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Reductive Cleavage of Cyclopentadienylmanganese Tricarbonyl

Mani S. Iyer

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**REDUCTIVE CLEAVAGE OF CYCLOPENTADIENYL-
MANGANESE TRICARBONYL**

by

Mani S. Iyer

**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
December 1991**

REDUCTIVE CLEAVAGE OF CYCLOPENTADIENYL- MANGANESE TRICARBONYL

Mani S. Iyer, M.A.

Western Michigan University, 1991

Since the isolation of ferrocene in 1951, it has been shown to behave like benzene and may be acylated, sulfonated, metalated, and arylated. Like benzene, it also resists hydrogenation.

Daniel Trifan and Louis Nicholas (1957) were the first to show that ferrocene can be smoothly degraded by lithium and ethylamine. The isolation of free cyclopentadienyl ion on hydrolysis of the reaction mixture indicates that the cleavage leads initially to cyclopentadienyl lithium salt. A similar procedure applied to cyclopentadienylmanganese tricarbonyl also resulted in the formation of cyclopentadienyl lithium salt. This, when added to ferrous chloride, gave ferrocene. This technique can be expanded to other π -bonded cyclopentadienyl-metal complexes.

ACKNOWLEDGEMENTS

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Last, but not the least, my deepest gratitude, thanks and appreciation are extended to my parents, my brother, and my sisters, for their love, support, sacrifice, and encouragement needed to bring this study to completion.

Mani S. Iyer

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
LIST OF TABLES	iv
CHAPTER	
I. INTRODUCTION	1
Methods of Ferrocene Synthesis	1
Properties	2
II. INTRODUCTION TO RESEARCH	18
III. RESULTS AND DISCUSSION	21
Conclusion	39
IV. EXPERIMENTAL PROCEDURES	42
REFERENCES	56

LIST OF TABLES

1. Relative Rates of Friedel-Crafts Acetylation of Aromatic Compounds.....	6
2. Qualitative Rates of Reduction of Ferrocene.....	10
3. GC-MS Data of Various Cp-Metal Complexes.....	30
4. Reductive Cleavage of Various Cp-Metal Complexes.....	40

CHAPTER I

INTRODUCTION

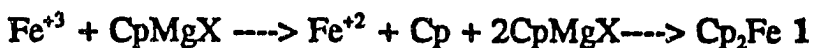
The ligands which formally contribute five electrons when bonded to a transition metal are called dienyl ligands. The most important dienyl ligand is the cyclopentadienyl group (Cp). The first cyclopentadienyl compound of a transition metal to be reported in 1951 was ferrocene¹. It is generally represented by $(C_5H_5)_2Fe$ and also written as $Fe(Cp)_2$. Ferrocenes are sandwich compounds, in which the Fe is sandwiched between two planar Cp groups. These compounds are generally known as metallocenes and their study is an important part of organometallic chemistry. Ferrocene was independently prepared by two different research groups².

Methods of Ferrocene Synthesis

By Oxidation of Cp Grignard Reagent

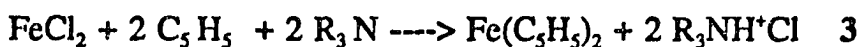
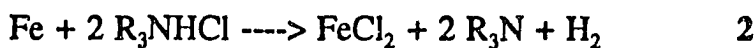
An attempt to synthesize fulvalene by oxidation of the cyclopentadienyl Grignard was unsuccessful; instead, a stable orange compound was isolated which was subsequently characterized and named ferrocene³. The ferric ion is first reduced by the Grignard reagent to ferrous ion which then

reacts to form ferrocene⁴. See equation 1.

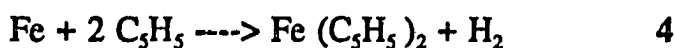


Direct Reaction Between Fe and Cp

Ferrocene, being one of the more stable metallocenes, can also be synthesized by methods not applicable to other metallocenes, that is, by reaction of Fe(II) and Cp-H at high temperatures. In this method, amines have been used as they facilitate the removal of protons from Cp and the formation of ferrocenes at relatively lower temperatures¹. See equations 2-4.



Net Reaction



Properties

Ferrocene is an orange solid which melts around 173°C. It obeys the effective atomic number rule or the 18 valence electron rule. The 18 electron rule and the concept of σ -donor/ π -acceptor synergism ("bonding and back bonding") represent the most rudimentary basis for discussing structure and

bonding in organotransition-metal compounds. The 18 electron rule (Sidgwick⁵, 1927) is based on the valence bond formation of localized metal ligand bonds; it states that thermodynamically stable transition-metal organometallics are formed when the sum of the d electrons plus the electrons conventionally regarded as being supplied by the ligands equals 18. In this way, the metal formally attains the electron configuration of the next higher noble gas. For example, in ferrocene, the Fe(II) ion contributes six electrons and each of the cyclopentadienyl ions also contributes six electrons.

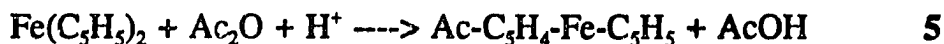
$$\text{Fe}^{+2} = 6$$

$$2 (\text{C}_5\text{H}_5)_2 = 12$$

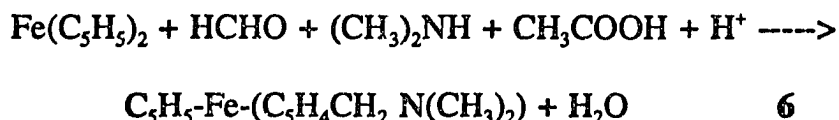
$$\text{Total Electrons} = 18$$

In the case of ferrocene, the total number of electrons is equal to 18 electrons (6+12) which is equal to a noble gas configuration and has no unpaired electron, hence it is diamagnetic. X-ray crystallographic studies reveal that ferrocene has a sandwich structure in which the Fe(II) is attached to two Cp rings in a pentagonal antiprismatic arrangement³. The arrangement of atoms in the ferrocene and the nature of binding between the central iron and Cp rings is well explained by molecular orbital theory. On the basis of molecular orbital theory, this bonding is considered to arise by the pairing of one electron from each ring with one of the unpaired d electrons of the iron atom, thus forming a single π bond between each ring and the iron atom.

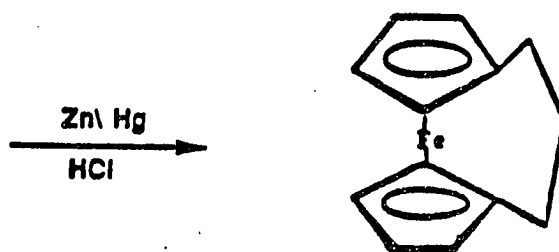
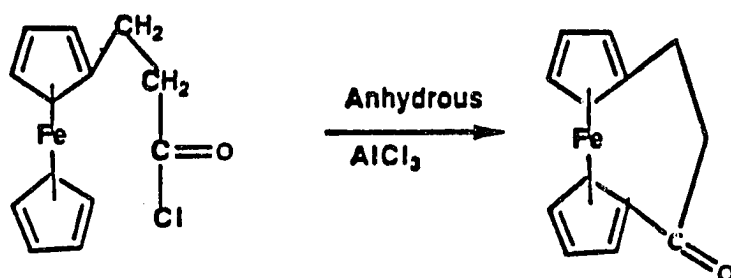
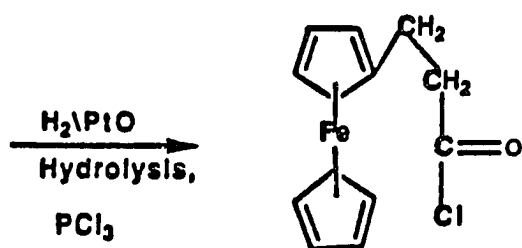
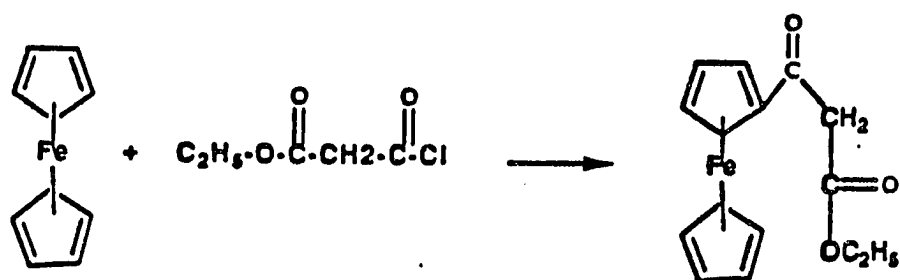
Ferrocene, in most of its chemical reactions, is similar to benzene. In fact, in some cases it is more reactive than benzene towards electrophilic reagents, thus indicating that in the case of the Cp ring, π -electrons are readily available. For example, its greater reactivity is illustrated by the acylation of ferrocene, using acetic anhydride in the presence of phosphoric acid as a catalyst⁶. See equation 5.



Ferrocene also undergoes the Mannich reaction by condensation of the ferrocene ring with formaldehyde and amines⁶. See equation 6.



In this respect again, ferrocene shows greater reactivity than benzene, which does not undergo the Mannich reaction. Ferrocene is deactivated by acylation. In order to introduce another acetyl group, the conditions employed are the same which are usually required for acylation of an aromatic ring. The 1,2-isomer with both acetyl groups on the same ring is obtained in very small quantity. The 1,1-isomer is the major product. The reluctance to form the 1,2-isomer is not surprising in view of the expected analogy with benzene. Acylation of the rings is generally used to bridge the two rings of ferrocene⁶ (Scheme I).



Scheme I

The high reactivity of ferrocene is evidenced qualitatively by the mild conditions under which acylation may be effected and more strikingly, by the observation that it is acylated even in the presence of a ten fold excess of anisole. A more quantitative measure of the reactivity has been obtained through competitive acylation studies, the results of which are shown in Table 1.⁶

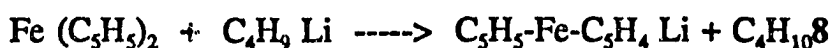
Table 1

Relative Rates of Friedel-Crafts
Acetylation Aromatic Compounds*

Compound	Relative Rate
1. Benzene	1.0
2. Acetyl Ferrocene	1.9×10^2
3. Mesitylene	2.9×10^3
4. Pentamethyl Benzene	1.3×10^4
5. Ferrocene	3.3×10^6

* In methylene chloride at 0°C.

Ferrocenes also undergo metallation, another type of reaction typical of aromatic ring systems. See equations 7-9.





