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**INVESTIGATION OF ELECTRON TRANSFER
FROM CARBONYLMETALLATE ANIONS
TO ELECTRON ACCEPTORS**

by

Joseph Kofi Agyin

**A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Arts
Department of Chemistry**

**Western Michigan University
Kalamazoo, Michigan
June 1993**

INVESTIGATION OF ELECTRON TRANSFER
FROM CARBONYLMETALLATE ANIONS
TO ELECTRON ACCEPTORS

Joseph Kofi Agyin, M.A.

Western Michigan University, 1993

This study investigated electron transfer potential of the carbonyl-metallate anions cyclopentadienylirondicarbonyl and methylcyclopentadienyliron-dicarbonyl anions to the electron acceptors 2,2-dinitropropane, 1,1-dinitrocyclohexane, α ,p-dinitrocumene, methyl cyclopentadienylmercury(II) chloride and iodide.

The findings from this study indicated that: (a) the expected products could not be obtained from reactions of the anions with the dinitro-substrates, and (b) the mercurials reacted with the anions but the expected products, (ferrocene and methylferrocene), was the minor product and an unexpected (methyl) cyclopentadienylirondicarbonylmercury(II)-chloride or iodide was the major product.

ACKNOWLEDGEMENTS

I wish to express my thanks and appreciation to my research advisor, Dr. William Kelly for his assistance and direction throughout this study.

My appreciation is expressed to the Chemistry Department, Western Michigan University for its financial support during my course of study.

Last, but not the least, my deepest gratitude and thanks are expressed to my wife, Christie, for her love and encouragement needed to bring this work to completion.

Joseph Kofi Agyin

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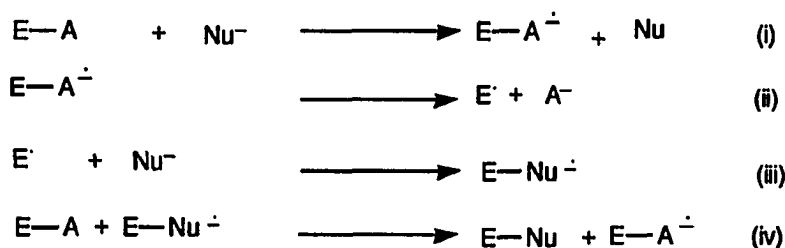
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BACKGROUND OF PROBLEM

Electron transfer chain substitution (ETCS) reactions have been studied extensively since their discovery in 1966. During this time the synthetic potential of these processes have been demonstrated. In particular, ETCS reactions are noteworthy because of the ease with which C-C bonds may be formed. In most cases the ETCS reactions occur cleanly, under mild conditions and with good yields of products. Also, because these reactions are rather insensitive to steric hindrance, they make possible the synthesis of highly branched C-C bonds which are unobtainable by other routes. The ETCS reaction is known to proceed via a multi-stage sequence involving radicals and radical anions. This process is summarized in scheme I.



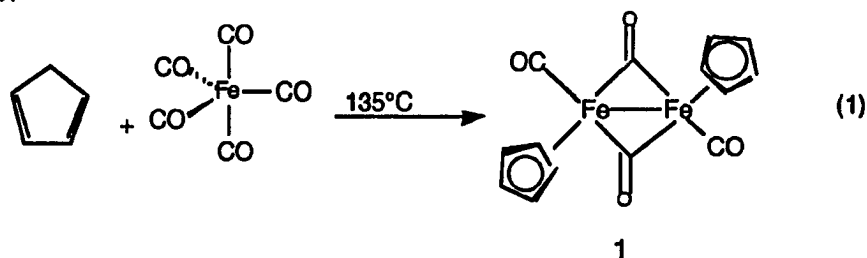
Scheme I

Common electron acceptor substrates involved in aliphatic ETCS reactions are α ,p-dinitrocumenes, gem-dinitroalkanes, α -nitro-halides, nitriles, -esters and -sulfones; as well as perfluoroalkyl iodides. The nucleofuge is the nitro group or the iodide. The nitro group is a good electron acceptor because it has low-lying Lowest Unoccupied Molecular

Orbitals (LUMO). The ETCS process is observed when electron donor nucleophiles such as azides, cyanide, selenates, sulfinates, thiolates, enolates, and nitronates are employed.

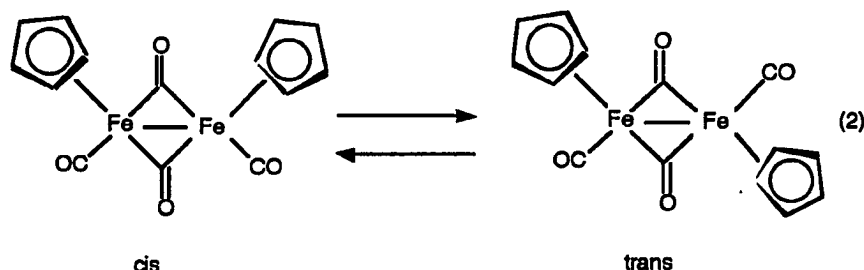
This research has been concerned with two fundamental questions: how widespread are reactions which proceed by ETCS pathways and how useful are such processes in synthesis? Accordingly, an attempt has been made to investigate the potential ETCS ability of a class of anions heretofore not studied in this regard: carbonylmetallate anions.

A carbonylmetallate anion which we have been particularly interested in studying is the cyclopentadienylirondicarbonyl anion, $(C_5H_5)Fe(CO)_2^-$. The $(C_5H_5)Fe(CO)_2^-$ anion is obtained by reductive cleavage of the dimer, $Cp_2Fe_2(CO)_4$ (1) ($Cp = C_5H_5$). Compound (1) is obtained by reacting ironpentacarbonyl with cyclopentadiene, as shown in eq. 1.



The product, $[C_5H_5Fe(CO)_2]_2$, has a structure which contains some unusual features. First, it contains both terminal and bridging carbonyl (CO) groups. Second, the diamagnetism of the compound and the short Fe-Fe distance indicate the presence of a metal-metal bond. The preceding structure (1) has been established in the solid state. The

$\text{Cp}_2\text{Fe}_2(\text{CO})_4$ molecule exists in solution as a mixture of cis and trans isomers with bridging CO groups, as shown in equation 2.



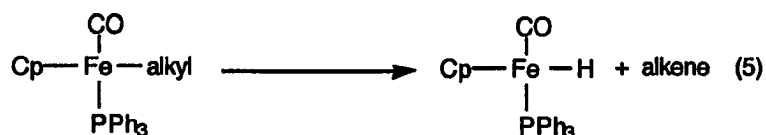
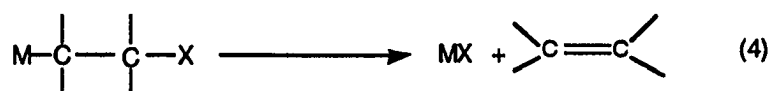
$^1\text{H NMR}$ resonances for the rings should appear at different positions and, this is observed at $-70\text{ }^\circ\text{C}$. However, at $28\text{ }^\circ\text{C}$ only a single sharp signal at the intermediate position is seen. Clearly, between $-70\text{ }^\circ\text{C}$ and room temperature, the rate by which the cis and trans isomers become interconverted becomes very rapid. This process cannot be a simple rotation because of the central rigid ring system. The NMR spectrum of the ^{13}C atoms of the CO groups shows that the cis-trans interconversion is accompanied by interchange of the CO groups between the bridging and terminal positions. The explanation for both these processes is that the CO bridges open in a concerted way to give a nonbridged $\text{Cp}(\text{OC})_2\text{Fe}-\text{Fe}(\text{CO})_2\text{Cp}$ intermediate in which rotation about Fe-Fe bond takes place. This rotation is followed by a reclosing of bridges. This may happen to produce either a cis or trans isomer, regardless of which one was present before ring opening.⁴

Like many organometallic compounds which contain metal-metal bonds, they may be reduced with metallic sodium to the monomeric

anions.² Thus sodium amalgam reduces tetrahydrofuran (THF) solutions of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ to the very air sensitive $\text{CpFe}(\text{CO})_2^-$, (eq. 3).



One of the distinctive properties of various binary carbonylmetallate anions is their nucleophilic character. Toward alkyl halide electrophiles, the reactivities span a range of more than 10^6 from $\text{Co}(\text{CO})_4^-$ to $\text{CpFe}(\text{CO})_2^-$ as listed in Table I.⁵ Reactions of carbonylmetallates such as $\text{CpFe}(\text{CO})_2^-$ with alkyl halides occur readily, although the alkyl derivative is not always formed. In some cases, the instability of the alkyl derivative (e.g; to β elimination) may be the cause of the failure to form stable alkyl derivatives. Formally, β -elimination involves cleavage of a β -bond in an organometal to produce unsaturation, equations 4 and 5.



Chemical studies with cyclopropylmethyl derivatives show that there is also a direct pathway, probably involving $\text{S}_{\text{N}}2$ displacement⁵ for the alkylation of $\text{CpFe}(\text{CO})_2^-$.



In other cases, electron transfer processes may be operative. For example, the observation of the electron spin resonance (esr) spectrum of the tropyli radical during the reaction with CpFe(CO)_2^- is most readily accommodated in this way.

