polymerization conditions.
Table 6: Ethylene/1-Hexene Copolymerization Results.

<table>
<thead>
<tr>
<th>Precatalyst</th>
<th>Activity$^a$</th>
<th>$M_w/M_n$</th>
<th>% 1-hexene</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>4.9 x 10^4</td>
<td>8.4</td>
<td>12</td>
</tr>
<tr>
<td>14</td>
<td>0.4 x 10^7</td>
<td>--</td>
<td>11</td>
</tr>
<tr>
<td>F</td>
<td>2.6 x 10^7</td>
<td>2.5</td>
<td>6</td>
</tr>
<tr>
<td>G</td>
<td>1.0 x 10^7</td>
<td>3.1</td>
<td>13</td>
</tr>
<tr>
<td>H</td>
<td>1.2 x 10^7</td>
<td>--</td>
<td>7</td>
</tr>
</tbody>
</table>

$^a$(g of polymer)/[(mol Zr)*p(C_2H_4)*h]

For use as ethylene or ethylene/1-hexene polymerization catalysts, there is no advantage to the C_5F_4N substituent over the C_6F_5 substituent. 13 and 14 both give comonomer incorporations of about 12%, which is similar to the results using G. Precatalyst G, however, is much more active and yields polymers with lower polydispersities.

**Conclusions.** Tetrafluoropyridyl-substituted zirconocene dichlorides were successfully synthesized and characterized. The polymerizations using these precatalysts were interesting but offered no practical advantages over the corresponding C_6F_5-substituted metallocenes. As a result, no other zirconocene dichlorides were made using the disubstituted Cp ligands, and no additional polymerization experiments were conducted.
Figure 8. GPC trace for polyethylene produced using 13 as catalyst
Figure 9. GPC trace for an ethylene-1-hexene copolymer produced using 13 as catalyst.
Chapter 6: Experimental

**General Procedures.** Standard inert-atmosphere techniques were used for all reactions. Pentafluoropyridine, FeBr₂, Mn(CO)₅Br, and Re(CO)₅Br were used as received from Aldrich. NaH was purchased as a 60% mineral oil dispersion from Aldrich, washed with hexanes, dried under vacuum, and stored in a glovebox. NaCp was made by the reaction of freshly distilled cyclopentadiene and NaH in THF. NMR spectra were recorded on a Varian Unity 400 or JEOL Eclipse 500 instrument. THF-d₈ was vacuum-transferred from Na/K alloy. Infrared spectra were recorded on a Midac M-series instrument operating at 1 cm⁻¹ resolution. Elemental analyses were performed by Desert Analytics (Tucson, AZ).

**Crystallography of Tricarbonyl[η⁵-1,3-bis(tetrafluoropyridyl)cyclopentadienyl]-manganese(I).** Glass-like yellow multicrystalline needles with poorly defined faces were crystallized by slow evaporation of hexanes. A single crystal (~0.4x0.3x0.2 mm³) was cut from a needle cluster, mounted on a glass fiber with epoxy, and centered on the goniometer of a Siemens (Bruker) P4 diffractometer. Unit cell parameters were determined by least squares refinement of 37 reflections that had been automatically centered on the diffractometer.³⁷ The Laue symmetry and systematic absences were consistent with the orthorhombic space group P₂₁₂₁₂₁. The structure was solved by direct methods and refined using the SHELXTL-NT v. 5.10 program package.³⁸ The final refinement involved an anisotropic model for all non-hydrogen atoms. All hydrogen atom parameters were refined independently.