These mono and dilithio products have been used to synthesize several ferrocenyl derivatives. In certain other reactions of ferrocene, the metal atom is directly involved⁶. One example is the intramolecular bonding of ferrocene alcohols (Figure 1). Another example is protonation by very strong acids, to give the cation Cp_2FeH^+ with bent rings. This protonation, occurring both

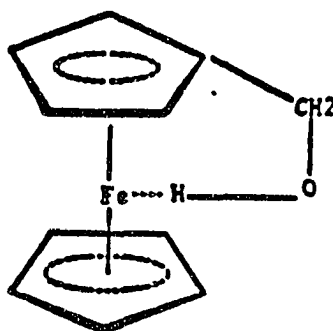
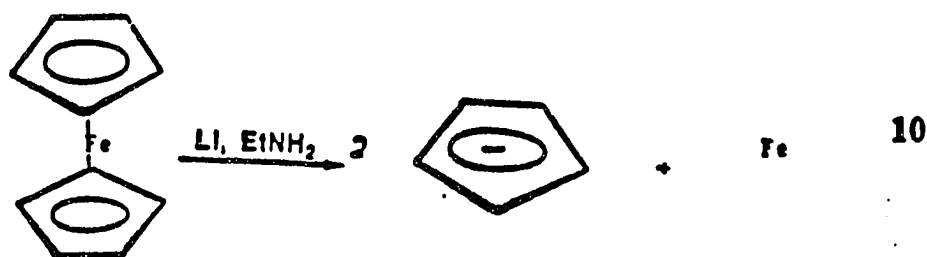


Figure 1

in Cp_2Fe and $\text{CpMn}(\text{CO})_3$, is suggested to proceed via initial attack on the metal⁶.

Few methods have been described for the mild, controlled degradation of ferrocene ring systems. The catalytic hydrogenation route to the dearomatization and collapse of the ferrocene molecule is unsuccessful. The resistance of ferrocene to catalytic hydrogenation over platinum has been reported by Woodward, Rosenblum and Whiting⁷. Attempts were also made

to hydrogenate ferrocene using the more active catalyst 5% rhodium on alumina in acetic acid, for periods up to several weeks, and these experiments have given similar negative results⁶. Under these conditions, benzene is completely hydrogenated in 5 minutes⁶. Fischer⁸ also reported the failure to hydrogenate ferrocene with Raney nickel in alcohol at 150°C and 150 atmospheres⁵. The use of alkali metals was investigated as a means of transferring an electron to the ferrocene nucleus to dearomatize the molecule. Trifan and Nicholas⁹ were first to show that ferrocene can be smoothly degraded by lithium and ethylamine. See equation 10.



Lithium does not react with ferrocene in refluxing ether, benzene or toluene. However, a reaction does occur at 200°C in mineral oil. In contrast to this slow reaction, however, rapid cleavage of ferrocene into metallic iron and cyclopentadiene is obtained by the use of lithium in ethylamine, the amine functioning as a solvent for lithium atoms. A series of quantitative

experiments were carried out to study ferrocene reduction by other alkali and alkaline earth metals, amines, and ammonia combinations. The progress of the reaction was followed by the rate of reflux and the appearance of black metallic iron. The rates are substantially lower using sodium than with lithium and lower in n-hexylamine than in ethylamine. The calcium-amine combination gives no reaction. In liquid ammonia, however, reductions with calcium, lithium, and sodium are all vigorous. The lithium-ethylamine combination appears to be the most convenient method and has therefore been selected for use in quantitative studies.

From the results (shown in Table 2), when compared with data on the reaction of sodium with various aromatic hydrocarbons, it may be estimated that in the series of aromatic compounds of increasing electron affinity, benzene << phenanthrene < naphthalene < anthracene, etc. Ferrocene is closer to benzene than to other members of this series. Although in view of the very much more rapid reaction of lithium-ethyl amine with ferrocene than with benzene, it would seem to be higher. Reaction periods of 8-10 hours are employed for benzene, while reaction of ferrocene gives good conversion in a few minutes. A typical ferrocene reduction using lithium and ethylamine for about 4-6 minutes resulted in the reduction of 73% of the initial ferrocene. The isolation of free cyclopentadienyl ion on hydrolysis of the reaction

Table 2
Qualitative Rates of Reduction of Ferrocene⁶

Metal	Amine	Description of initial reaction
1. Li	Ethylamine:	Vigorous reaction, Black iron formed.
2. Na	Ethyl amine	Gradual appearance of Black iron, slow reaction.
3. Ca	Ethyl amine	No reaction.
4. Mg	Ethyl amine	No reaction.
5. Li	n-Hexylamine	Gradual appearance of Black iron, very slow reaction.
6. Na	n-Hexylamine	Some darkening only after 0.5 hours.
7. Ca	n-hexylamine	No Reaction even at boiling.
8. Li	Liquid ammonia	Vigorous reaction, Black iron formed.
9. Na	Liquid ammonia	Vigorous reaction, Black iron formed.

mixture indicates that the cleavage leads initially to cyclopentadienyl-lithium.

The cleavage reaction proceeds by initial electron transfer from the lithium metal to the ferrocene. Attack on the ferrocene aromatic system has a

different consequence from the parallel attack on a benzenoid aromatic system. In the latter case, the π -electrons are displaced to give resonance stabilized negative ion free radicals, with no consequent molecular rupture¹⁰ (Figure 2).

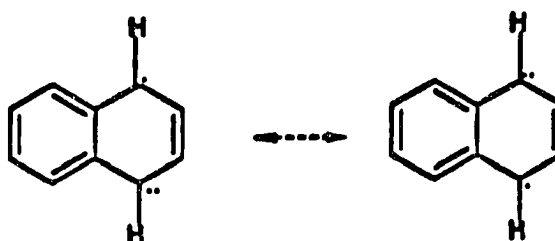


Figure 2

Similarly, it seems reasonable to suggest that in the analogous instance of the electron transfer to one of the five carbon rings of ferrocene, the π -electrons are displaced to the conjugated double bond orbital of the cyclopentadienide ion with resulting detachment from the iron atom. The remaining radical fragment presumably separates into free iron and cyclopentadienyl radical, which in turn may abstract hydrogen from solvent or an electron from lithium (Figure 3). The mass spectra of ferrocene and ferrocene derivatives exhibit a strong peak at mass number 121, correspond-

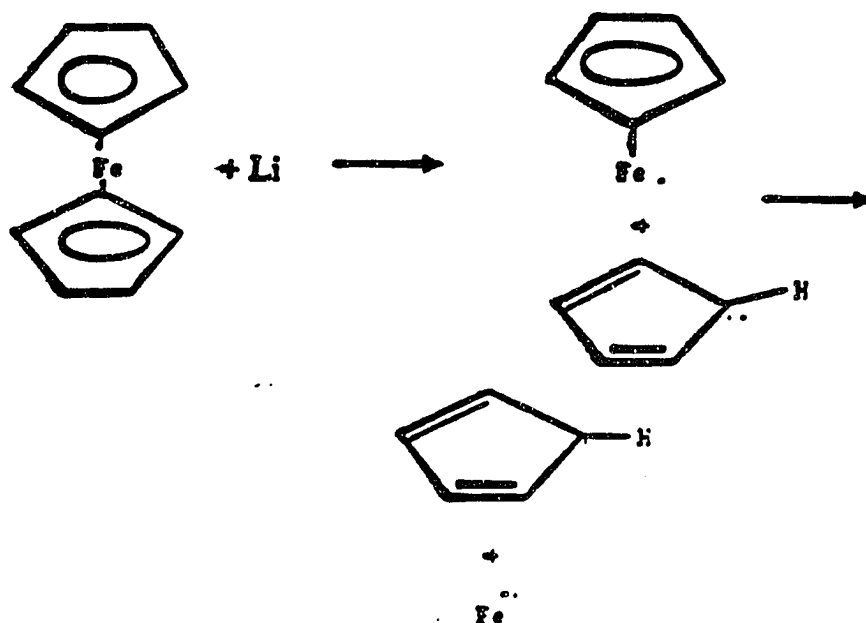


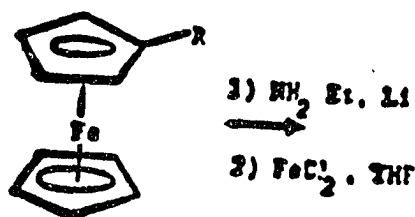
Figure 3

ing to the C_5H_5 fragment which may be interpreted as evidence of some appreciable degree of stability of this cyclopentadienyl-iron entity.

If the same reaction were applied to a mono substituted ferrocene, a mixture of cyclopentadienyl-lithium results. Addition of ferrous chloride should convert this into a mixture of starting material, disubstituted ferrocene, and ferrocene. If the first step is complete and if the second takes the statistical course, then 50% of the starting material(II) would be recovered along with 25% of the disubstituted product(III) and 25% unsubstituted ferrocene.

Osgerby and Pauson¹¹ studied the reductive cleavage of dimethyl-

aminomethylferrocene ($R=CH_2NMe_2$); since it may be made quantitatively by direct aminomethylation of ferrocene, whereas the corresponding disubstituted product cannot be obtained in this way. It was found that a relatively large excess of lithium was required to effect even 80% completion of the first stage. Subsequent addition of ferrous chloride then afforded the three products in very nearly the statistical ratio (Figure 4). It was also found that free dimethylamino cyclopentadiene could not be isolated from the initial reaction mixture, which emphasized the value of direct treatment with ferrous chloride. Cyanoferrocene and methylthioferrocene failed to yield products other than ferrocene itself in a similar reaction. In both cases, it appears reasonable to assume that the disubstituted cyclopentadienyl lithium does not survive under the vigorous reduction conditions.



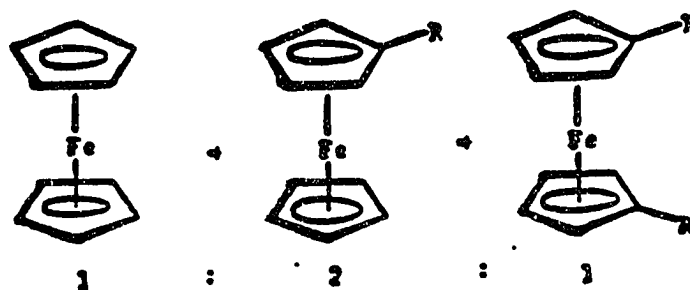


Figure 4

Manganocene, bis(cyclopentadienyl) manganese, was prepared and characterized in 1954 by the research group of Wilkinson and Fischer¹². This compound was found to be rather atypical among the metallocenes being a high spin ionic compound. Shortly after the discovery of manganocene, it was determined that this compound could be converted to cyclopentadienylmanganese tricarbonyl by treatment with carbon monoxide under pressure^{13,14,15,16}. The first preparation of cyclopentadienylmanganese tricarbonyl was described in 1954¹⁷ and involves the carbonylation of $\text{Mn}(\pi\text{-C}_5\text{H}_5)_2$. Although the reaction can run at a pressure of one atmosphere of carbon monoxide, somewhat better yields arise if the synthesis is carried out under moderate pressure (800 p.s.i) at 250°C. A 50% yield via this procedure is reported¹⁴. Another preparation of this compound, described in 1962¹⁷, involves the carbonylation of a mixture of $\text{MnCl}_2(\text{Py})_2$,

cyclopentadiene and Mn metal in DMF at a pressure of 300 atmosphere and 180°C. Hydrogen is also added to the reaction system. After cooling and releasing pressure the reaction mixture is hydrolysed and then steam distilled, the product being obtained in about 70% yield. The synthesis of methylcyclopentadienylmanganese tricarbonyl may be accomplished in the same fashion. The preparation of cyclopentadienylmanganese tricarbonyl from the reaction of $\text{Ti}(\text{C}_5\text{H}_5)_3$ and $\text{MnCl}(\text{CO})_5$ has also been reported¹⁸. An extensive organic chemistry was developed around this compound which was found to behave rather like ferrocene, showing a proclivity towards aromatic type reaction at the cyclopentadienyl ligand. A closely related complex methylcyclopentadienylmanganese tricarbonyl has been produced commercially for use as an antiknock agent for gasoline.