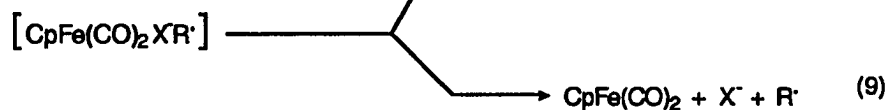
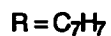
Table 1

Nucleophilicity of Metallate Anions Toward Alkyl Halides;
Relationship With Oxidation Potentials

Metallate Anion	$k_{\text{rel}}^{\text{b}}$	$-E_{1/2}$
CpFe(CO)_2^-	7×10^7	2.2
Re(CO)_5^-	2.5×10^4	2.3
CpW(CO)_3^-	$\sim 5 \times 10^2$	-
Mn(CO)_5^-	77	1.7
CpCr(CO)_3^-	4	1.3
Co(CO)_4^-	1.00	1.0

^a Data reported by R.E. Dessy et al; J. Amer. Chem. Soc; 1966,88, 5121.

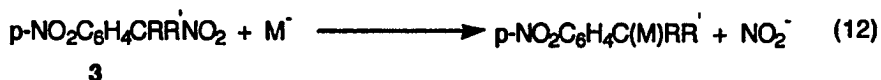
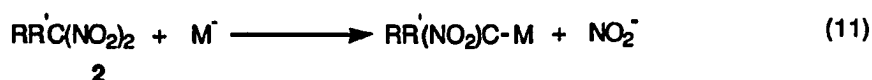
^b These relative nucleophilicities were measured electrochemically in 1,2-dimethoxyethane solution in the presence of tetrabutylammonium perchlorate. The nucleophilicity of Co(CO)_4^- is arbitrarily taken as 1.



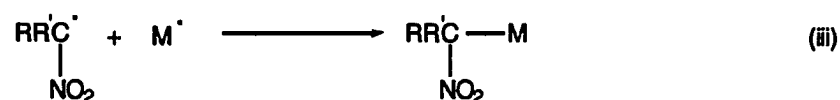
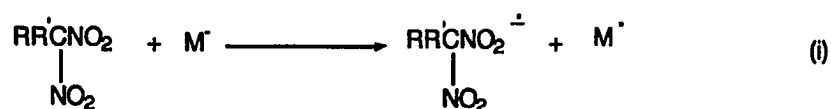
In these examples, the alkylated products are known to be stable thermally, and the radicals cannot arise via a secondary process such as the subsequent homolysis of the alkyl-iron bond.

INTRODUCTION TO RESEARCH

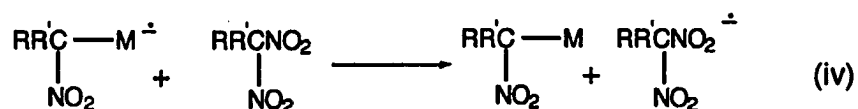
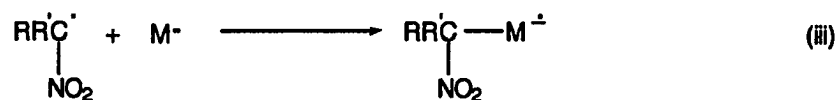
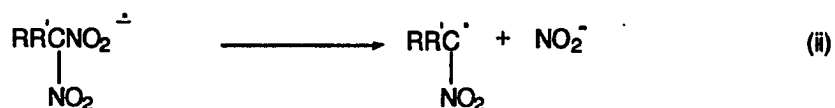
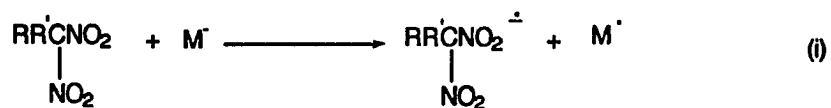
We planned to investigate whether carbonylmetallate anions can replace a nitro group in gem-dinitroalkanes **2** and α ,p-dinitrocumene **3**, and if so whether a chain or non-chain process is involved.



Compounds such as **2** and **3** have been known to rapidly undergo ETCS reactions with various anions. $\text{S}_{\text{N}}2$ displacement of a hindered nitro group is an extremely unlikely process. The substrates are easily reduced (reduction potentials -1.5V) and there is a correlation between rate of electron transfer and substrate reduction potential. Thus the initial electron transfer should occur even when metallate anions with less negative oxidation potentials are employed. Once initiated, the reaction should follow one of two possible pathways -a simple radical coupling leading to product, i.e.; scheme II; or an ETCS radical-anion mechanism, scheme III.



Scheme II

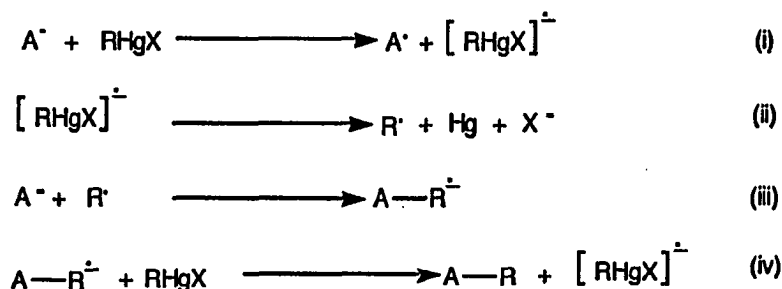


Scheme III

It has been reported that organomercury halides will participate in free-radical chain reactions as shown below.¹¹



The reaction proceeds via a multi-stage sequence involving radicals and radical anions. The process is summarized in Scheme IV.



Scheme IV

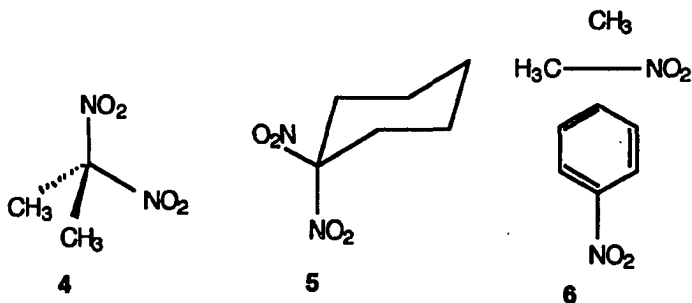
With this idea in mind, we have also sought to investigate the reaction of $\text{CpFe}(\text{CO})_2^-$ with the organomercurial compound, RHgX ($\text{R} = \text{C}_5\text{H}_5$). Should the reaction proceed as proposed above, then we expect to have a coupling between $\text{CpFe}(\text{CO})_2^-$ and the alkyl group of the mercurial to form $\text{CpFe}(\text{CO})_2\text{-R}$. This should decompose by established pathways to the very stable ferrocene.

The reaction may go by a chain or non-chain pathway. Chain or a non-chain processes can be differentiated by employing standard techniques developed for ETCS reactions. A radical process will be greatly affected by even small amounts of a scavenger present. Radical traps such as di-*tert*-butylnitroxide, as well as oxidizing agents such as *p*-dinitrobenzene inhibit ETCS reactions. If the reaction involves a chain

mechanism with a long chain length then even small amounts of inhibitor will have a significant effect. Should no inhibition be observed, the concentration of the inhibitor will gradually be increased. A non-chain radical reactions will require stoichiometric amounts of inhibitor for an effect.

STATEMENT OF PROBLEM

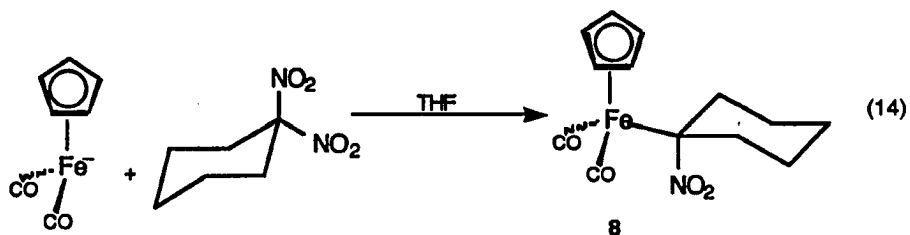
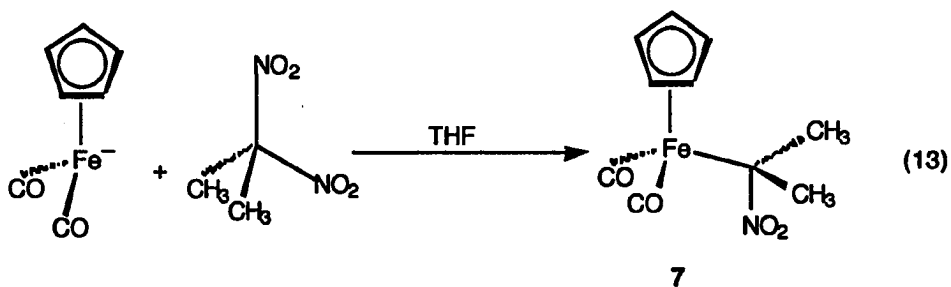
To date, there is no evidence of carbonylmetallate anions reacting with organic substrates by a radical chain process. This work is aimed at investigating the ability of the cyclopentadienylirondicarbonyl anion, $C_5H_5Fe(CO)_2^-$, to undergo possible electron transfer chain substitution (ETCS) reactions. In this regard, the $C_5H_5Fe(CO)_2^-$ anion has been utilized to react with nitro-compounds **4**, **5**, and **6** which are known to be good electron acceptor substrates.