**Crystallography of Tricarbonyl[η⁵-(tetrafluoropyridyl)cyclopentadienyl]rhenium(I).** One large colorless plate (5 x 5 x .4 mm³) was grown by slow evaporation of a toluene solution at room temperatures. The crystal was cut, mounted on a glass fiber with epoxy, and centered on the goniometer of a Siemens (Bruker) P4 diffractometer. Unit cell parameters were determined by least squares refinement of 41 reflections that had been automatically centered on the diffractometer.³⁷ Intensity data were collected, processed³⁷ and corrected for absorption.³⁸ The structure was solved by direct methods and refined

using the SHELXTL NT v5.10 program package.\(^{38}\) Unit cell dimensions were consistent with the triclinic system, and the space group \(P\bar{1}\) was assigned. The final refinement involved an anisotropic model for all non-hydrogen atoms. All hydrogen atom parameters were refined independently. The program package SHELXTL-NT was used for the ensuing molecular graphics generation.\(^{38}\)

**Electrochemical Measurements.** Single-sweep cyclic (CV) and Osteryoung square-wave (OSWV) voltammograms were obtained for 10 and 11 at nominal concentrations of about 2 mM in \(\text{CH}_2\text{Cl}_2\) using 0.10 M tetra(n-butylammonium) hexafluorophosphate at the electrolyte and activated alumina as an internal desiccant. The apparatus was a BioAnalytical Systems BAS-100B automated digital potentiostat with a platinum disk working electrode, a platinum wire auxiliary electrode, and an \([\text{Ag|AgCl}]\) reference electrode. The cell was purged thoroughly with argon prior to measurement. CV sweeps were initialized at 0 mV, scanned to +1800 mV, and reversed to 0 mV, at a scan rate of 100 mV s\(^{-1}\). Wave parameters (|\(E_{\text{ox}} - E_{\text{red}}|, I_c/I_{a}\)) similar to internal ferrocene suggested substantially reversible Fe\(\text{II}\)|Fe\(\text{III}\) couples for 10 and 11. Shifts in oxidation potential relative to internal ferrocene were obtained using OSWV. The cell voltage was swept from 0 mV to 1700 mV with a step resolution of 4 mV, a square-wave amplitude of 25 mV, a frequency of 15 Hz, and 256 samples per point. Voltammograms were analyzed using BAS100W software, version 2.0.\(^{39}\) We thank Prof. Karen J. Brewer for the use of her electrochemical equipment.

**\(\text{Tetrafluoropyridyl)cyclopentadiene (1)}\).** Sodium cyclopentadienide (9.6 g, 0.11 mol), and NaH (3.8 g, 0.16 mol) was stirred in 150 mL of THF. Pentafluoropyridine (10.5 g, 0.062 mol) was slowly added to the flask by syringe. The mixture was stirred under reflux for 15 h. The mixture was cooled, and the THF was evaporated. Hexanes (100 mL) was added to the residue, and the sides of the flask were scraped with a spatula. An ice-cold 20% aqueous \(\text{NH}_4\text{Cl}\) solution (100 mL) was then added to the mixture to hydrolyze any unreacted NaH, and the mixture was stirred for 20 min. The organic layer was separated, and the aqueous layer was extracted with additional hexanes. The organic


layers were combined and dried over MgSO 4 . The mixture was filtered through alumina and evaporated to afford 9.6 g (0.045 mol, 72%) of a pale yellow solid. $^1$H NMR (400 MHz, CDCl 3 ): $\delta$ 7.56 (m, 1 H), 6.84 (m, 1 H), 6.76 (m, 1 H), 3.62 (m, 2 H). $^{19}$F NMR (376 MHz, CDCl 3 ): $\delta$ -94.10 (ddd, 2 F), -144.04 (ddd, 2 F). $^1$H $^{13}$C NMR: $\delta$ 141.5 (t, $J_{CF} = 8.4$ Hz, CH), 138.95 (t, $J_{CF} = 3.8$ Hz, CH), 133.0 (s, CH), (C missing), 44.2 (t, $J_{CF} = 4.6$ Hz, CH 2 ). Satisfactory elemental analysis was not obtained.

**Sodium (Tetrafluoropyridyl)cyclopentadienide (4).** (Tetrafluoropyridyl)cyclopentadiene (5.44 g, 0.0253 mol) was dissolved in 100 mL THF. This solution was added by pipet to NaH (0.911 g, 0.0380 mol), stirred for two hours at room temperature, and then filtered to remove excess NaH. The filtrate was evaporated, and the product residue was dried overnight in a high vacuum ($10^{-5}$ torr) at 80 °C. Pentane (100 mL) was then added to the residue to extract any unreacted ligand or its dimer. The mixture was filtered, and the product collected on the filter to afford a 71% yield (4.26 g, 0.0180 mol) of a tan solid after drying. $^1$H NMR (400 MHz, THF-d 8 ): $\delta$ 6.69 (m, 2 H), 6.02 (m, 2 H). $^{19}$F NMR (376 MHz, THF-d 8 ): $\delta$ -98.7 (m, 2 F), -148.58 (m, 2 F).