Cyclopentadienylmanganese tricarbonyl, sometimes also named cymantrene, is a yellow crystalline species, M.P 77°C. It is quite volatile, subliming at room temperature in vacuo. It is soluble in most of the organic solvents, unaffected by water, and only slightly decomposed by air oxidation over a long period of time. The infra-red spectrum contains two $\nu(\text{CO})$ absorption bands at 2023 and 1923 cm^{-1} ¹².

Systems containing only one $\pi\text{-C}_5\text{H}_5$ ring include $(\pi\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$, $(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$, $(\pi\text{-C}_5\text{H}_5)\text{NiNO}$, and $(\pi\text{-C}_5\text{H}_5)\text{CuPr}_3$. The ring-to-metal

bonding in these cases can be accounted for by a conceptually simple modification of the picture given previously for $(\pi\text{-C}_5\text{H}_5)_2\text{M}$ systems. In each case, a principal axis of symmetry can be chosen so as to pass through the metal atom and intersect the ring plane perpendicular at the ring center; in other words the $\text{C}_5\text{H}_5\text{M}$ group is a pentagonal pyramid, symmetry C^{5v} . The single ring may then be considered to interact with the various metal orbital in about the same way as do each of the rings in the sandwich system. The only difference is that opposite to this single ring is a different set of ligands.

Ellis, Faltynek, and Hentges¹⁷ used sodium hexamethylphosphoramide in the reductive cleavage of cyclopentadienylmanganese tricarbonyls for the generation of metal carbonyl anions, including the first non-intermetal carbonyl trianions²⁰. Their previous observations that the compounds $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}$ and W) are cleanly converted to the corresponding dianions $\text{M}(\text{CO})_5^{2-}$ by alkali metals in hexamethylphosphoramide suggested that this procedure might also be a useful route to η^5 -cyclopentadienyl substituted metal carbonyl dianions, of which $(\text{C}_5\text{H}_5)\text{V}(\text{CO})_3^{2-}$ is the only previously known example^{21,22}. Treatment of methylcyclopentadienylmanganese tricarbonyl with sodium in HMPA afforded only carbonylmetallate anions. This indicated that decomplexation had occurred between the metal nucleus and the cyclopentadienyl group. The subsequent fate of the cyclopentadienyl ring

under these vigorous conditions was not discerned.

CHAPTER II

INTRODUCTION TO RESEARCH

Trifan and Nicholas⁹ have shown that ferrocenes cleave easily under reductive conditions, with subsequent good survival of the cyclopentadiene ring. However Ellis' work suggested that the cleavage of cymantrene leads to the destruction of the released cyclopentadienyl ring. We wanted to determine if conditions could be found that would easily decomplex half sandwich complexes with good survival of the cyclopentadienyl ring. Since cyclopentadienylmanganese tricarbonyl and related half metallocenes show behavior similar to ferrocene, they can be substituted with a wide variety of substituents. Thus decomplexation of various substituted half-sandwich metallocenes might provide a useful route for the preparation of substituted cyclopentadienes; compounds which are difficult to prepare by other methods (Figure 5). Furthermore, the reductive cleavage of cyclopentadienyl half-sandwich complexes, and subsequent recomplexation with Fe(II) to form ferrocenes offer an attractive route for the preparation of conducting organometallic polymers from starting compounds such as polyvinylcyclop-

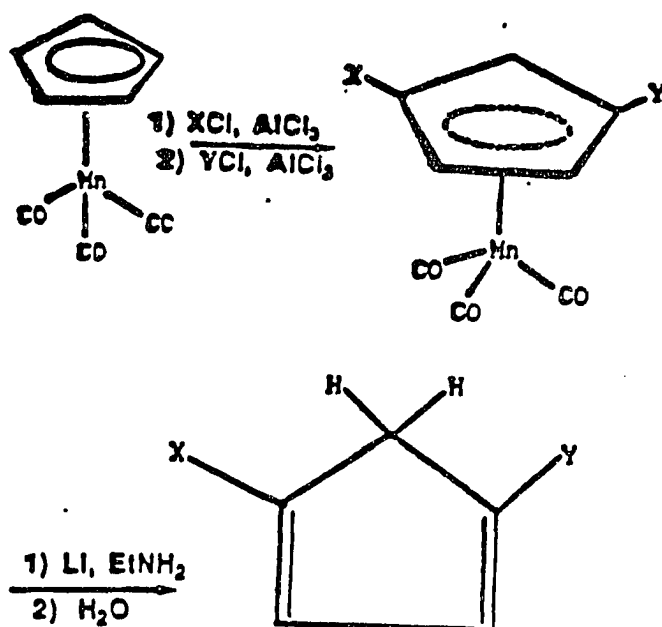


Figure 5

tadienemanganese tricarbonyl²³ (Figure 6). However, before work of this scope can be started, the chemistry involved must be well established through the study of simple model systems. Thus we investigated the reductive cleavage of the following compounds:

1. Methylferrocene.
2. 1:1 mixture of methylferrocene and ferrocene.
3. Cyclopentadienylmanganese tricarbonyl.
4. Methylcyclopentadienylmanganese tricarbonyl.

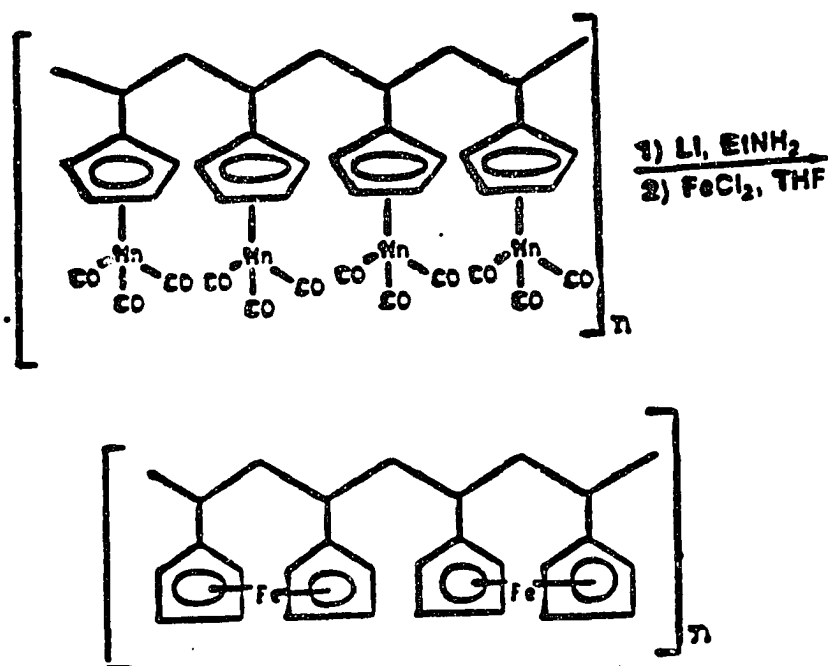


Figure 6

5. 1:1 mixture of cyclopentadienylmanganese tricarbonyl and methyl cyclopentadienylmanganese tricarbonyl.
6. Cyclopentadienylcobalt dicarbonyl.
7. Benzoylcyclopentadienylmanganese tricarbonyl.
8. 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane.

CHAPTER III

RESULTS AND DISCUSSION

In order to optimise the reaction conditions and gain experience working with a system which, based on published work, should undergo reaction, we first studied the reductive cleavage of methylferrocene. Methylferrocene is a stable solid metallocene which is readily available from several commercial suppliers. Since the methyl group is an electron donating group, we wanted to investigate if this would have any effect on the reaction. Initial treatment of methylferrocene with lithium metal in ethylamine resulted in a vigorous reaction and the resultant solution was added to a large excess of ferrous chloride suspended in tetrahydrofuran (THF). The residue, obtained after removing the solvent under reduced pressure, was purified on a silica gel column using 10% ether and hexane mixture as the solvent to elute the residue through the column. Under these conditions, ferrocenes, which are non-polar compounds, are first off the column. The cleaned product was studied by GC-MS technique. The data showed that the resultant product was a mixture of three components: ferrocene (25%, retention time 2.3

minute), methylferrocene (50%, retention time 3.0 minute), and 1,1'-dimethylferrocene (25%, retention time 3.6 minute). We confirmed our assignments by comparing the observed GC/MS with those obtained from authentic samples of ferrocene, methylferrocene and 1,1'-dimethylferrocene (Figure 7).

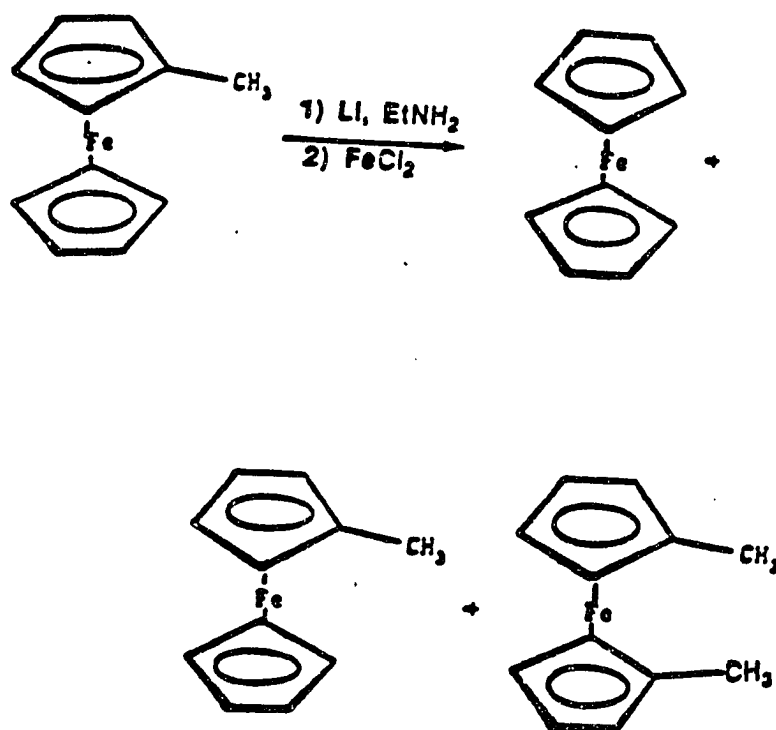


Figure 7

The ratio of products observed in the reaction of methylferrocene is explainable if one were to consider the random statistical combination of equal amounts of components A and B, i.e., 25% A-A, 50% A-B and 25% B-B. Thus, the product ratio suggests that all of the methylferrocene is cleaved initially, giving rise to equal amounts of cyclopentadienide and methylcyclopentadienide anions which condense with Fe(II) according to the statistical norm. The isolated yield of the red oil consisting of the ferrocene mixture was 0.65 g. Since the product mixture had a nominal molecular weight of methylferrocene, this corresponds to 32% mass balance.