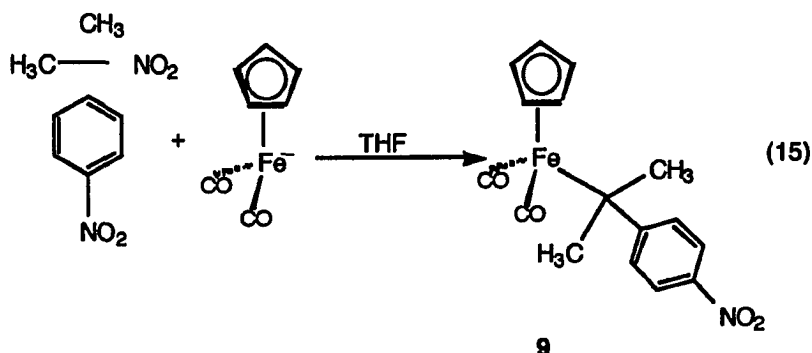


RESULTS AND DISCUSSION

Reaction With Gem-dinitro Substrates

This part of the work was aimed at synthesizing the compounds **7**, **8** and **9** by the reactions indicated below by a modified version of the procedure developed by Robert J. Angelici for alkylation of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2^-$ (equations 13-15).²





The reactions were carried out in a 1000 mL 3-neck round-bottom flask with a stopcock fused to the bottom. An inert atmosphere is provided by a stream of nitrogen gas. Sodium amalgam is prepared by stirring mercury with sodium metal. This reaction was highly exothermic. After the amalgamation is complete and the flask has cooled to room temperature, dry THF is added followed by dicyclopentadienyl diirontetracarbonyl, $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$. The system is then flushed with nitrogen for five minutes. The speed of the stirrer is adjusted with a rheostat until the amalgam is being vigorously mixed with the THF solution. After thirty minutes, the violet color of the $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ solution turns greenish-yellow. The sodium amalgam is then drained off through the stopcock at the bottom of the flask. A THF solution of the nitro-compound is prepared under nitrogen and transferred by a transfer needle slowly into the $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ solution while stirring. After stirring for 12 hours at room temperature, the reaction mixture is transferred into a 500 mL round-bottom flask and rotovaped to dryness.²

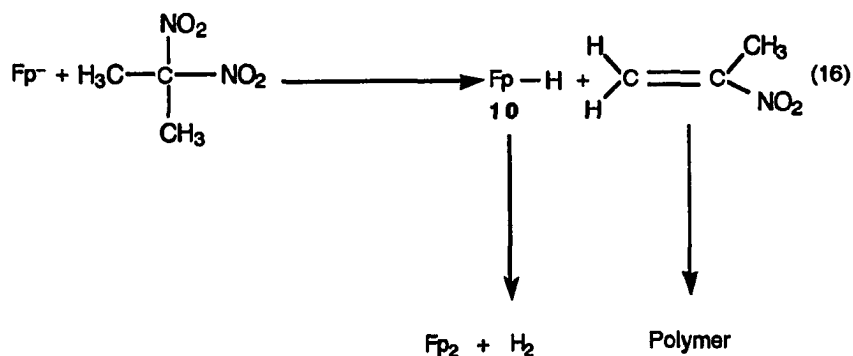
The crude reaction mixture is dissolved in chloroform and run through a column of activity 1 neutral alumina packed in pentane. The column is then developed with benzene followed by chloroform. Any

product obtained is characterized by melting point determination, IR, NMR and GC-MS.

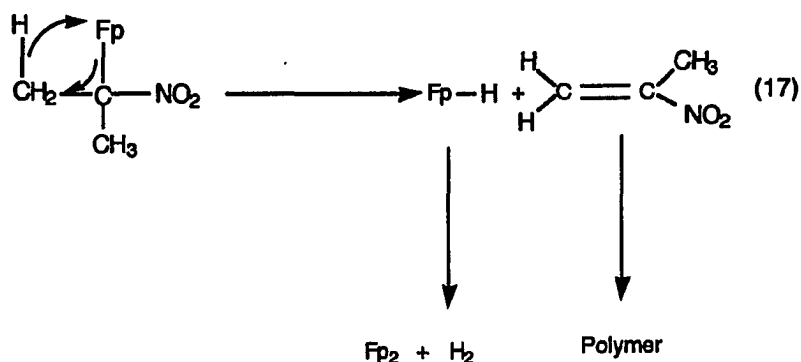
However, in all experiments employing gem-dinitro substrates none of the expected products were obtained. What is obtained is a black greasy material which does not dissolve in common solvents like chloroform, ethanol or acetone. One interesting observation was that even when 1:1 stoichiometric amounts of reactants are used, some $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ is always recovered, while none of the starting nitro-compound is. All the reactions were performed at room temperature and the reaction time was 12 hours.

The fact that none of the expected products were observed in this work could be because the products were unstable under the reaction conditions, as was pointed out in the introduction. Also the formation of the greasy material and the $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ dimer might suggest two things.

The $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2^-$ anion quite possibly acts as a base and abstracts a β -hydrogen to form $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$ (compound **10**) which is known to dimerize readily. After proton abstraction, the 2,2-dinitropropane, for example, can then form 2-nitropropene which can undergo polymerization to form the black greasy material obtained.

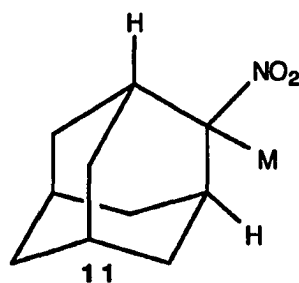


Another possible explanation is that the product does in fact form, but then it reacts further by an intra-molecular β -hydrogen elimination to afford a polymer and the dimer as shown below:



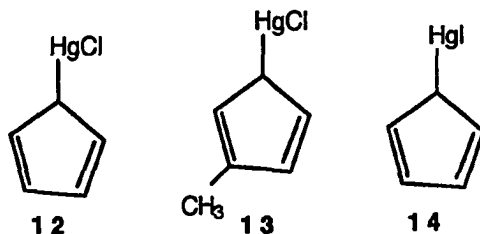
However, from this study, it is inconclusive as to whether or not a reaction takes place to form the expected product. I believe one way by which this can be verified is by forming the 2,2-dinitroadamantyl derivative, **11**.

The extraordinary stability of the bridgehead compound, **11**, eliminates any possibility of a β -elimination and should afford the expected product. In other words the adamantyl system is precluded from forming the double bond which would otherwise violate Bredt's rule.

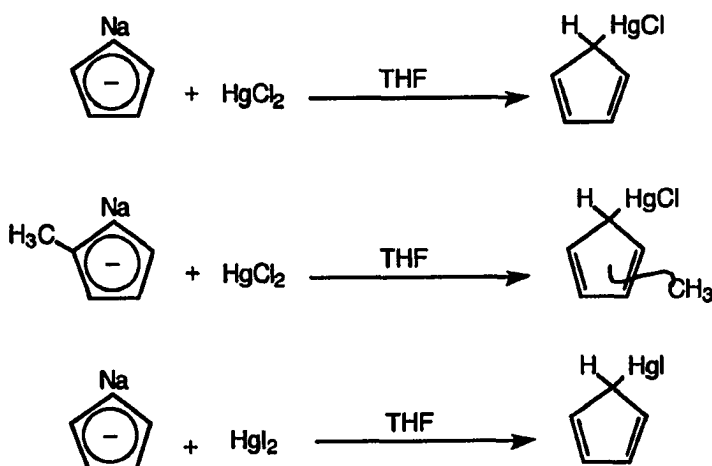


Reactions With Organomercurials

The second area of this research involved the use of alkyl substituted mercury halide salts as the electron acceptor substrates. As mentioned earlier, these compounds are known to be good electron acceptors. Accordingly, we set out to prepare the cyclopentadienylmercury halides **12**, **13**, and, **14**, for use in this in this case. If these mercury halides do indeed undergo a substitution process, then the isolated product should be the very stable ferrocene which can be easily isolated and identified.