**1,3-Bis(tetrafluoropyridyl)cyclopentadiene (2).** Sodium cyclopentadienide (1.23 g, 0.0140 mol) and NaH (2.3 g, 0.096 mol) was stirred in 100 mL of THF. Pentafluoropyridine (5.11 g, 0.0302 mol) was added to the flask slowly by syringe. The mixture was stirred and refluxed for 4 days. The solvent was evaporated, and dichloromethane (100 mL) was added to the residue. An ice-cold 20% aqueous NH 4 Cl solution (100 mL) was then added to the mixture to hydrolyze any unreacted NaH, and the biphasic mixture was stirred for 30 min. The biphasic mixture was filtered through Celite, and the organic layer was separated. The aqueous layer was extracted twice with additional dichloromethane, and the organic layers were combined and dried over anhydrous magnesium sulfate. The mixture was then filtered through alumina and evaporated to afford a yellow solid. $^1$H-NMR analysis showed that the solid comprised a mixture of C 5 F 4 N-substituted cyclopentadienes. The solid was dissolved in 15/85 ethyl acetate/hexanes and was loaded onto a (4 cm x 30 cm) column of silica gel, which was eluted with the same ethyl acetate/hexanes mixture. The first band eluted from the column afforded 1,3-bis(tetrafluoropyridyl)cyclopentadiene (1.16 g, 3.19 mmol, 23%) as a pale yellow solid. NMR analysis revealed the presence of two hydrogen shift isomers.
in a 5:1 ratio. Data for major isomer 2a: $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 7.70 (m, 2 H), 4.26 (m, 2 H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$): $\delta$ -91.34 (m, 4 F), -139.27 (m, 4 F). Data for minor isomer 2b: $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 7.84 (s, 1 H), 7.49 (m, 1 H), 3.96 (s, 2 H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$): $\delta$ -90.63 (m, 2 F), -91.48 (m, 2 F), -139.88 (m, 2 F), -140.61 (m, 2 F). Anal. Calcd for C$_{15}$H$_4$F$_8$N$_2$: C, 49.47; H, 1.11; N, 7.69. Found: C, 49.38; H, 0.93; N, 7.70.

1,2-Bis(tetrafluoropyridyl)cyclopentadiene (3). From the chromatographic separation described above, a second band was eluted to yield 1,2-bis(tetrafluoropyridyl)-cyclopentadiene (0.80 g, 2.20 mmol, 15%). NMR analysis revealed the presence of two hydrogen shift isomers in a 3.5:1 ratio. Data for 3a: $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 7.01 (dt, $J$ = 5.2, 2 Hz, 1 H), 6.82 (dt, $J$ = 5.2, 1.2 Hz, 1 H), 3.80 (s, 2 H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$): $\delta$ -90.20 (m, 2 F), -90.52 (m, 2F), -141.83 (m, 2 F), -142.42 (m, 2 F). Data for 3b: $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 7.07 (s, 2 H), 3.62 (s, 2 H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$): $\delta$ -89.51 (m, 4 F), -140.77 (m, 4 F). Anal. Calcd for C$_{15}$H$_4$F$_8$N$_2$: C, 49.47; H, 1.11; N, 7.69. Found: C, 49.55; H, 0.92; N, 7.70.