In order to study this, we took a 1:1 mixture of ferrocene and methylferrocene and treated it with lithium and ethylamine. It resulted in the formation of cyclopentadienyl lithium salt and methyl cyclopentadienyl lithium salt in 3:1 ratio. This was then transferred into a suspension of anhydrous ferrous chloride in THF. The product obtained after removing the solvent(THF) reduced pressure was passed through a silica gel column and was eluted by using 10% ether and 90% hexane mixture as the solvent. The purified product was then studied by GC-MS technique. The data obtained showed that the product was a mixture of 34% ferrocene, 32% methyl-3-ferrocene, and 34% dimethylferrocene (Figure 8). The first preliminary experiments with ferrocene and methylferrocene provided experience in the

isolation and identification of ferrocene products derived from the reductive cleavage

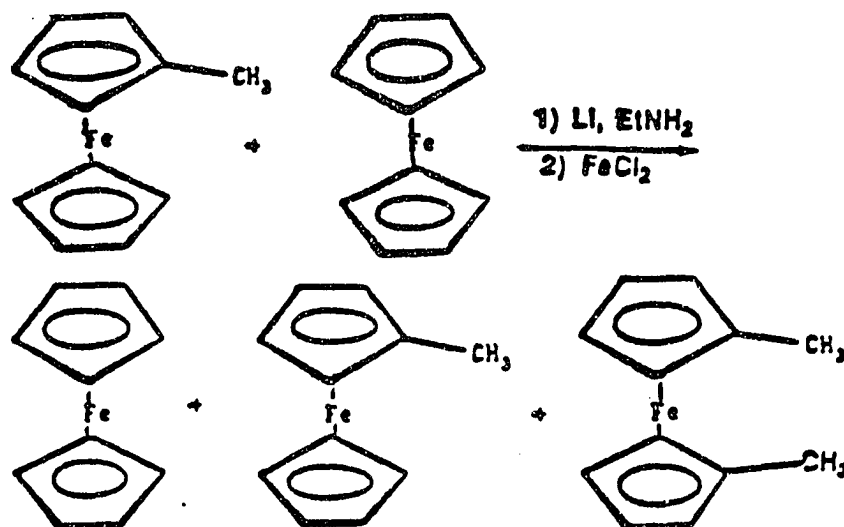


Figure 8

reactions. Since cyclopentadienes are very reactive species, they undergo Diels-Alder cyclodimerization and other polymerization reactions quite readily. Thus, they are hard to isolate and characterize. Ferrocenes, on the other hand, are quite stable and easy to isolate and identify. In all subsequent experiments involving the reductive cleavage of half-metallocene compounds, the cyclopentadienes were recondensed with Fe(II) to form ferrocenes, rather than attempt to isolate the cyclopentadiene itself. We then repeated Ellis'¹⁷ work on cyclopentadienylmanganese tricarbonyl to check for the survival of the cyclopentadiene ring. Cyclopentadienylmanganese tricarbonyl in hexamethylphosphoramide (HMPA) was treated with excess sodium metal until the

blue color of the solvated electrons persisted. The resulting solution was transferred to ferrous chloride in THF and stirred overnight. The usual work-up and purification gave a viscous brown oil which was analyzed by GC-MS. The absence of a peak in the GC-MS corresponding to the starting manganese complex was noted. Since the cyclopentadienylmanganese tricarbonyl starting material has a R_f on the TLC different than that of ferrocene, it would have been isolated under the work-up conditions if present. The absence of the starting complex suggests that it was entirely consumed during the reaction. The GC-MS analysis did indicate the presence of trace amounts of ferrocene, identified by comparison with authentic sample. The major component was an uncharacterized material with a M^+ of 198 (Figure 9). The purification of this unexpected compound of molecular weight 198 was carried out by column chromatography by using a silica gel column and mixture of 10% ether and 90% hexane as the solvent. Because of the extreme viscosity of the unknown product, a small amount of solvent was trapped in the compound even after heating under vacuum (0.05 mm Hg) for 6 hr.

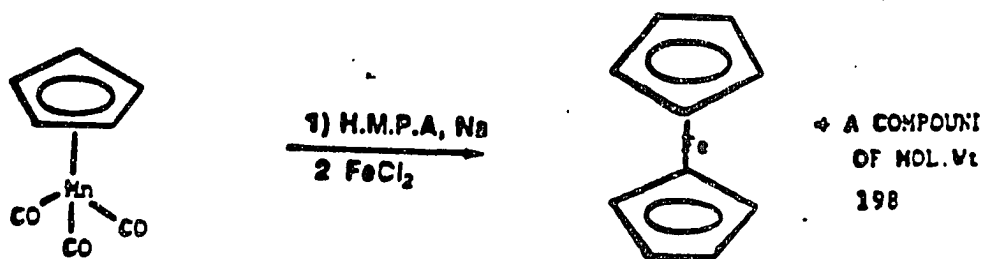


Figure 9

Attempts to recrystallize the material from various solvents were unsuccessful. An attempt to purify by vacuum distillation resulted in the decomposition of the sample. A qualitative test on this compound was performed; it showed that it burned with a nonsooty flame and did not leave any metallic residue indicating the absence of any metal in the complex. It even showed negative for sodium fusion test and prussian blue test for nitrogen. The IR spectrum taken in a chloroform solution, showed strong C-H stretching and C-H bending absorption bands ($2941, 2796, 1368\text{ cm}^{-1}$). This compound of molecular weight 198 might have been formed either by a three fold Diels-Alder reaction of the cyclopentadiene (Figure 10)

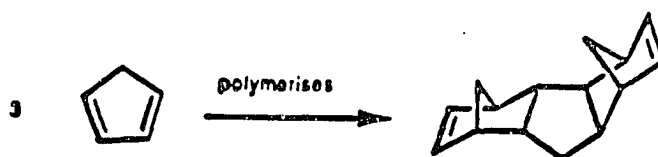


Figure 10

or by a three unit oligomer of some long polycyclopentadiene. It may be formed from ionic polymerization (Figure 11).

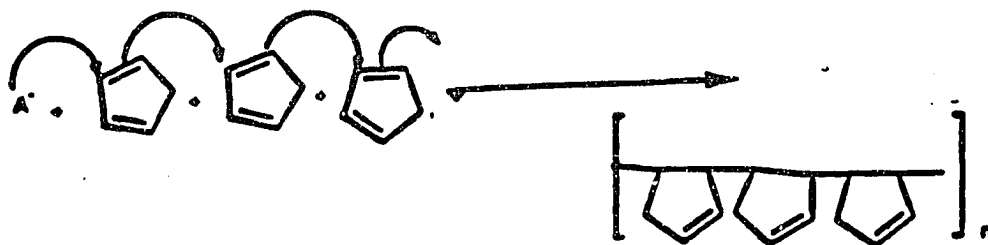


Figure 11

As the reductive cleavage of cyclopentadienylmanganese tricarbonyl with sodium metal and HMPA gave a very low yield of ferrocene, we tried the modification of Trifan and Nicholas method. We treated cyclopentadienylmanganese tricarbonyl with lithium metal and ethylamine and the product obtained was treated with ferrous chloride in THF. The solvent (THF) was removed under reduced pressure. The residue obtained was cleaned by passing it through a silica gel column and using a 10% ether and 90% hexane mixture as the solvent. It was then studied by GC-MS technique. The product formed had a retention time of 2.3 minutes and molecular weight of 186. Comparison of the GC-MS of this reaction product with authentic ferrocene showed it to be identical in retention time. The yield was around 81%. The interesting part of this reaction was that no starting material was recovered. The modification proved to be an excellent route for the preparation of the Cp anion with very good survival of the anion as shown by good yield of ferrocene (Figure 12).

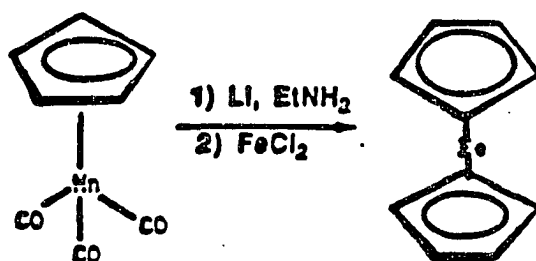


Figure 12

When methyl cyclopentadienylmanganese tricarbonyl was treated with lithium metal and ethylamine, it resulted in the formation of methylcyclopentadienyl lithium salt which, when treated with ferrous chloride in THF, formed dimethylferrocene. The residue obtained after removing the solvent under reduced pressure was passed through a silica gel column and eluted by using 10% ether and 90% hexane mixture. The cleaned product had a retention time of 3.6 minutes and a molecular weight of 214. The formation of dimethylferrocene was confirmed by comparing the product with an authentic original sample of dimethylferrocene. We found that this reaction works even better (Figure 13).

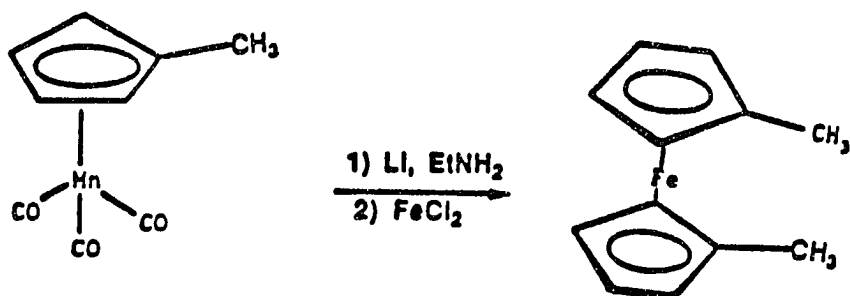


Figure 13

When a mixture of $\text{CpMn}(\text{CO})_3$ and $\text{Me CpMn}(\text{CO})_3$ was taken in 50% ratio and treated with lithium metal and ethyl amine and later transferred to a suspension of anhydrous ferrous chloride in THF, a mixture of ferrocene (25%), methyl ferrocene (50%), and dimethyl ferrocene (25%) was obtained in statistical amount (Figure 14).