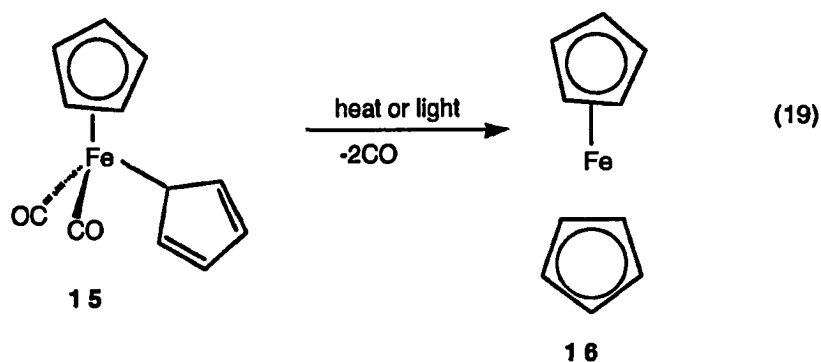
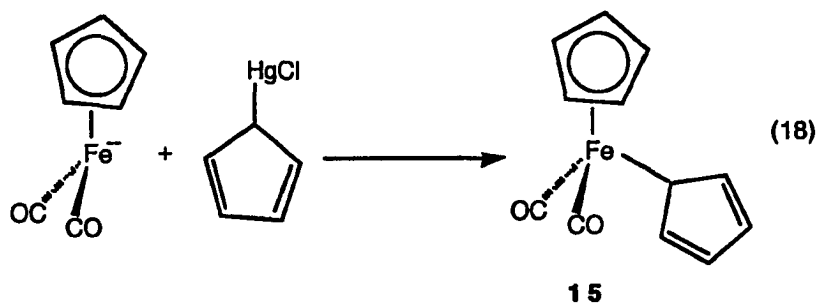


The cyclopentadienylmercury(II) halides were prepared from the reaction of the corresponding mercury(II) halide with a cyclopentadienide anion:

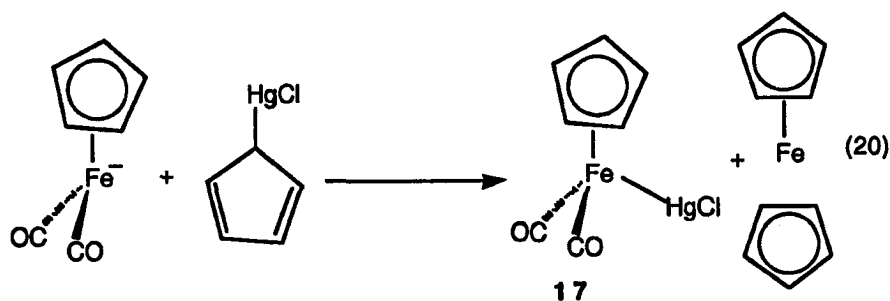


The mercury(II) halide was stirred in tetrahydrofuran (THF) under a nitrogen atmosphere. A solution of the sodium cyclopentadienide in THF was added and the solution was stirred for 2.0 hours under nitrogen. The cyclopentadienylmercury(II) halide was used as prepared $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ prepared as in (I) above was then transferred by needle under nitrogen pressure into the round-bottom flask containing the mercurial compound while stirring. The reaction mixture was allowed to stir for five hours, and then the reaction was quenched by pouring the mixture into cold water. This was then extracted with ether and the ether extract backwashed with water. The ether extract was dried with anhydrous magnesium sulfate for 1 hour, filtered and concentrated to a volume of 5 mL by vacuum distillation. The crude reaction mixture is separated by column chromatography on a column of neutral alumina packed in pentane. The column was eluted in succession with pentane, 5% ether in pentane, 10% ether in pentane, and chloroform. Ferrocenes elute first with pentane while $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgX}$ elutes last with chloroform. Products obtained are characterized as before by melting point determination, NMR, IR and GC-MS.

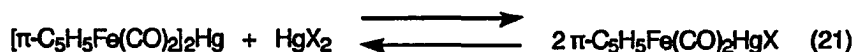
In this part of my work, the $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2$ and the mercury(II) substrate were expected to react according to the Russel²³ reaction to yield the bis-cyclopentadienyl-iron dicarbonyl intermediate (Equation 18). Ferrocene should then form from the bis-cyclopentadienyl-iron dicarbonyl intermediate (compound 15) by decomposition with loss of carbon monoxide, through a thermal or photo-initiated radical process, (equation 19)



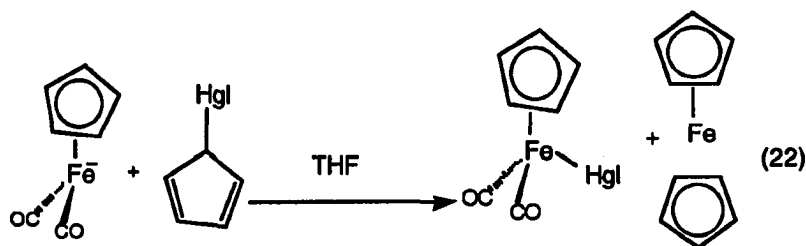
However, the reaction of a 1:1 mole ratio of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2^-$: $\text{C}_5\text{H}_5\text{HgCl}$ (equation 21) afforded only 5.3% of the expected product, ferrocene, and 36% of a rather unexpected compound cyclopentadienylirondicarbonyl-mercuric chloride 17.



Compound **17** was isolated as golden yellow crystals with a melting point of 115 °C. It has two carbonyl (C=O) IR peaks at 2017 cm⁻¹ and 1971 cm⁻¹. It shows a proton NMR peak at 5.14 ppm. The GC-MS spectrum shows a molecular ion peak of 186 indicating that the compound decomposes on the column to form ferrocene. Compounds of π -cyclopentadienyl transition metal-mercury complexes of the type π -C₅H₅Fe(CO)₂HgX (X= Cl, Br, I, or SCN) are reported in the literature.¹⁸ These have been synthesized by exchange between $[\pi$ -C₅H₅Fe(CO)₂]₂Hg and HgX₂ in acetone solution.

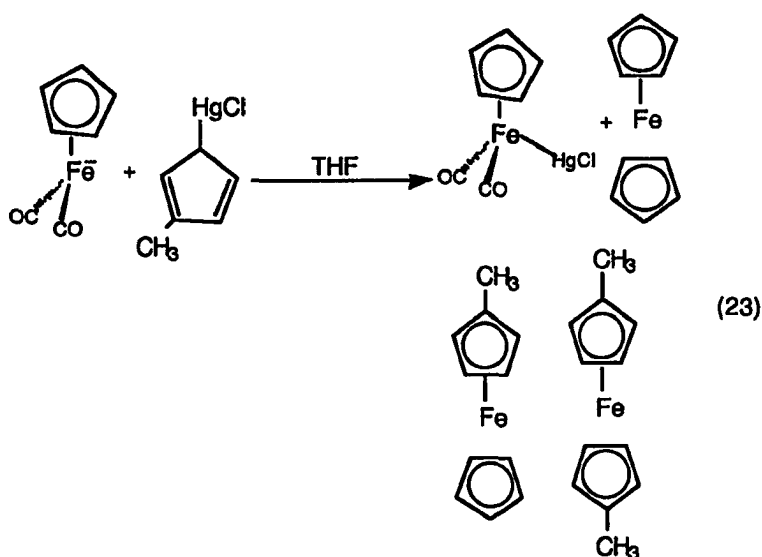


Consistent with reaction 21, the reaction of cyclopentadienyl-iron dicarbonyl anion with cyclopentadienyl-mercury(II)iodide (reaction 22) affords ferrocene and cyclopentadienyl-iron-dicarbonyl-mercury(II)iodide which has a melting point of 117 °C.



Replacement of compound **12** in reaction 20 with methylcyclopentadienylmercuric chloride **13** affords 41% of product **20** and an unexpected mixture of ferrocenes as depicted in reaction 24 below.

Overall, **17** is the major product while the mixture of ferrocenes is the minor. Among the mixture of ferrocenes, 1-methylferrocene, which is the expected product in this reaction, is the major product.



The GC-MS spectra for the mixture of ferrocenes are indicated in Figures 1, 2, and 3.

Reaction of 1-methylcyclopentadienyl-iron dicarbonyl anion **18** with cyclopentadienylmercury(II)iodide (reaction 23) affords 1-methylcyclopentadienyl-iron dicarbonylmercury(II)iodide as the major product (11.2%) and again a mixture of ferrocenes. The relative proportion of the mixture of ferrocenes is as follows: ferrocene (5.7%); 1-methylferrocene (90.7%); 1,1'-dimethylferrocene (3.6%). Another product which was obtained albeit in small yields (<1%) in the organomercurial reactions is the bis-organomercurial, $\text{Fe}_2\text{Hg}(\text{Fe}=\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5)$.

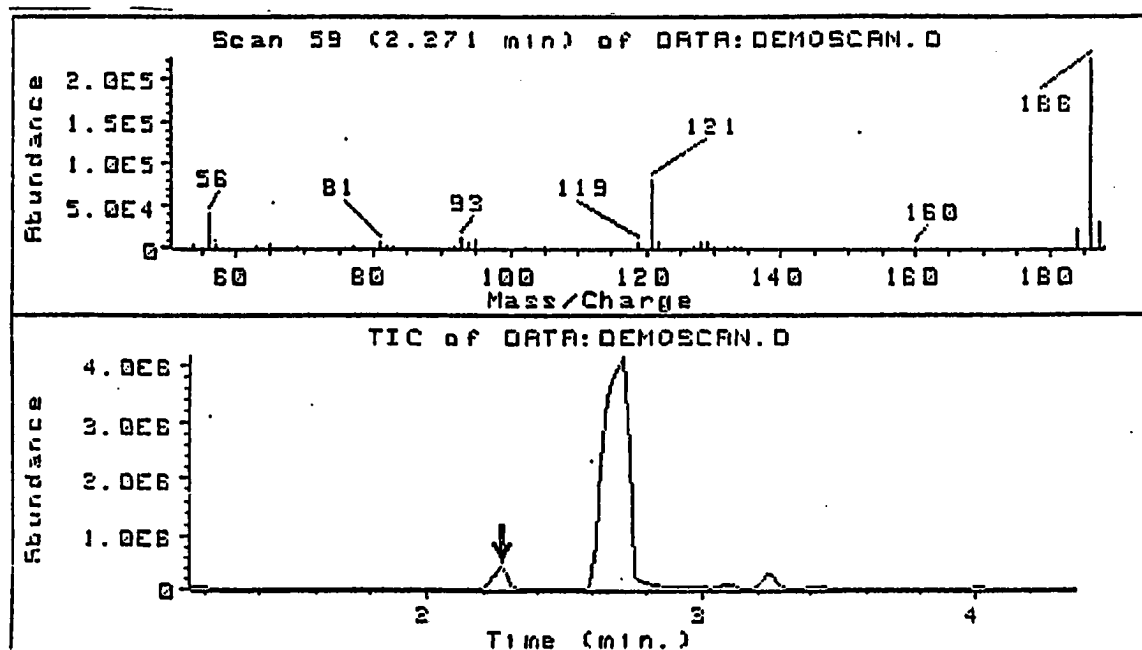


Figure 1. GC-MS of Mixture of Ferrocenes Obtained From Reaction of Fp^- With CpHgCl .