Sodium 1,3-Bis(tetrafluoropyridyl)cyclopentadienide (5). A solution of 1,3-bis(tetrafluoropyridyl)cyclopentadiene (1.5 g, 0.0041 mol) in THF (20 mL) was added slowly by pipet to 1.5 g of NaH (0.062 mol). The mixture was stirred for 4 h at 25 °C, and then filtered to remove excess NaH. The filtrate was evaporated. Pentane (50 mL) was added to the residue to dissolve unreacted 1,3-bis(tetrafluoropyridyl)-cyclopentadiene, and the mixture was stirred for 30 min. The mixture was filtered, and the precipitate was washed twice with 15 mL of pentane and dried to afford 1.18 g of a bright yellow solid (0.00306 mol, 75%). $^1$H NMR (500 MHz, THF-d$_8$): $\delta$ 7.54 (septet, $J$ = 2 Hz, 1 H), 6.69 (m, 2 H). $^{19}$F NMR (470 MHz, THF-d$_8$): $\delta$ -100.32 (m, 4 F), -149.29 (m, 4 F).

Sodium 1,2-Bis(tetrafluoropyridyl)cyclopentadienide (6). A solution of 1,2-bis(tetrafluoropyridyl)cyclopentadiene (0.41 g, 0.0011 mol) in THF (20 mL) was added slowly by pipet to 1.1 g (0.046 mol) NaH. The mixture was stirred for 4 h at 25 °C and then filtered to remove excess NaH. The filtrate was evaporated. Toluene (20 mL) was added to the residue, and the mixture was stirred for 30 min. The mixture was filtered,
and the precipitate was washed with 10 mL of toluene and then dried. A brown solid was obtained (0.28 g, 0.72 mmol, 65%). $^1$H NMR (500 MHz, THF-$d_8$): $\delta$ 6.49 (d, $J = 3.5$ Hz, 2 H), 6.05 (t, $J = 3.5$ Hz, 1 H). $^{19}$F NMR (470 MHz, THF-$d_8$): $\delta$ -99.90 (m, 4 F), -149.76 (m, 4 F).

**Tricarbonyl[$\eta^5$-(tetrafluoropyridyl)cyclopentadienyl]manganese(I) (7Mn).** A mixture of Mn(CO)$_5$Br (0.23 g, 0.87 mmol), sodium (tetrafluoropyridyl)cyclopentadienide (4, 0.23 g, 0.97 mmol), and THF (30 mL) was stirred under reflux for 24 h. The THF was evaporated, and the residue was dissolved in 40 mL of hot toluene. The solution was filtered, and the toluene was then removed by evaporation to afford a bright orange solid. This solid was then purified by column chromatography using a 1 inch x 10 inch column of silica gel with toluene as the mobile phase. The initial band afforded 0.22 g of a yellow solid (0.630 mmol, 75%). IR (decane): $\nu_{CO}$ (cm$^{-1}$) = 2035 (A$_1$), 1959 (E). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.80 (s, 2 H), 3.90 (s, 2 H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$): $\delta$ -91.78 (m, 2 F), -140.86 (m, 2 F). Satisfactory elemental analysis was not obtained.

**Tricarbonyl[$\eta^5$-(tetrafluoropyridyl)cyclopentadienyl]rhenium(I) (7Re).** A mixture of Re(CO)$_5$Br (0.23 g, 0.57 mmol), sodium (tetrafluoropyridyl)cyclopentadienide (0.145 g, 0.612 mmol), and THF (30 mL) was stirred under reflux for 24 h. The THF was then evaporated, and the resulting crude product was dissolved in 30 mL of hot toluene. The solution was filtered, and the solvent was evaporated. The product was purified by column chromatography using a 1 inch x 10 inch silica gel column and eluted using toluene, followed by further purification by recrystallization from a hexanes/toluene mixture to afford 0.11 g of a white solid (0.23 mmol, 37%). IR (decane): $\nu_{CO}$ (cm$^{-1}$) = 2037 (A$_1$), 1951 (E). $^1$H NMR (360 MHz, CDCl$_3$): $\delta$ 6.16 (s, 2 H), 5.52 (s, 2 H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$): $\delta$ -89.87 (m, 2 F), -140.46 (m, 2 F). Anal. Calcd for C$_{13}$H$_4$F$_4$NO$_3$Re: C, 32.24; H, 0.83; N, 2.89. Found: C, 32.48; H, 0.54; N, 2.86.