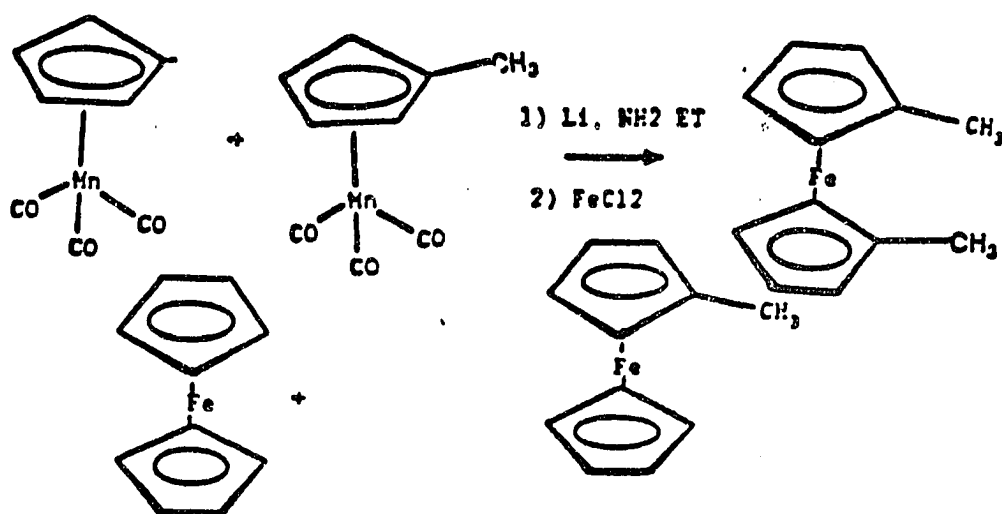


Figure 14

Shown in Table 3 are the GC-MS data of cyclopentadienylmanganese tricarbonyl and other compounds. After successfully carrying out reductive cleavage of cyclopentadienylmanganese tricarbonyl and methylcyclopentadienylmanganese tricarbonyl, we wanted to check if this method could apply to other similar types of metallocenes. So we tried the reductive cleavage of cyclopentadienylcobalt dicarbonyl by treating it with lithium salt and ethylamine. The product obtained was transferred to a suspension of anhydrous ferrous chloride in THF. After removing the solvent under reduced pressure, the residue was cleaned by passing it through the silicagel column and a mixture of 10% ether and hexane was used to elute it through the column. The cleaned product was studied by the GC-MS technique. The product formed in the reaction was found to be ferrocene. The yield was around

42% (Figure 15).

Table 3

GC-MS Data of Various Cp-Metal Complexes

Compound	Molecular weight	Retention time minutes	Base peak
1. Cyclopentadienyl manganese tricarbonyl	204	1.405	204
2. Methyl cyclopentadienyl manganese tricarbonyl	218	1.711	134
3. Ferrocene	186	2.309	186
4. Methyl ferrocene	200	3.002	56
5. Dimethyl ferrocene	214	3.656	214

Column type: Crosslinked Methyl Silicone gum.
12 mm * 0.2 mm * 0.33 μ m thickness
400 plates/m

Column temperature: 150°C

Head pressure: 31 pa.

When we found that this technique of reductive cleavage could be successfully applied to other half sandwich metallocenes, we decided, at

this point, to study the reductive cleavage of different derivatives of cyclopentadienylmanganese tricarbonyl, that is, on benzoylcyclopenta-

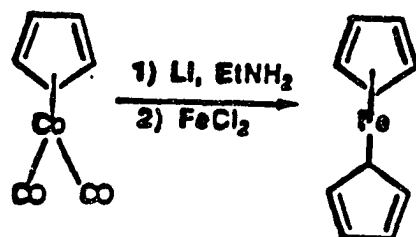


Figure 15

dienylmanganese tricarbonyl and the 1,3-bis (cyclopentadienylmanganese tricarbonyl)propane complex. The basic idea of studying the benzoyl derivative was to see if the acyl group effects reaction. The 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane complex was chosen as a model for the reductive cleavage of polyvinyl cyclopentadienylmanganese tricarbonyl.

CpMn(CO)_3 can be alkylated and acylated by using aluminum chloride as a catalyst. The alkylation reaction required only catalytic quantities of aluminium chloride. For acylation, where one mole of aluminum chloride co-ordinates strongly with the oxygen of the resulting ketone, only slightly more than one mole of catalyst was required. The

acylation of CpMn(CO)_3 gives only one isomer. The acylation reaction with CpMn(CO)_3 was first carried out and studied by Kozikowski, Maginn, and Love²². It was prepared by treating CpMn(CO)_3 with benzoyl chloride and aluminum chloride in the usual Friedel-Crafts manner. The compound obtained was analyzed by TLC and shown to be a mixture of ketone and starting material. Column chromatography on silica gel separated the polar ketone product from the unreacted starting material. The product was authenticated by infrared spectroscopy, GC-MS technique and also by its melting point. The melting point of the compound was found to be around 73- 74°C which is same as the literature value (Figure 16). This compound was then treated with ethylamine and lithium metal. The resulting solution was transferred to a suspension of ferrous chloride in THF. It was then

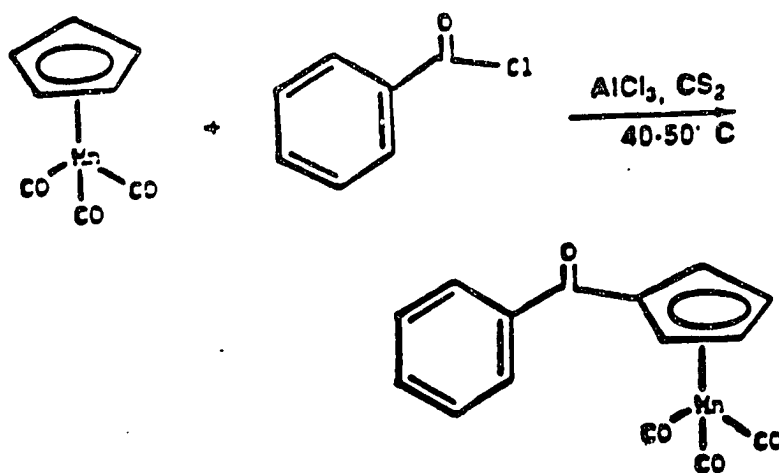


Figure 16

filtered and treated to remove all the solvent(THF). The residue obtained was purified by column chromatography and studied by GC-MS technique. It was found that in the reductive cleavage of benzoylcyclopentadienylmanganese tricarbonyl some amount of methylcyclopentadienylmanganese tricarbonyl was formed showing a retention time of 1.7 minutes and a M^+ weight of 218. We are not able to mechanistically prove how the methyl derivative was formed, but it was authenticated by comparison of the GC-MS to the authentic sample. This compound was formed in trace amount and a large amount of an unknown compound of M^+ 198 and having a retention time of 3.0 minutes was formed. Thus reductive cleavage of the benzoyl group attached to the cyclopentadienylmanganese tricarbonyl was not successful. Interestingly, we found that whenever the Cp ring does not survive in the reaction we seem to get the unknown compound of retention time 3.0 minutes and M^+ 198 (Figure 17).

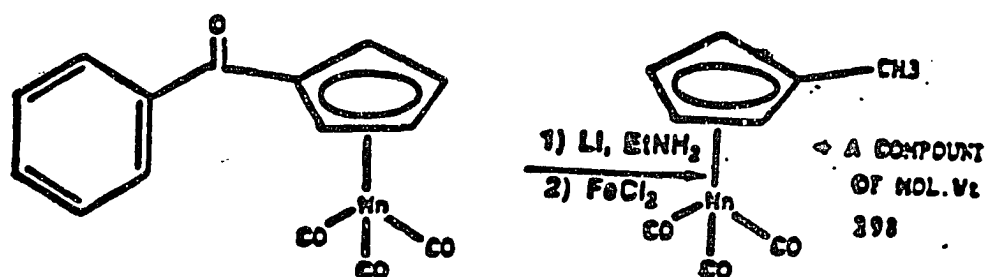


Figure 17

At this point, we wanted to synthesise 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane and study the reductive cleavage of this compound by treating with lithium metal, ethylamine, and later with ferrous chloride. This should give rise to ferrocenophane (Figure 18). This forms a model compound for synthesising a conducting polymer from polyvinylcyclopentadienylmanganese tricarbonyl. However, it had to be synthesized first.

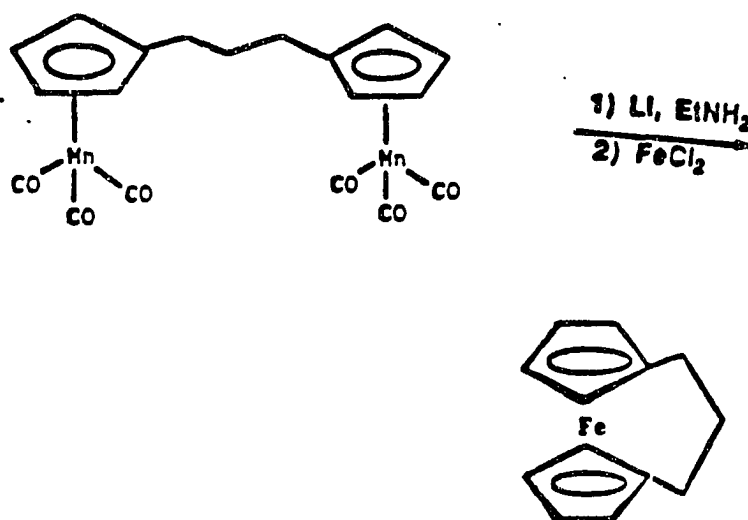
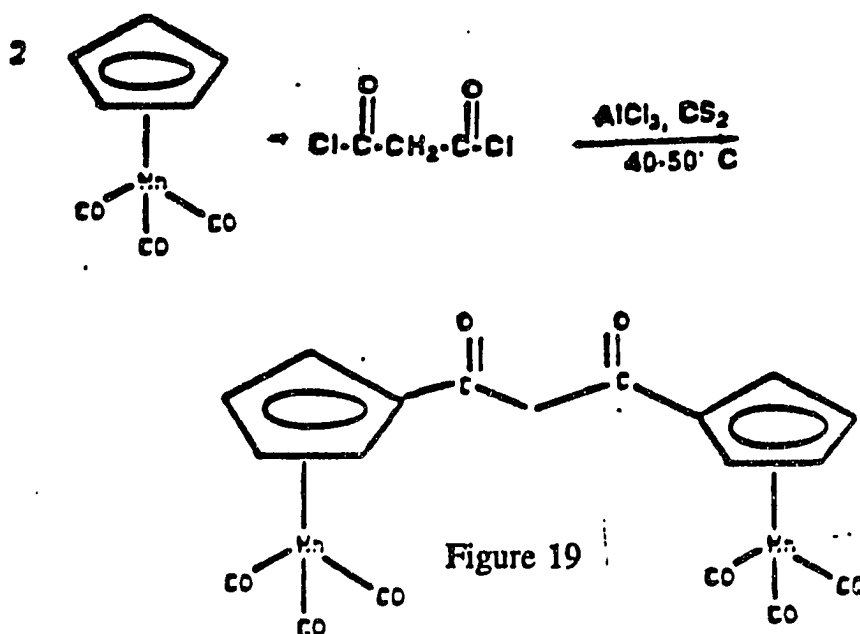


Figure 18

The diketone of 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane was synthesized by the usual Friedel-Crafts method by treating one equivalent of malonyl chloride with two equivalent of $\text{CpMn}(\text{CO})_3$ and aluminium chloride in carbon disulfide (Figure 19). This compound was confirmed by Fourier transform infrared spectroscopy, which showed a terminal carbonyl group around $1943, 2023 \text{ cm}^{-1}$, a broad enolate peak around 1650 cm^{-1} , and a OH



peak around 3450 cm^{-1} . It was also confirmed by GC-MS and NMR (Figure 20).