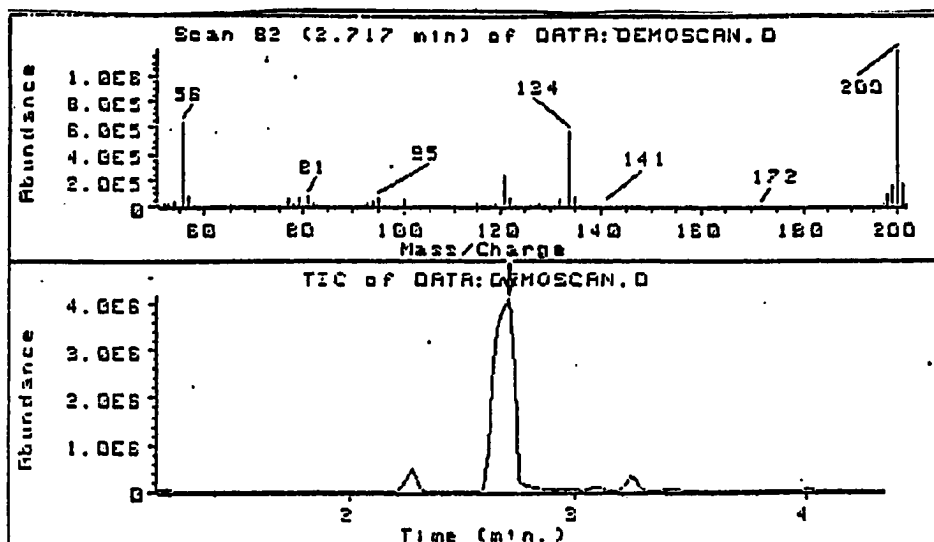


Figure 2. GC-MS of Mixture of Ferrocenes Obtained From Reaction of Fp^+ with MeCpHgCl .

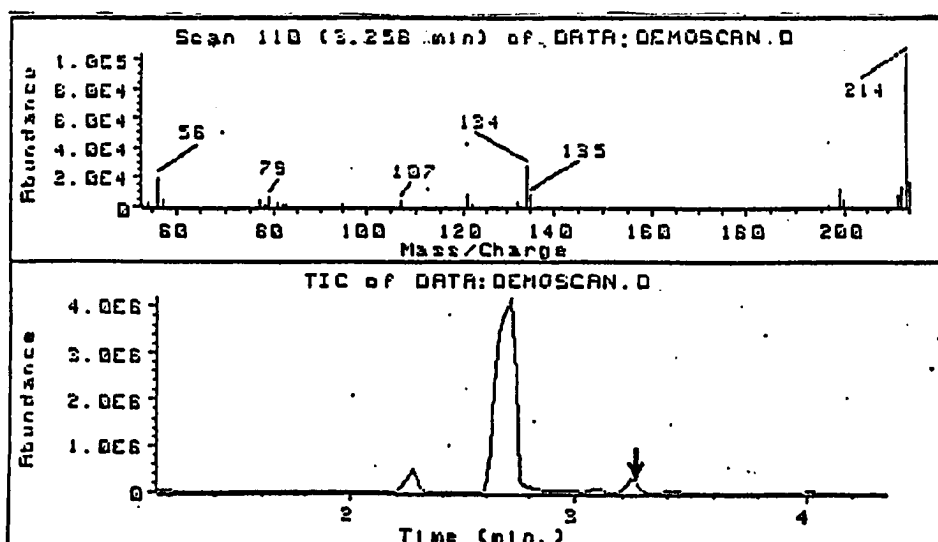
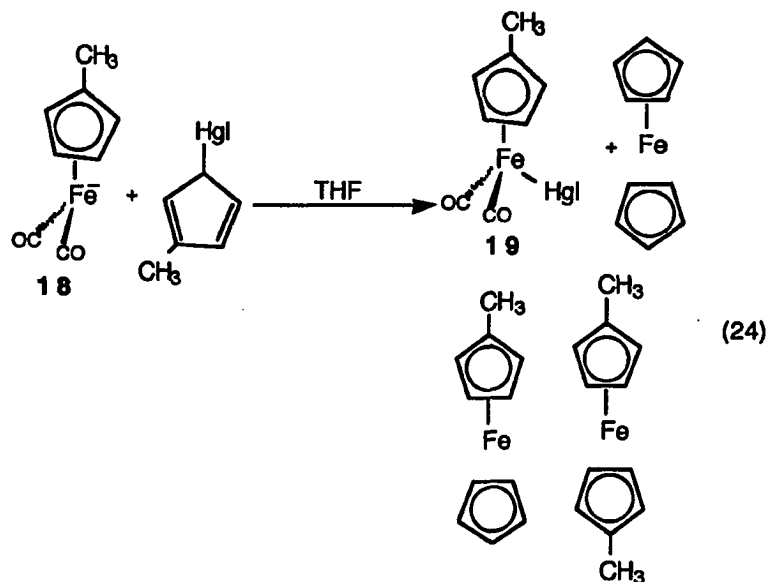
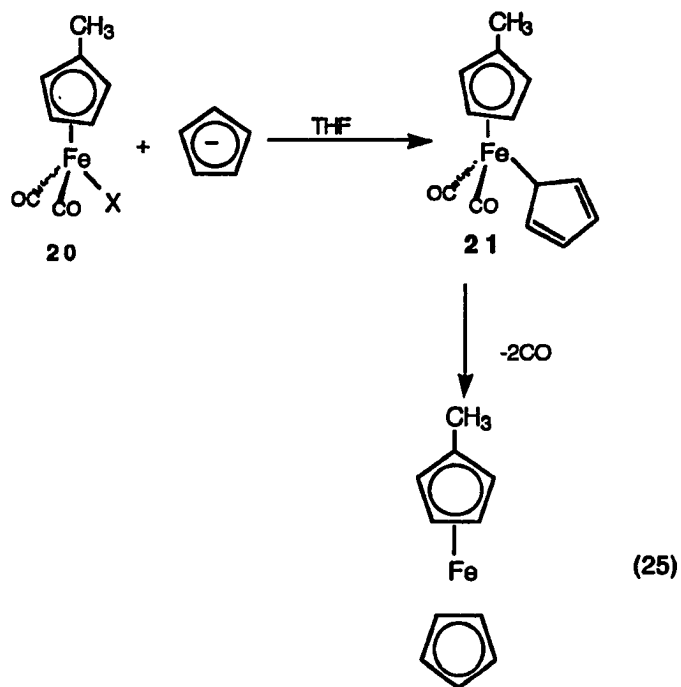
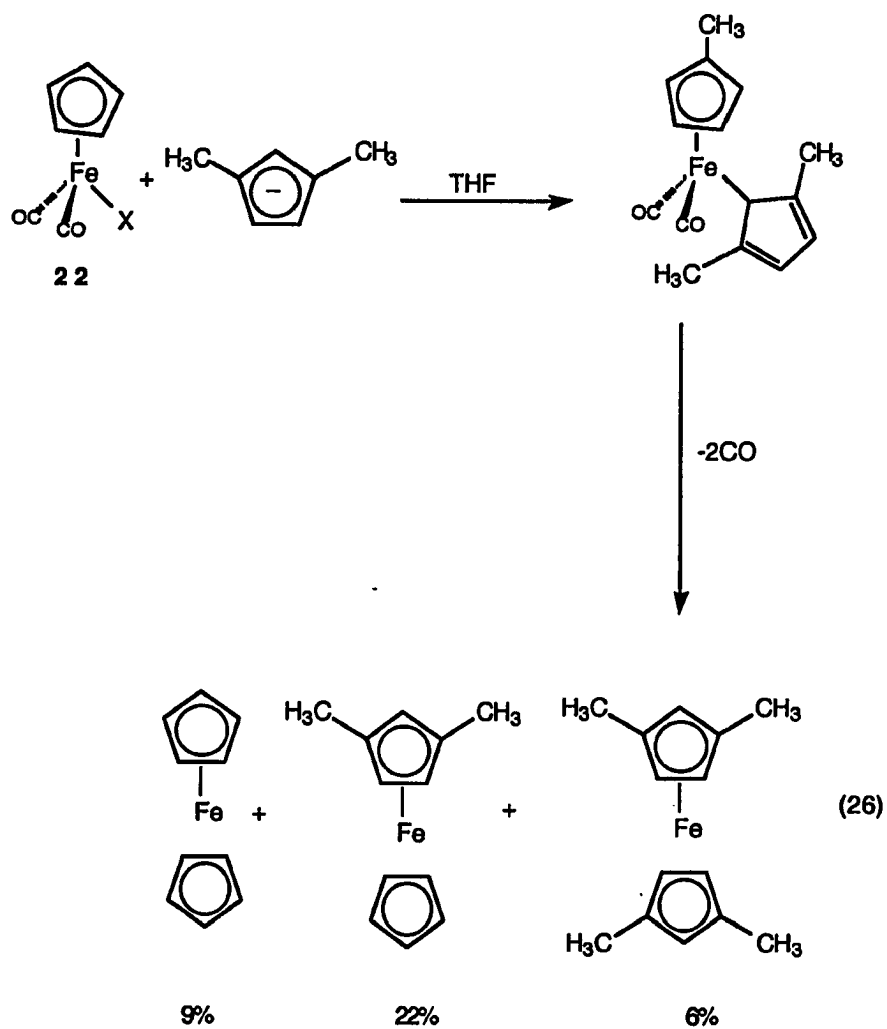