**Tricarbonyl[$\eta^5$-1,3-bis(tetrafluoropyridyl)cyclopentadienyl]manganese(I) (8Mn).** A mixture of Mn(CO)$_5$Br (0.146 g, 0.531 mmol), sodium 1,3-bis(tetrafluoropyridyl)-cyclopentadienide (0.20 g, 0.52 mmol), and THF (30 mL) was stirred under reflux for 24 h. The solvent was then evaporated, and the residue was dissolved in 30 mL of hot
toluene. The solution was filtered, and the toluene was evaporated to afford an orange solid. The product was recrystallized from a hexanes/toluene mixture to afford 0.10 g of a bright yellow solid (0.20 mmol, 38%). IR (decane): $\nu_{\text{CO}}$ (cm$^{-1}$) = 2041 (A$_1$), 1974, 1968 (E). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.35 (s, 1 H), 5.77 (s, 2 H). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -91.10 (m, 4 F), -141.22 (m, 4 F). Anal. Calcd for C$_{18}$H$_3$F$_8$N$_2$O$_3$Mn: C, 43.05; H, 0.60; N, 5.58. Found: C, 43.05; H, 0.33; N, 5.49.

**Tricarbonyl[η$^5$-1,3-bis(tetrafluoropyridyl)cyclopentadienyl]rhenium(I) (8Re).** A mixture of Re(CO)$_5$Br (0.24 g, 0.60 mmol), sodium 1,3-bis(tetrafluoropyridyl)cyclopentadienide (0.23 g, 0.59 mmol), and THF (25 mL) was stirred under reflux for 24 h. The solvent was evaporated, and the residue was dissolved in 25 mL of hot toluene. The solution was filtered, and the toluene was then evaporated. The crude product was further purified by dissolving it in toluene and filtering it through alumina. 0.12 g of a colorless viscous oil was obtained (0.19 mmol, 40%). IR (decane): $\nu_{\text{CO}}$ (cm$^{-1}$) = 2043 (A$_1$), 1964, 1961 (E). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.86 (s, 1 H), 6.29 (s, 2 H). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$): $\delta$ -88.96 (m, 4 F), -139.96 (m, 4 F).

Elemental analysis was not obtained.

**Tricarbonyl[η$^5$-1,2-bis(tetrafluoropyridyl)cyclopentadienyl]manganese(I) (9Mn).** A mixture of Mn(CO)$_5$Br (0.11 g, 0.40 mmol), sodium 1,2-bis(tetrafluoropyridyl)cyclopentadienide (0.31 g, 0.80 mmol), and THF (25 mL) was stirred under reflux for 24 h. The solvent was evaporated, and the residue was dissolved in 25 mL of hot toluene. The solution was filtered, and the toluene was evaporated to afford an orange solid. This solid was recrystallized twice from a toluene/hexanes mixture to afford 0.10 g of a yellow solid (0.20 mmol, 50%). IR (decane): $\nu_{\text{CO}}$ (cm$^{-1}$) = 2041 (A$_1$), 1972, 1965 (E). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.43 (d, $J = 3.5$ Hz, 2 H), 5.12 (t, $J = 3.5$ Hz, 1 H). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -88.56 (m, 4 F), -137.26 (m, 4 F). Anal. Calcd for C$_{18}$H$_3$F$_8$N$_2$O$_3$Mn: C, 43.05; H, 0.60; N, 5.58. Found: C, 43.31; H, 0.49; N, 5.58.

**Tricarbonyl[η$^5$-1,2-bis(tetrafluoropyridyl)cyclopentadienyl]rhenium(I) (9Re).** A mixture of Re(CO)$_5$Br (0.25 g, 0.66 mmol), sodium 1,2-bis(tetrafluoropyridyl)cyclopentadienide (0.26 g, 0.64 mmol), and THF (50 mL) was stirred under reflux for 24 h. The solvent was evaporated, and the resulting crude product was dissolved in hot
toluene (50 mL). The solution was filtered, and the toluene was evaporated to afford a pale yellow solid. This solid was recrystallized from a hexanes/toluene mixture to afford 0.23 g of a white solid (0.36 mmol, 57%). IR (decane): $\nu_{\text{CO}}$ (cm$^{-1}$) = 2043 (A$_1$), 1964, 1956 (E). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.99 (d, $J = 3.5$ Hz, 2 H), 5.68 (t, $J = 3$ Hz, 1 H). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -87.93 (m, 4 F), -136.95 (m, 4 F). Anal. Calcd for C$_{18}$H$_3$F$_8$N$_2$O$_3$Re: C, 34.13; H, 0.48; N, 4.42. Found: C, 33.65; H, 0.21; N, 4.27.