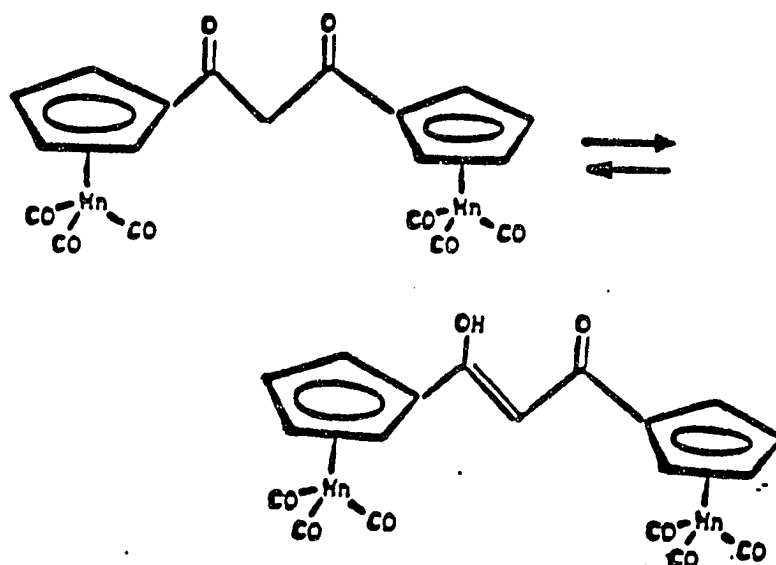


Figure 20

The diketone was then reduced to 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane. Initially, catalytic reduction was tried, employing platinum oxide and hydrogen gas at 30 p.s.i. This method was able to efficiently reduce acetophenone and acetyl ferrocene. But, when this method was tried on benzoylcyclopentadienylmanganese tricarbonyl, no reduction took place. This might be due to the poisoning of the catalyst by carbon monoxide. Clemenson reduction employing zinc amalgam and hydrochloric acid also failed to give reduction. The reduction of this compound was finally carried out by treating it with lithium aluminum hydride and aluminum chloride in ether^{11,24} to form 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane (Figure 21).

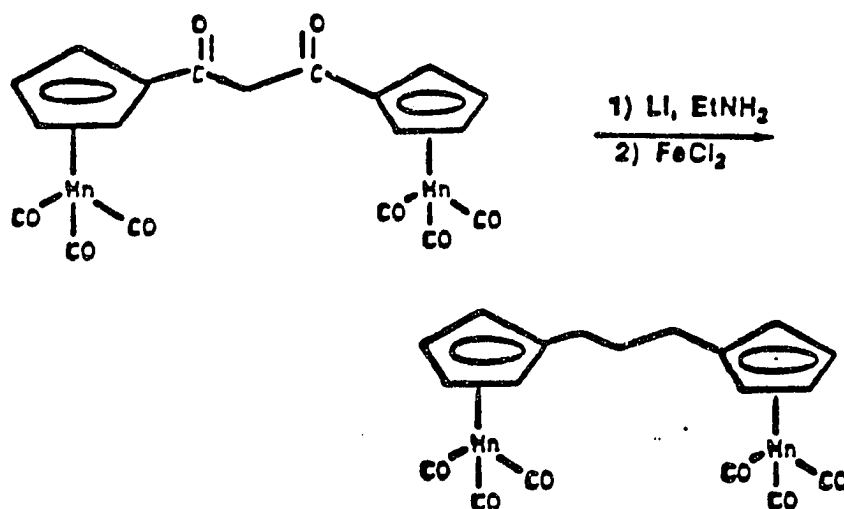


Figure 21

The diketone of 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane could also be synthesised by a different method by treating an equivalent of cyclopentadienylmanganese tricarbonyl with succinic anhydride in presence of aluminum chloride with carbon disulfide as a solvent. It results in the formation of a ketoacid⁸. This is an alternate model compound with one extra carbon increase with compared to 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane (Figure 22).

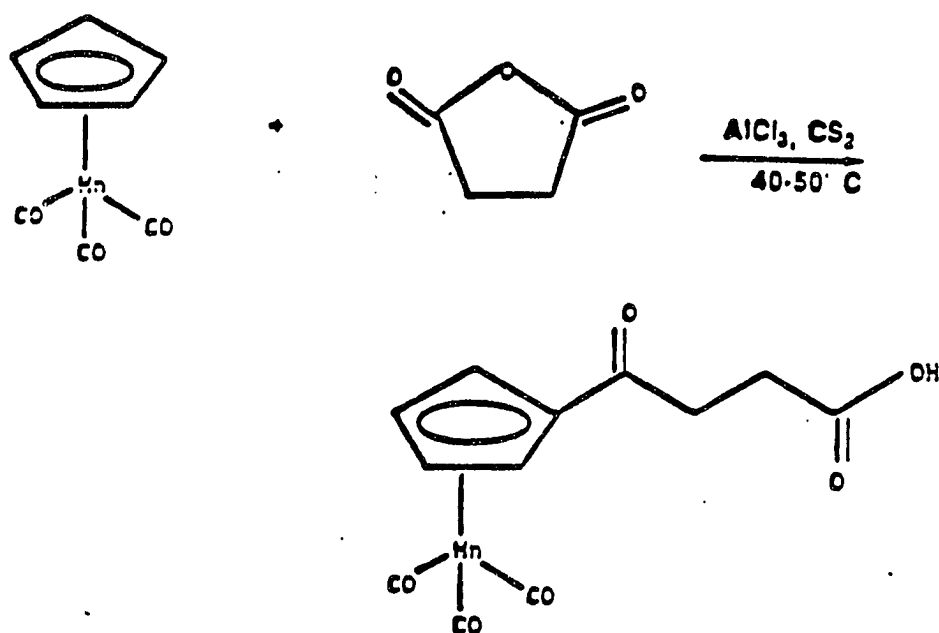


Figure 22

Time constraints prevented the completion of the alternate model. The ketoacid formed can be treated with another equivalent of cyclopentadienylmanganese tricarbonyl in polyphosphoric acid resulting in the form-

ation diketone of 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane with four carbon in between the two cyclopentadienyl rings (Figure 23). The diketone of 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane was reduced to 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane

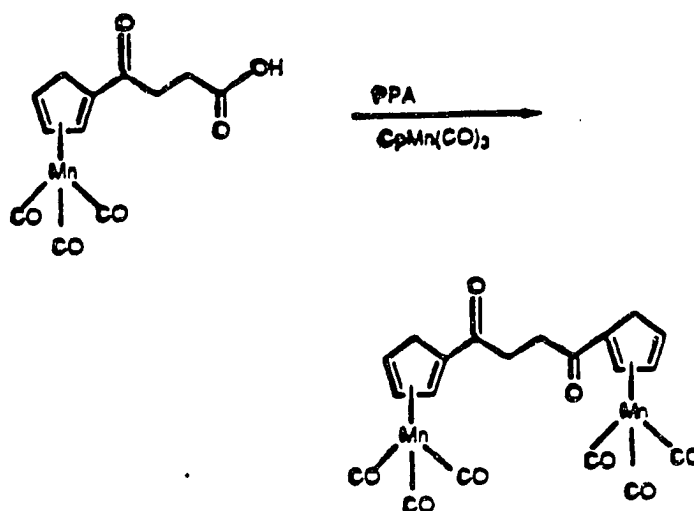


Figure 23

by treating it with lithium aluminum hydride and aluminum chloride¹⁸.

The 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane was then reductively cleaved by using lithium metal and ethyl amine. The resultant product was transferred to a ferrous chloride solution in THF. The product obtained in the reductive cleavage was cleaned by passing it through a silica gel column and eluted by using a mixture of 10% ether and 90% hexane. It was studied by GC-MS technique. The molecular weight of 452 of the molecular ion with retention time 3.5 minutes in the GC-MS suggested the

formation of (3,3) ferrocenophane. The yield was around 12%. We were able to see only the dimer in GC-MS (Figure 24).

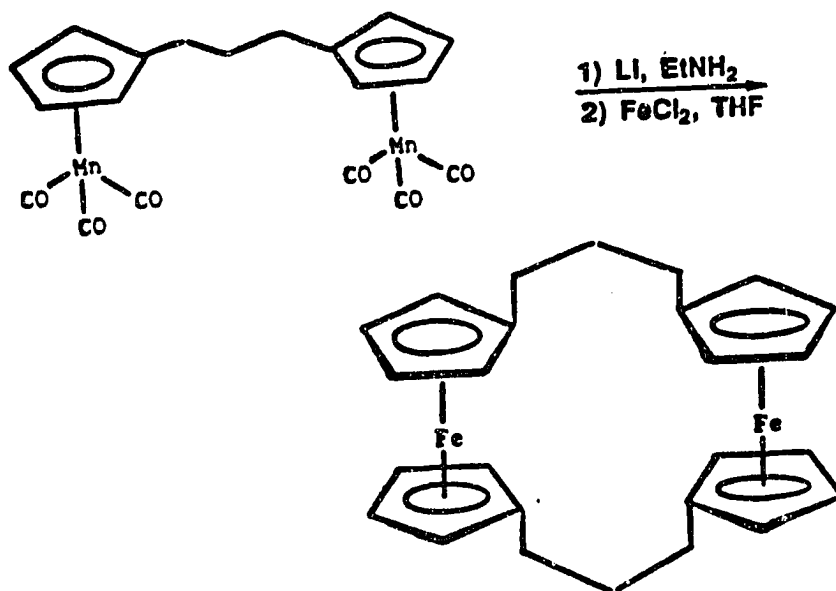


Figure 24

Conclusion

Thus we can see from Table 4 that the method of reductive cleavage is easily applied to sandwich compounds like ferrocene. We also found that this technique could be successfully extended to half sandwich compounds like $\text{CpMn}(\text{CO})_3$, $\text{MeCp}(\text{CO})_3$, and $\text{Cp}(\text{CO})_3$. Thus, we can generalise that most of the half metallocene compounds should cleave in a manner similar to ferrocene on treating with lithium metal, ethyl amine and ferrous chloride. But this method failed in case of benzoylcyclopentadienylmanganese tri-

carbonyl. Instead of the expected 1,1'-biphenylferrocene as a product, an unknown complex of M^+ 198 having a retention of 3.0 minute was formed