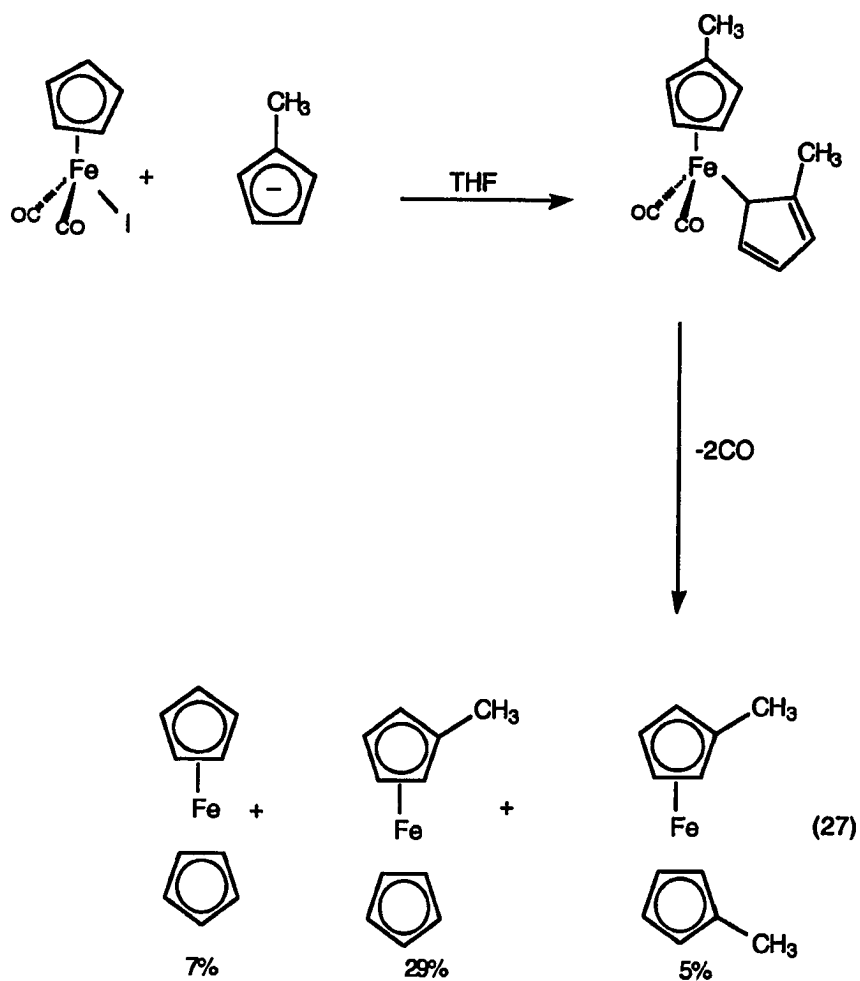
Figure 3. GC-MS of Mixture of ferrocenes Obtained From Reaction of MeFp^+ With CpHgCl .

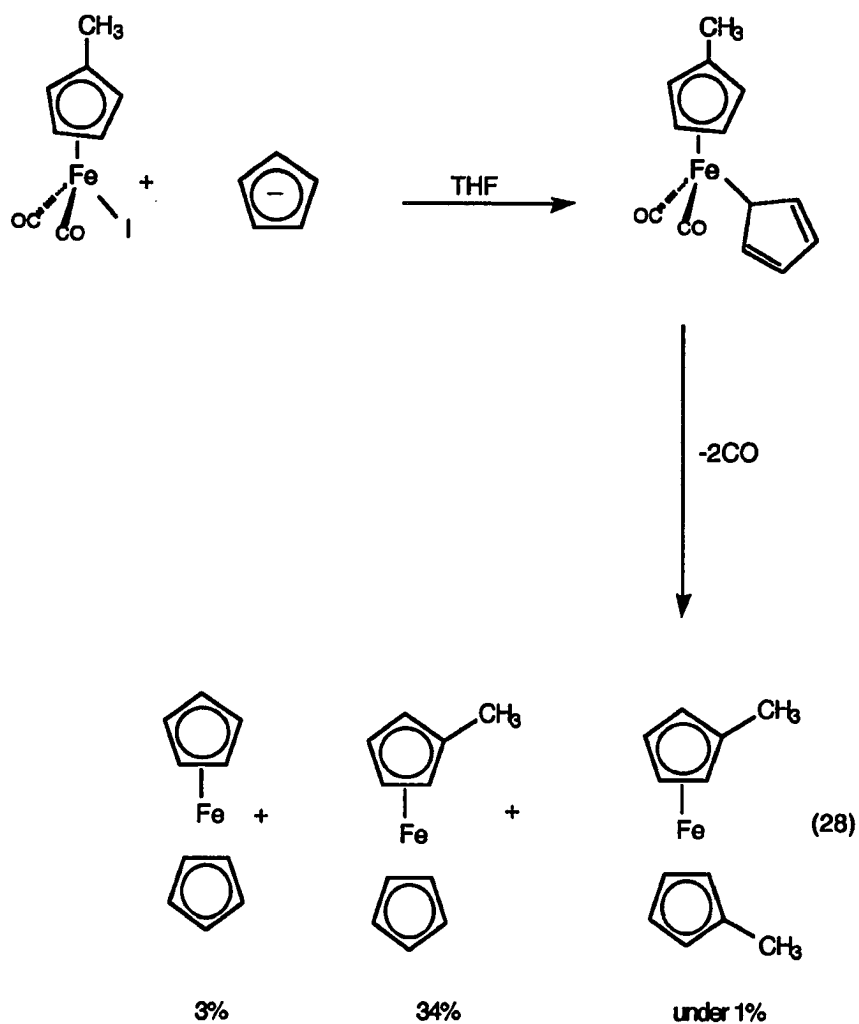


The mixture of ferrocenes obtained in this work bears a striking resemblance to the results of an investigation undertaken previously in our laboratory.²⁵ Seeking an efficient route for the preparation of 1,3-dimethylferrocene, uncontaminated by the 1,1'- and 1,2- regioisomers, the following process developed by Wilkinson was employed. Accordingly, $\text{CpFe}(\text{CO})_2\text{I}$ (compound 20, $\text{X} = \text{I}$) was treated with potassium 1,3-cyclopentadienide, (equation 25). However, Dr. Kelly obtained a mixture of ferrocene products. In addition to the desired 1,3-dimethylferrocene, ferrocene and 1,1',3,3'-tetramethylferrocene were formed in relatively large amounts. Similarly, he also observed that when $\text{CpFe}(\text{CO})_2\text{I}$ was reacted with the anion, methylcyclopentadienide, a mixture of ferrocenes was likewise obtained, (equation 26). When he carried out the inverse of equation 27, that is reacting methylcyclopentadienyl-iron dicarbonyl iodide with the anion Cp^- ferrocene and 1,1'-dimethylferrocene were still observed, albeit in small amounts (equation 28).

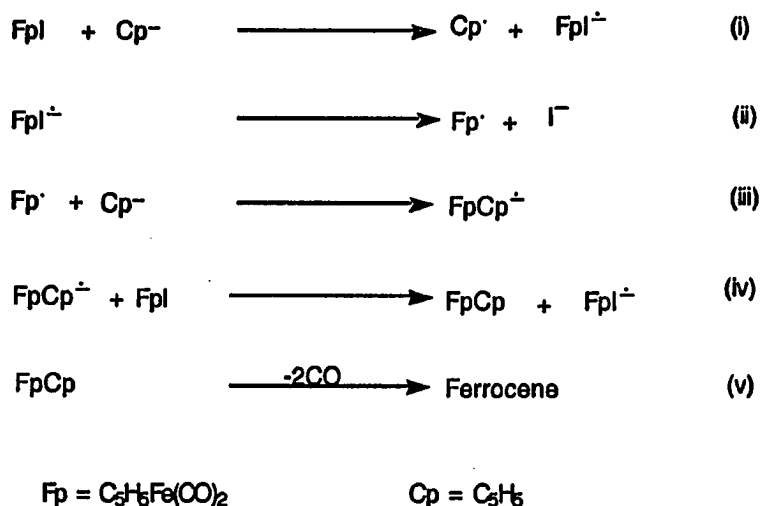








A plausible mechanism for this reaction is outlined in Scheme V.