1,1'-Bis(tetrafluoropyridyl)ferrocene (10). A mixture of iron(II) bromide (0.300 g, 1.39 mmol), sodium (tetrafluoropyridyl)cyclopentadienide (0.34 g, 1.43 mmol), and THF (50 mL) was stirred under reflux for 24 h. The solvent was evaporated, and toluene (50 mL) was added to the crude product. The mixture was then heated and filtered. The toluene was evaporated, and the crude product was recrystallized from a hexanes/toluene mixture to afford 0.23 g of a red solid (0.48 mmol, 66%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.97 (s, 4 H), 4.57 (s, 4 H). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -91.88 (m, 4 F), -141.86 (m, 4 F). Anal. Calcd for C$_{20}$H$_8$F$_8$N$_2$Fe: C, 49.62; H, 1.67; N, 5.79. Found: C, 49.81; H, 1.44; N, 5.83.

1,1',3,3'-Tetrakis(5-tetrafluoropyridyl)ferrocene (11). A mixture of iron(II) bromide (0.061 g, 0.28 mmol), sodium 1,3-bis(tetrafluoropyridyl)cyclopentadienide (0.17 g, 0.44 mmol), and THF (25 mL) was stirred under reflux for 5 h. The solvent was evaporated, and the residue was dissolved in 25 mL of toluene. The solution was heated and filtered, and the toluene was evaporated to afford 0.12 g of an orange solid (0.15 mmol, 70%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.68 (s, 2 H), 5.30 (s, 4 H). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -89.64 (m, 8 F), -140.68 (m, 8 F). Anal. Calcd for C$_{30}$H$_{16}$F$_{16}$N$_4$Fe: C, 46.06; H, 0.77; N, 7.16. Found: C, 45.87; H, 0.85; N, 7.24.

1,1',2,2'-Tetrakis[5-(tetrafluoropyridyl)cyclopentadienyl]ferrocene (12). A mixture of iron(II) bromide (0.06 g, 0.3 mmol), sodium 1,2-bis(tetrafluoropyridyl)-cyclopentadienide (0.21, 0.54 mmol), and THF (50 mL) was stirred under reflux for 24 h. The solvent was evaporated, and the residue was dissoluded in 50 mL of toluene. The solution was heated and filtered, and the toluene was evaporated. The resulting solid was purified by recrystallization from a hexanes/toluene mixture to afford 0.07 g of an orange solid (0.09 mmol, 33%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.07 (s, 4 H), 5.03 (s, 2 H). $^{19}$F
NMR (470 MHz, CDCl₃): δ -89.11 (m, 8 F), -139.28, (s, 8 F). Satisfactory elemental analysis was not obtained.

**Dichlorobis[η⁵-(tetrafluoropyridyl)cyclopentadienyl]zirconium(IV)** (13). A mixture of ZrCl₄(THF)₂ (1.03 g, 2.73 mmol), sodium (tetrafluoropyridyl)cyclopentadienide (1.23 g, 5.19 mmol) and toluene (400 mL) was stirred at 110 °C for 3.5 h. The hot solution was filtered, and the filtrate was evaporated. Hexane (200 mL) was added to the crude product, and the mixture was stirred for 1 h and then filtered. The white solid was collected on the filter and dried (0.99 g, 1.7 mmol, 65%). ¹H NMR (500 MHz, THF-­d₈): δ 7.20 (m, 2 H), 6.91, (t, J = 2.5, 2 H). ¹⁹F NMR (470 MHz, THF-­d₈): δ -93.63 (m, 4 F), -141.76 (m, 4 F). Elemental analysis was not obtained.