Table 4

Reductive Cleavage of Various Cp-Metal Complexes

Starting material	Product
1. Methyl ferrocene.	Mixture of ferrocene, methylferrocene, and 1,1'-dimethylferrocene in the ratio of 1:2:1.
2. 1:1 mixture of ferrocene and methyl ferrocene.	Ferrocene (34%), methyl ferrocene (32%), and 1,1'-dimethylferrocene (32%).
3. $CpMn(CO)_3$	Ferrocene (40%).
4. $MeCpMn(CO)_3$	1,1'-Dimethylferrocene (60%).
5. 1:1 mixture of $CpMn(CO)_3$ and $MeCpMn(CO)_3$	Mixture of ferrocene, methylferrocene, and 1,1'-dimethylferrocene in the ratio of 1:2:1.
6. $CpCo(CO)_2$	Ferrocene (42%).
7. Benzoylcyclopentadienyl manganese tricarbonyl M^+ 198.	Trace amounts of $CpMn(CO)_3$ and a unknown compound of
8. 1,3-bis(cyclopentadienyl manganese tricarbonyl) propane.	(3,3) ferrocenophane (12%).

along with some trace amount of $MeCp(CO)_3$. Thus, we found that whenever

the Cp ring does not survive in the reaction, we seem to get this unknown compound of M^+ 198. This technique was successfully applied to the decomplexation of bis (cyclopentadienylmanganese tricarbonyl) propane. But instead of the expected monomer ferrocenophane, a dimer 3,3'ferrocenophane was isolated.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The melting points were determined in open capillaries using a Unimelt laboratory device apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet 5DXC spectrometer. Nuclear magnetic resonance spectra (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 (12 * 0.2 mm * 0.33 μ m thickness, 400 plates/m). The gas chromatograph was attached to a 5970 series mass selective detector. All solvents were purified by distillation. Anhydrous tetrahydrofuran (THF) was prepared by continuous reflux over sodium metal under a nitrogen atmosphere. Benzophenone was used as an indicator. The formation of purple colored solution indicated that the THF solution is completely dried. The glasswares were dried overnight in an oven at temperature 150°C.

Ferrocene and methylferrocene were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin and were used as received.

Cyclopentadienylcobalt dicarbonyl and methylcyclopentadienyl-manganese tricarbonyl were obtained from Strem Chemical Company, Newburyport, Massachusetts and were used as received. Benzoylcyclopentadienyl-manganese tricarbonyl and 1,3-bis-(cyclopentadienylmanganese tricarbonyl) propane were prepared as described.

1. Preparation of Ferrous Chloride. This follows a literature procedure²⁵. To a 300 ml three necked flask fitted with a condenser and inlet for admission of nitrogen were added anhydrous ferric chloride and 100 mL of dry THF (prepared as mentioned). Iron powder (4.70 g, 0.0085 mole) was added and the resultant suspension was refluxed under nitrogen for 4.5 hrs, this gave ferrous chloride as a gray solid suspended in a brown liquid. This suspension was used as is in the next reaction.

2. Preparation of 1,1'-dimethylferrocene by reductive cleavage of methylferrocene. The following procedure is a modification of the method of Trifan and Nicholas⁹. Methylferrocene (2.0 g, 0.010 mole) was added to a 100 mL round bottom flask. It was dissolved in 30 mL of ethylamine. Ethylamine (bp 16.6°C) is a gas at room temperature. The round bottom flask containing the methylferrocene was cooled to -78°C by an external dry ice-isopropanol bath. Ethylamine was introduced through an inlet tube and condensed in the flask. The solution containing the ethylamine and

methylferrocene was allowed to stir until all the methylferrocene was completely dissolved. The ethylamine solution of methylferrocene was transferred via cannula to a clean dry 200 mL three neck flask equipped with nitrogen inlet and containing an excess of lithium metal (1.2g, 0.1730 mol). Upon addition, a vigorous reaction ensued with the formation of a black precipitate and the solution was allowed to stir for 25 mins. It was then transferred to a grey solid suspension of anhydrous ferrous chloride (prepared as in 1.). This solution was allowed to stand over night whereupon the ethylamine evaporated off. The resulting THF solution was filtered free of solids and the filtrate was removed under pressure to get a yellowish brown colored residue (0.8 g). The residue obtained was dissolved in 3.0 mL of hexane and purified by passing through a column containing silica gel (length 20 x 2.5 cm) and eluted by a solvent mixture of 10% ether and 90% hexane. The first 500 mL was collected and the solvent removed under pressure to give a red oil (0.65). The red oil was studied by GC-MS technique. Analysis of the data showed that the product formed was a mixture of ferrocene (25%, retention time(rt) 2.3 min, m/e: 186, 121, 56), methylferrocene (50%, rt 3.0 min, m/e: 200, 134, 121, 56), 1,1'-dimethylferrocene (25%, rt 3.6 min, m/e: 214, 134, 121, 56). The results were checked by comparing with authentic samples.

3. Reductive Cleavage of 1:1 mixture of methylferrocene and ferrocene by using lithium metal and ethyl amine. The procedure used was same as described in (2.). Methylferrocene (1.0 g, 0.0050 mol) and ferrocene (1.0 g, .0054 mol) were taken in 1:1 ratio as a starting material. The final product was a red oil (0.65 g). The red oil was studied by GC-MS technique. The analysis showed that the product contained a mixture of ferrocene (34%, rt 2.3 min, m/e: 186, 121, 56), Methylferrocene (32%, rt 3.0 min, m/e: 200, 121, 134, 56), 1,1'-dimethylferrocene (34%, rt 3.6 min, m/e: 214, 134, 121, 56). The results were authenticated by comparing with the original samples of ferrocene, methylferrocene, and 1,1'-dimethylferrocene.

4. Reductive cleavage of cyclopentadienylmanganese tricarbonyl using sodium metal and hexamethylphosphoramide (HMPA). The following procedure is a modification of the method of Ellis et al¹⁹. Cyclopentadienylmanganese tricarbonyl (1.0 g, 0.0049 mole) was added to 100 mL round bottom flask. It was dissolved in 30 mL of ethylamine. Ethylamine (bp 16.6°C) is a gas at room temperature. The round bottom flask containing the cyclopentadienylmanganese tricarbonyl was cooled to -78°C by an external dry ice-isopropanol bath. Ethylamine was introduced through an inlet tube and condensed in the flask. The solution containing the ethylamine and cyclopentadienylmanganese tricarbonyl was allowed to stir until all the

cyclopentadienylmanganese tricarbonyl was completely dissolved. The ethylamine solution of cyclopentadienyl-manganese tricarbonyl was transferred via cannula to a clean dry 200 mL three neck flask equipped with nitrogen inlet containing an excess of sodium metal (1.2 g, 0.0857 mol). Upon addition, a vigorous reaction ensued with the formation of a blue colored solution and the solution was allowed to stir for 45 mins. It was then transferred to a grey suspension of anhydrous ferrous chloride (prepared as in 1.). This solution was allowed to sit overnight. It was filtered by vacuum filtration and the filtrate was removed under reduced pressure to get a pale yellow colored residue (0.45 g). The residue was dissolved in 1.5 mL of hexane and cleaned by passing through a column containing silica gel (length 20 * 1.5 cm) and eluted by a solvent mixture of 10% ether and 90% hexane. The first 500 mL was collected and rotavaped to give reddish brown oil (0.30 g). It was studied by GC-MS and NMR. GC-MS : rt 2.3 min, m/e: 186, 121, 56, rt 3.0 min, m/e: 198, 121, 107, 91, 71, 55; NMR (CDCl_3) δ 7.73(d), 7.69(m), 5.44(bs), 4.85(bs), 3.34 ppm(m).

5. Reductive cleavage of cyclopentadienylmanganese tricarbonyl using lithium metal and ethylamine. The following procedure is a modification of the method of Trifan and Nicholas⁹. Cyclopentadienyl-manganese tricarbonyl (1.0 g, 0.0049 mole) was added to 100 mL round bottom flask. It was

dissolved in 30 mL of ethylamine. Ethylamine (bp 16.6°C) is a gas at room temperature. The round bottom flask containing the cyclopentadienylmanganese tricarbonyl was cooled to -78°C by an external dry ice-isopropanol bath. Ethylamine was introduced through an inlet tube and condensed in the flask. The solution containing the ethylamine and cyclopentadienylmanganese tricarbonyl was allowed to stir until all the cyclopentadienylmanganese tricarbonyl was completely dissolved. The ethylamine solution of cyclopentadienylmanganese tricarbonyl was transferred via cannula to a clean dry 200 mL three neck flask equipped with nitrogen inlet containing an excess of lithium metal (1.2 g, 0.1730 mol). Upon addition, a vigorous reaction ensued with the formation of a black precipitate and the solution was allowed to stir for 25 mins. It was then transferred to a grey suspension of anhydrous ferrouschloride (prepared as in 1.). This solution was allowed to sit overnight. It was filtered by vacuum filtration and the filtrate was removed under reduced pressure to get pale yellow colored residue (0.7 g). The residue was dissolved in 1.5 mL of hexane and cleaned by passing through a co-lumn containing silica gel (length 20 * 1.5 cm) and eluted by a solvent mixture of 10% ether and 90% hexane. The first 500 mL was collected and removed under reduced pressure to give a yellowish brown liquid which solidified on standing to a solid (0.4 g). The compound was dried and

recrystallized by using petroleum ether. It was also studied by GC-MS and NMR. Mp 173°C (lit. 174-176°C). GC-MS (m/e): 186, 121, 56; ^1H NMR (CDCl_3) δ 4.43 ppm (bs).

6. Reductive cleavage of methlcyclopentadienylmanganese tricarbonyl using lithium metal and ethylamine. The procedure used was same as described in (4.). Methylcyclopentadienylmanganese tricarbonyl (1.5 g, 0.0070 mol) was taken as the starting material. The final product was a yellowish brown oil which solidified on standing to a solid (0.9 g). It was recrystallized by using petroleum ether. The solid was found to be 1,1'-dimethylferrocene. Mp 37°C (lit. 37-39°C); GC-MS (m/e): 200, 134, 121, 56. ^1H NMR (CDCl_3) δ 2.00 (s, 6H), 4.46 (m, 4H), and 4.8 ppm (m, 4H).