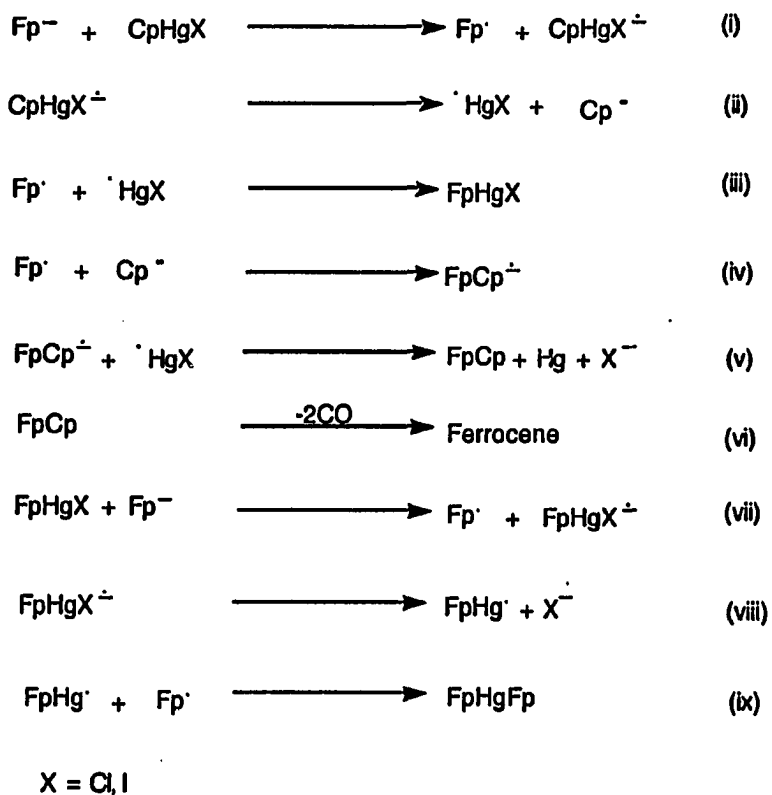


Scheme V

The similarity of the results between the previous work done in this laboratory and this work, with respect to the mixture of ferrocenes when the two different routes are taken suggests a similarity of mechanism. The bis-FpCp (compound **15**) seems to be the common intermediate involved. The products obtained from the above reactions indicate an electron transfer process. These products are consistent with the mechanism proposed in Scheme VI below.

As pointed out in the introduction, the standard way of determining whether or not a reaction proceeds by a chain or a non-chain mechanism is by using a radical trap such as di-tertbutylnitroxide. In this work, reaction is observed in the presence of 5 mole% of di-tertbutylnitroxide. In fact, in the presence of 5 mole% of the above radical trap, 24% of FpHgCl is produced while in the presence of 20 mole% of the trap 20%, of FpHgCl

was produced. Thus there is very little effect of the radical trap on the reaction. My conclusion is that either the reaction involves a non-chain



Scheme VI

process or it is a chain process with an extremely short chain propagation length. The results are summarized in Table 2 below.

Table 2

Effect of di-*tert*-butylnitroxide on Reaction 20 (page 18)

Amount of di- <i>tert</i> -butylnitroxide (mole percent)	Amount of FpHgCl isolated (mass percent)
0	36
5	24
20	20

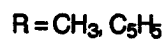
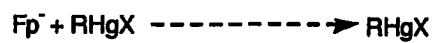
Inhibition studies were also done using various amounts of *m*-dinitrobenzene and the results are shown in Table 3.

Table 3

Effect of *m*-dinitrobenzene on Reaction 20 (page 18)

Amount of <i>m</i> -dinitrobenzene (mole percent)	Amount of FpHgCl isolated (mass percent)
0	36
5	25
20	22

Reaction of the Fp⁻ anion with methylmercuric chloride and phenylmercuric chloride, respectively, were also tried.



In either case, there was no evidence of the expected product.

CONCLUSION

This work has come out with an convenient way by which FpHgX can be synthesized, instead of the alternative method reported in the literature whereby it is produced by a disproportionation reaction between Fp_2Hg and HgX_2 :



Electron transfer from the carbonylmetallate anion Fp^- is still uncertain from this study with the gem-dinitroalkanes. More studies need to be done in this regard, probably with 2,2-dinitroadamantane. However, products obtained from the second part of this work of reaction between Fp^- and the organomercurials suggest electron transfer. On the other hand, the inhibition studies do not support the fact of a free radical chain process. Further studies need to be done in this area too.

EXPERIMENTAL PROCEDURE

All the preparations described below involving the cyclopentadienylirondicarbonyl anion and the dimer, and the organomercurials were carried out in a nitrogen atmosphere. Tetrahydrofuran (THF) was purified before use by distillation in nitrogen over sodium metal. Benzophenone was used as an indicator. The formation of a purple colored solution indicated that the THF solution was completely dry.

Melting points were determined in open capillary tubes using a Unimelt laboratory device and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet 5DXC spectrometer. Nuclear magnetic resonance (NMR) were determined on a Bruker 200 MHz instrument. The gas chromatograph used was a Hewlett Packard 5890 series. It had a crosslinked methyl silicone gum column. Attached to the gas chromatograph was a Hewlett Packard 5970 series mass selective detector.

Cyclopentadienylirondicarbonyl dimer, gem-dinitroalkanes and the alkylmercury halides were prepared as described.

1. Preparation of 2,2-Dinitropropane. This was prepared according to a literature procedure.²³ A mixture of 4.75 g (50 mmol) of 94% 2-nitropropane, 3.00 g (75 mmol) of sodium hydroxide, and 25 mL of water was stirred until a homogeneous solution was formed. Methylene chloride (25 mL) was added and the mixture was cooled with an ice-water bath. A solution of 14.0 g (0.20 mmol) of sodium nitrite in 25 mL of water, and 3.30

g (10 mmol) of potassium ferricyanide in 10 mL of water, were added consecutively with stirring. The reaction temperature rose to 42 °C before subsiding, and the mixture was then stirred for 1 hr at 25 °C. The aqueous layer was separated and was extracted twice with methylene chloride, and the combined organic layers were washed with saturated sodium chloride, dried over magnesium sulfate, and distilled to give 5.50 g (82%) of 2,2-dinitropropane.

2. Preparation of 1,1-Dinitrocyclohexane. This was prepared according to a literature procedure.²⁴ Under nitrogen, nitrocyclohexane (1.24 g, 0.0096 mol) was added to a rapidly stirred solution of sodium hydroxide (0.48 g, 0.012 mol) in methanol (20 mL) and water (25 mL). After 10 min a clear yellow solution was obtained, and this was added, dropwise under nitrogen, in the course of 30 min to give a vigorously stirred solution of potassium ferricyanide (16.25 g, 0.050 mol) and sodium nitrite (6.90 g, 0.100 mol) in water (100 mL) over which pentane (200 mL) had been layered. The reaction mixture was stirred for an additional 60 min, the two phases were separated, and the aqueous phase was extracted twice with 100-mL portions of pentane. The pentane phase and extracts were combined, washed with 100 mL of water, and dried (MgSO₄). Removal of the pentane gave 1.79 g of crude product, which on vacuum distillation gave 1.48 g (88% yield) of VPC-pure 1,1-dinitrocyclohexane as a colorless liquid (bp 77-79 °C, 1.5 mmHg). On standing this crystallized: mp 33-34 °C; ¹H NMR (CDCl₃) δ 1.60 (m, 6 H), 2.50 (m 4 H).

3. Preparation of C₅H₅Fe(CO)₂Na and CH₃C₅H₄Fe(CO)₂Na.

This reaction was carried out in a 250 mL 3-neck round-bottom flask with a

2 mm bore stopcock fused to the bottom, which was equipped with a mechanical stirrer and a condenser. The flask was flushed with a stream of nitrogen for 5 min. With the nitrogen flowing, the condenser was removed and 15 mL of mercury and 1.0 g (43 mmol) of freshly cut sodium metal were put into the flask. The mixture was stirred vigorously for 30 min. After the amalgamation was complete and the flask had cooled to room temperature, 50 mL of dry THF were added and stirring continued for another 5 min. Then 2.5 g (7 mmol) of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ were added. The condenser was replaced and the system was flushed with nitrogen for 5 min and the nitrogen was turned off. The speed of the stirrer was adjusted with a rheostat until the amalgam was vigorously mixed with the THF solution. After 30 min, the solution had turned from violet to greenish-yellow. The amalgam was then drained through the stopcock at the bottom of the flask. This solution was used for subsequent reactions as needed. The bis-dimethyldicyclopentadienyldiiron tetracarbonyl was prepared, as indicated above, from methylcyclopentadiene and iron pentacarbonyl. The dimer was likewise cleaved with sodium amalgam to obtain $\text{CH}_3\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{Na}$.

4. Preparation of α ,p-Dinitrocumene. This follows the literature procedure given by Kornblum.¹³ Under nitrogen, a mixture of 10.1 g (60 mmol) of p-dinitrobenzene and 6.3 g (66 mmol) of the lithium salt of 2-nitropropane²⁴ was dissolved in 95 mL of dimethylsulfoxide (DMSO) and the solution was stirred for 3 hr after which it was poured into ice-water and extracted with benzene. The benzene extract was washed with water and dried (MgSO_4), and the solvent was removed by evaporation.