**Dichloro(cyclopentadienyl)[η⁵-(tetrafluoropyridyl)cyclopentadienyl]zirconium(IV)** (14). A mixture of CpZrCl₃(DME) (1.23 g, 3.49 mmol), sodium (tetrafluoropyridyl)-cyclopentadienide (0.79 g, 3.33 mmol) and toluene (400 mL) was stirred at 110 °C for 2.5 h. The hot solution was filtered, and the toluene was evaporated. Hexane (200 mL) was added to the crude product, and the mixture was stirred for 1 h and then filtered. The white product was collected on the filter and dried (1.07 g, 2.43 mmol, 69%). ¹H NMR (500 MHz, THF-­d₈): δ 7.56 (s, 2 H), 7.10 (m, 2 H), 6.60 (s, 5 H). ¹⁹F NMR (470 MHz, THF-­d₈): δ -94.93 (m, 2 F), -144.00 (m, 2 F). Elemental analysis was not obtained.

**Polymerization studies.** All catalyst activations and polymerizations were conducted as described below. The [(C₅F₄N)Cp]₂ZrCl₂ precatalyst is used as an example. In a glove box, 20.2 mg of precatalyst was weighed into a 10-mL volumetric flask and toluene was added to give a 0.00342 M precatalyst stock solution. 1.53 mL of this stock solution was injected by syringe into a separate 10-mL volumetric flask containing 603 mg of solid MAO. The flask was filled with additional toluene to give a 0.00053 M solution. This solution was stirred for 20 minutes, after which 9.0 mL of the activated Zr/MAO solution was loaded into a syringe. The reactor was a 1-L glass vessel fitted with a thermal resistor, motorized stir bar, condenser, gas dispersion tube, and septum. The reactor was dried in an oven for at least 24 h before use, evacuated (50 mtorr), and refilled with nitrogen. Dry, deoxygenated toluene was added to the reactor under nitrogen flow from a pressurized solvent column. The reactor was placed in a temperature regulated water bath and stirring was begun. When the temperature equilibrated to 50 °C, 50 mg of solid
MAO was added under a nitrogen purge to scavenge any unwanted moisture. In a copolymerization, 20 mL of freshly distilled 1-hexene was then added by syringe through the septum. Ethylene was bubbled into the solution and exhausted to an oil bubbler. When the temperature of the reactor equilibrated to 50 °C, the 9 mL of the Zr/MAO solution was injected through the septum. After 10 minutes the polymerization was terminated by injecting 20 mL of acidified methanol (5% HCl). In a copolymerization, the polymerization mixture was rotary-evaporated until about 20 mL of liquid was left, to which 150 mL of acidified methanol (5% HCl) was added to precipitate any dissolved polymer. In a homopolymerization, the polymerization mixture was added directly to 300 mL of the acidified methanol solution. The mixture was then filtered, and the polymer collected on a Buchner funnel. The polymer was dried in a vacuum oven (50 mtorr) at 80 °C for 24 h.

The $^{13}$C NMR spectra of the copolymer samples were obtained at 120 °C in 10-mm tubes using a trichlorobenzene/1,1,2,2-tetrachloroethane-$d_2$ (95:5) solvent mixture. Hexene incorporation (mol%) was determined according to the method described by Randall. GPC analysis was done at Dow Chemical using a Waters Alliance GPCV 2000 instrument. 15 ± 1.0 mg of the sample was dissolved in 13.0 mL of 1,2,4-trichlorobenzene containing 300 ppm w/w Ionol (used as a marker). The solutions were shaken at 160 °C for 2 h and then filtered. A flow rate of 1.0 mL/min. was used at a temperature of 50 °C. The injector was set to inject 200 μL at 135 °C. The columns were heated to 135 °C and included Polymer Laboratories 10 μm Mixed B, SN 10 M-Mixed B-113-158, 131-55 and 131-57. A refractive index detector was used.

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Vita

Andrea Warren was born and raised in Suffolk, Virginia. She is the daughter of Henry George and Nancy Warren, both of Suffolk. She received her Bachelor of Science in chemistry in 1999 from the College of William and Mary, where she did research under Dr. David Thompson. In August 2001 she received her Master of Science degree in chemistry from Virginia Tech.