7. Reductive cleavage of 1:1 mixture of methlcyclopentadienylmanganese tricarbonyl and cyclopentadienylmanganese tricarbonyl using lithium metal and ethylamine. The procedure used was same as described in (4.). Methylcyclopentadienylmanganese tricarbonyl (1.0 g, 0.0050 mol) and cyclopentadienylmanganese tricarbonyl (1.0 g, 0.0049 mol) were taken as starting materials. The final product was a red oil (0.45). The red oil was studied by GC-MS. The analysis showed that the product was a mixture of ferrocene (34%, rt 2.3 min, m/e: 186, 121, 56), methylferrocene (32%, rt 3.0 min, m/e: 200, 134, 121, 56), 1,1'-dimethylferrocene (34%, rt 3.6 min, m/e:

214, 134, 121, 56). The results were authenticated by comparing with original samples of ferrocene, methylferrocene, and 1,1'-dimethylferrocene.

8. Reductive cleavage of cyclopentadienylcobalt dicarbonyl using lithium metal and ethylamine. The following procedure is a modification of the method of Trifan and Nicholas⁹. Cyclopentadienylcobalt dicarbonyl (2.0 g, 0.010 mole) was added to 100 mL round bottom flask. It was dissolved in 30 ml of ethylamine. Ethylamine (bp 16.6°C) is a gas at room temperature. The round bottom flask containing the cyclopentadienylcobalt dicarbonyl was cooled to -78°C by an external dry ice-isopropanol bath. Ethylamine was introduced through an inlet tube and condensed in the flask. The solution containing the ethylamine and cyclopentadienylcobalt dicarbonyl was allowed to stir until all the cyclopentadienylcobalt dicarbonyl was completely dissolved. The ethylamine solution of cyclopentadienylcobalt dicarbonyl was transferred via a cannula to a clean dry 200 mL three neck flask equipped with nitrogen inlet containing an excess of lithium metal (1.2g, 0.1730 mol). Upon addition, a vigorous reaction ensued with the formation of a black precipitate and the solution was allowed to stir for 25 mins. It was then transferred to a grey solid suspension of anhydrous ferrous chloride (prepared as in 1.). This solution was allowed to stand overnight whereupon the ethylamine evaporated off. The resulting THF solution was filtered free of

of solids and the filtrate was removed under reduced pressure to give a yellowish brown colored residue (0.8 g). The residue obtained was dissolved in 3.0 mL of hexane and purified by passing through a column containing silica gel (length 20 x 2.5 cm) and eluted by a solvent mixture of 10% ether and 90% hexane. The first 500 mL was collected and removed under reduced pressure to give a yellowish brown liquid which solidified on standing (0.42 g). The solid was recrystallized by using petroleum ether. Its melting point was determined and was studied by GC-MS and ^1H NMR. Mp 175°C (lit. 174- 175°C). Analysis of the data showed that the product formed was ferrocene(25%, retention time(rt) 2.3 min, m/e: 186, 121, 56), ^1H NMR (CDCl_3) δ 4.43 ppm (bs). The compound was authenticated by comparing it with an original sample.

9. Preparation of benzoylcyclopentadienylmanganese tricarbonyl. This follows the literature procedure²². Additions of aluminum chloride (8.7g 0.0650 mol) in small portions to a stirred mixture of cyclopentadienylmanganese tricarbonyl (10.2 g, 0.0500 mol) and benzoyl chloride (7.05 g, 0.0500 mol) in 100 mL carbon disulfide resulted in a small rise in temperature and evolution of hydrogen chloride. When addition was complete (ca 25 mins) the mixture was heated to reflux for 4 hrs., cooled, hydrolyzed with cold dilute hydrochloric acid and the organic layer was separated. The solution

was evaporated to dryness, and the solid residue dissolved in hexane and dried over calcium sulfate, concentration of the solution yielded a yellowish colored solid (8.0 g). The solid was recrystallized from benzene-petroleum ether. Mp 73.5°C (lit. 73.5-74.5°C); ^1H NMR (CDCl_3) δ 4.9 (m, 2H), 4.6 (m, 2H), and 7.2 ppm (bs, 6H); IR (CHCl_3) 2023, 1948 and 1641 cm^{-1} ; GC-MS (m/e): 308, 252, 224, 132, 55.

10. Preparation of diketone of 1,3-bis(cyclopentadienyl)manganese tricarbonyl) propane. Addition of aluminum chloride (6.0 g 0.045 mol) in small portions to a mixture of cyclopentadienyl manganese tricarbonyl (3.0 g, 0.0150 mol), malonyl chloride (1.06 g, 0.0075 mol) and 130 mL of carbon disulfide, in a three necked flask, resulted in a small rise in temperature and evolution of hydrogen chloride. When addition was complete (ca 30 mins) the mixture was heated to reflux for 4 hours, cooled, hydrolyzed with cold dilute hydrochloric acid and the organic layer separated. The solution was evaporated to dryness, and the solid residue dissolved in hexane and dried over calcium sulfate, concentration of the solution yielded a reddish brown oil (0.75 g). The diketone was confirmed by IR, NMR, and GC-MS. IR (CHCl_3) 3450, 2023, 1948, and 1650 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.91 (m, 4H), 4.6 (m, 4H), and 1.5 ppm (s, 2H); GC-MS (m/e): 476, 272, 212, 188, 131, 71.

11. Reductive cleavage of benzoylcyclopentadienylmanganese tricarbonyl. The following procedure is a modification of the method of Trifan and Nicholas⁹. Benzoylcyclopentadienylmanganese tricarbonyl (2.0 g, 0.0065 mole) was added to 100 mL round bottom flask. It was dissolved in 30 mL of ethylamine. Ethylamine (bp 16.6°C) is a gas at room temperature. The round bottom flask containing the benzoylcyclopentadienylmanganese tricarbonyl was cooled to -78°C by an external dry ice-isopropanol bath. Ethylamine was introduced through an inlet tube and condensed in the flask. The solution containing the ethylamine and benzoylcyclopentadienylmanganese tricarbonyl was allowed to stir until all the benzoylcyclopentadienylmanganese tricarbonyl was completely dissolved. The ethylamine solution of benzoylcyclopentadienylmanganese tricarbonyl was transferred via a cannula to a clean dry 200 mL three neck flask equipped with nitrogen inlet containing an excess of lithium metal (2.5 g, 0.3571 mol). Upon addition, a vigorous reaction ensued with the formation of a black precipitate and the solution was allowed to stir for 25 mins. It was then transferred to a grey suspension of anhydrous ferrous chloride (prepared as in 1.). This solution was allowed to sit overnight. It was filtered by vacuum filtration and the filtrate was removed under reduced pressure to give a pale yellow colored oil (1.2 g). The residue was dissolved in 1.5 mL of hexane and

cleaned by passing through a column containing silica gel (length 20 * 1.5 cm) and eluted by a solvent mixture of 10% ether and 90% hexane. The first 500 mL was collected and rotavaped to give a yellowish brown liquid (0.8 g). The compound was studied by GC-MS. The data showed that it formed a very small amount of methylcyclopentadienylmanganese tricarbonyl but a very large amount of a compound of molecular weight 198. This compound was separated and studied by GC-MS, NMR, IR. It was analyzed to be a polymer of cyclopentadiene. GC-MS (m/e): 198, 121, 107, 91, 71, 55; ^1H NMR (CDCl_3) δ 7.73(d), 7.69(m), 5.44(bs), 4.85(bs), 3.34 ppm(m); IR (CHCl_3) 2941, 2796, 1857, 1732, 1368, 1114 cm^{-1} .

12. Preparation of 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane. This follows the literature procedure for reduction of acetylcyclopentadienylmanganese tricarbonyl⁸. To 1.96 g (0.0147 mol) of aluminum chloride in 50 mL ether, was added with cooling 1.0 g (0.0263 mol) of lithium aluminum hydride in 100 mL ether, followed by 0.5 g (0.0095 mol) of the diketone of 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane and allowed to reflux for 4 hrs. The mixture was treated with to yield 40% of 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane. The crude product was purified by passing through a silica gel column (length 20 * 1.5 cm) and eluted by a mixture of 10% ether and 90% hexane. The first 300

mL was collected and removed under reduced pressure to give a reddish brown liquid (0.13 g). This was studied by IR, NMR, and GC-MS. In the IR the absence of the enolate peak and the OH peak indicated the absence of the dicarbonyl in the compound. The GC-MS data showed different fragments at different retention time. IR 2023 and 1948 cm^{-1} ; ^1H NMR δ 4.79 (m, 4H), 4.64 (m, 4H), 1.00 (m, 2H) and 1.5 ppm (m, 4H); GC-MS rt 2.8 min, m/e: 232, 55, rt 7.5 min, m/e: 218, 55.

13. Reductive cleavage of 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane. The following procedure is a modification of the method of Trifan and Nihcolas⁹. 1,3-Bis(cyclopentadienylmanganese tricarbonyl) propane (0.13 g, 0.0030 mol) was added to 100 mL round bottom flask. It was dissolved in 30 mL of ethylamine. Ethylamine (bp 16.6°C) is a gas at room temperature. The round bottom flask containing the 1,3-bis-(cyclopentadienylmanganese tricarbonyl) propane was cooled to -78°C by an external dry ice-isopropanol bath. Ethylamine was introduced through an inlet tube and condensed in the flask. The solution containing the ethylamine and 1,3-bis(cyclopentadienylmanganese tricarbonyl) propane was allowed to stir until all the 1,3-bis(cyclopentadienylmanganese tricarbonyl) was completely dissolved. The ethylamine solution of 1,3-bis(cyclopentadienylmanganese tricarbonyl) was transferred via a cannula to a clean dry 200 mL

three neck flask equipped with nitrogen inlet containing an excess of lithium metal (1.2 g, 0.1730 mol). Upon addition, a vigorous reaction ensued with the formation of a black precipitate and the solution was allowed to stir for 25 mins. It was then transferred to a grey suspension of anhydrous ferrous chloride (prepared as in 1.). This solution was allowed to sit overnight. It was filtered by vacuum filtration and the filtrate was removed under reduced pressure to get a pale yellow colored oil (0.03 g). The residue was dissolved in 1.5 mL of hexane and cleaned by passing through a column containing silica gel (length 20 * 1.5 cm) and eluted by a solvent mixture of 10% ether and 90% hexane. The first 500 mL was collected and removed under reduced pressure to give yellowish brown liquid which solidified on standing to a solid (12%, 0.0016 g). The compound was studied by GC-MS and NMR. The compound was found to be (3,3) ferrocenophane. GC-MS (m/e): 452, 281, 143, 71, 56. ^1H NMR (CDCl_3) δ 3.92(m 8H), 3.72(m, 8H), 1.78(t,4H), 1.00 ppm(m, 2H).

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