Chromatography of the crude product followed by two recrystallizations gave 8.15 g of the title compound, mp 67-68 °C.

5. Reaction of $C_5H_5Fe(CO)_2Na$ with 2,2-dinitropropane. 2,2-Dinitropropane (1.9 g) was dissolved in 50 mL of THF under a nitrogen atmosphere. A THF solution of $C_5H_5Fe(CO)_2Na^2$ was transferred by a syringe into the 2,2-dinitropropane solution and allowed to react at room temperature for 12 hr. The crude reaction mixture was suction filtered to obtained 2 g of a black greasy material (possibly a polymer). The solvent was removed from the filtrate and the solid obtained was adsorbed on activity 1 neutral alumina and eluted with benzene to afford 0.5 g of the starting material $[C_5H_5Fe(CO)_2]_2$. There was no evidence of the expected product. When the procedure was repeated with 1,1-dinitrocyclohexane and α,p -dinitrocumene¹³ instead of the 2,2-dinitropropane, again none of the expected products were isolated. Again in this case, a black greasy material was obtained.

6. Reaction of $C_5H_5Fe(CO)_2Na$ with C_5H_5HgCl . A solution of cyclo-pentadienylmercury chloride (14.0 mmol) was prepared by reacting mercury(II) chloride (3.8 g) dissolved in 50 mL of THF with 7 mL of a 2 M solution of C_5H_5Na in THF. The reaction was allowed to run for 2 hr. A THF solution of $C_5H_5Fe(CO)_2Na$ (5.0 g, 14.0 mmoles) was transferred by a needle into the mercurial compound solution and reaction was continued for 5 hr. The reaction mixture was poured into cold water and then extracted with ether. The ether extract was dried with magnesium sulfate, filtered and concentrated to a volume of 5 mL. The products were purified by chromatography on a column of activity 1 neutral alumina. The column was eluted with pentane, 5% ether in pentane, 10% ether in

pentane, and then chloroform. Three products were obtained and they were analyzed by ^1H NMR, IR and GC-MS spectroscopic techniques. The first product was identified as ferrocene (0.14 g 5.3%). A ^1H NMR spectrum of this product showed only one predominant Cp signal at 4.3 ppm. It showed no carbonyl IR signal. GC-MS: r.t. 2.3 min, m/e: 56, 121, 186. A yellow-orange band of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{Hg}$ immediately following the ferrocene band was observed. The mercury derivative was isolated by evaporation of the eluate to give 0.13 g of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{Hg}$. The ^1H NMR spectrum of this product showed a sharp Cp signal at 5.2 ppm. IR(CHCl_3) 1925.4, 1959.4, 1991.0 cm^{-1} . the GC-MS spectrum showed the same peaks as ferrocene, indicating that this compound is relatively unstable and decomposes readily to form ferrocene. A yellow band of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$ was also observed. Evaporation of the chloroform eluate followed by recrystallization from chloroform-pentane afforded 2.1 g (36%) of the golden yellow crystals of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$. It had a melting point of 115 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 4.9S; ^{13}C NMR (CDCl_3) 80 ppm, 207 ppm; IR (CHCl_3) 1971, 2017 cm^{-1} .

7. Reaction of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ with $\text{CH}_3\text{C}_5\text{H}_4\text{HgCl}$. Methylcyclopentadiene (1.12 g, 14 mmol) and potassium hydride (0.34 g) were stirred together in THF (20 mL) for 2 hr. To the THF solution of the resulting $\text{CH}_3\text{C}_5\text{H}_4\text{K}$ was added mercuric chloride (3.8 g, 14 mmol) and the solution was stirred for another 2 hr. A THF solution of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ (14 mmol) was added and the reaction mixture stirred for 5 hr. The reaction mixture was then treated and analyzed as in 2 above. A golden yellow compound 2.4 g (41.2%) was isolated and later identified as compound 17 ($\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$). The NMR and IR spectra were the

same as compound **17** found in 5 above. Also 0.11 g of a yellow solid was obtained. The IR spectrum of this compound in CHCl_3 indicated no carbonyl signal. GC-MS analysis indicated 3 components: (a) r.t. 2.3 min, m/e: 56, 121, 186 identified as ferrocene (39%), (b) rt. 2.7 min, m/e: 56, 121, 134, 200 identified as methylferrocene (57%) and (c) rt. 3.3 min, m/e : 56, 134, 214 identified as 1,1'-dimethylferrocene (10%).

8. Reaction of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ with $\text{C}_5\text{H}_5\text{HgI}$. A solution of cyclopentadienylmercury iodide (5.48 g, 14.0 mmol) was prepared by reacting mercuric iodide (14 mmol), dissolved in 50 mL of THF, with 7 mL of a 2.0 M solution of $\text{C}_5\text{H}_5\text{Na}$ in THF. The reaction was allowed to go for 2 hr. A THF solution of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ (14.0 mmol)² was added to the mercurial solution and stirred for 5 hr. The reaction mixture was poured into 200 mL of cold water and extracted with ether. The ether extract was dried over magnesium sulfate, filtered and concentrated to a volume of 3 mL. The crude products were purified by chromatography on a column of activity 1 neutral alumina and eluted with pentane and chloroform. The hexane eluent upon evaporation produced 0.23 g (8%) of ferrocene: melting point 173-174 °C, ^1H NMR showed a sharp signal at δ 4.3 ppm, GC-MS: r.t. 2.3 min, m/e : 56, 121, 186. It showed no IR signal. The chloroform eluent produced 1.0 g (15%) of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgI}$, **18**, melting point 117°C, ^1H NMR (CDCl_3) : δ 4.9 ppm, IR spectrum (CHCl_3) : 1964, 2010 cm^{-1} .

9. Reaction of $\text{CH}_3\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{Na}$ with $\text{C}_5\text{H}_5\text{HgI}$. The procedure used was the same as that described in 6, except for the use of $\text{CH}_3\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{Na}$ instead of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$. A yellow solid (0.29 g) was obtained which, submitted to GC-MS analysis, was shown to be a

mixture of ferrocene (5.7%), methylferrocene (90.7%), and 1,1'-dimethylferrocene (4%). The major product obtained from this reaction was compound **19**, (0.82 g, 11%), melting point 105 °C. IR spectrum (CHCl_3): 1961.4, 2007.3 cm^{-1} , ^{13}C NMR (CDCl_3) δ 14.0, 78.9, 100, 215 ppm.

10. Reaction of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ with $\text{C}_5\text{H}_5\text{HgCl}$ in the presence of di-*tert*-butylnitroxide. A solution of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ (14 mmol) in THF (50 mL) was added to a solution of cyclopentadienylmercury chloride prepared *in situ* by reacting mercury (II) chloride (3.8 g, 14 mmol), dissolved in THF (50 mL), with 7 mL of a 2 M solution of $\text{C}_5\text{H}_5\text{Na}$ in THF. Five mole% of di-*tert*-butylnitroxide was added. The reaction mixture was stirred for 5 hr and quenched with ice-cold water. It was extracted twice with 30 mL portions of diethyl ether. The combined extracts were dried over MgSO_4 . After evaporating the solvent, the crude reaction mixture was purified by column chromatography. The progress of the reaction was monitored by determining the amount of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$ after 10 min of reaction time. In the presence of 5 mole % of the free radical trap, di-*tert*-butylnitroxide, 1.4 g (24%) of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$ was obtained. Only a small amount of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{Hg}$ (0.05 g) was obtained. However, in the presence of 20 mole % of the inhibitor 1.1 g (20%) of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$ was obtained. There was no evidence of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{Hg}$. Thus in these reactions, no appreciable inhibition was observed.

11. Reaction of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$ with CH_3HgX / $\text{C}_5\text{H}_5\text{HgX}$. A solution of Fp^- (14.0 mmol) in tetrahydrofuran (THF), prepared as in 8 above, was added to a solution of methyl mercuric chloride (3.52 g, 14.0 mmol) in THF (5.0 mL) and stirred for 5 hr. The THF was evaporated and

the crude reaction mixture was transferred to a sublimation probe connected to a high vacuum line. After 15 min there was no evidence of the expected volatile orange waxy compound, $C_5H_5Fe(CO)_2CH_3$, on the cold finger of the sublimation probe. Column chromatography of the crude reaction mixture on activity 1 neutral alumina using hexane afforded Fp_2Hg (1.58 g) and $FpHgCl$ (0.31 g). In the other reaction, C_6H_5HgBr (0.29 g, 14.0 mmol in THF, 15 mL) was added to a THF solution of Fp^- (14.0 mmol) and stirred for 5 hr. The solvent was evaporated and the crude reaction mixture was purified by chromatography on a column of activity 1 neutral alumina and eluted with a gradient of 5% ether in pentane, 10% ether in pentane, and chloroform. A yellow product was obtained, melting point 112-113 °C. IR: 1970 cm^{-1} and 2016 cm^{-1} ; 1H NMR 4.89 ppm; ^{13}C NMR: 80.23 ppm, 206 ppm. Less than 1% of Fp_2Hg was obtained. There was no evidence of the expected compound, $FpHgC_6H_5$.

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