

AROMATIC CARBENE TRANSITION METAL COMPLEXES

By

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to my wife,

Anelia,

for her love, understanding, and help

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AROMATIC CARBENE TRANSITION METAL COMPLEXES

By

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Chairman: William M. Jones
Major Department: Chemistry

Aromatic carbene transition metal complexes are classified as carbene complexes which possess an intraligand $(4N+2)$ pi electron system. To date, no carbocyclic carbene complex with $(4n+2)$ pi electrons where $n \geq 1$ has been reported. The synthesis of η^1 -cycloheptatrienyldiene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate ($Fp[\text{cycloheptatrienyldiene}]\text{HFP}$), a six pi electron carbocyclic aromatic carbene complex, is a first step in filling this void. The same methodology was also successfully applied by Kawada to the synthesis of cycloheptatrienyldiene(penta-carbonyl)tungsten, the first neutral transition metal complex of cycloheptatrienyldiene. This synthetic method was also readily applicable to the synthesis to two ten pi electron carbocyclic carbene complexes, namely, η^1 -4,5-benzocycloheptatrienyldiene- η^5 -cyclopentadienyldicarbonyliron

hexafluorophosphate (Fp[4,5-benzocycloheptatrienyli-
dene]HFP), and η^1 -3,4-benzocycloheptatrienyli-
dene- η^5 -cyclopentadienyl-
dicarbonyliron hexafluorophosphate, (Fp[3,4-benzocyclohepta-
trienylidene]HFP).

The synthesis of Fp[cycloheptatrienyli-
dene]HFP was accomplished via hydride abstraction from 1-, 2-, and 3-
(cyclopentadienyliron dicarbonyl)cycloheptatrienes. In turn,
these cycloheptatriene complexes were prepared by reaction
of 1-, 2-, and 3-lithiocycloheptatrienes with cyclopenta-
dienyliron dicarbonyl iodide. The ^1H nmr, ^{13}C nmr, and ir
spectra indicate that there is a greater and more highly
delocalized positive charge on the carbene ligand of Fp[cyclo-
heptatrienyli-
dene]HFP than η^1 -benzocyclobutenylidene- η^5 -
cyclopentadienyliron hexafluorophosphate, Fp[benzocyclo-
butenyli-
dene]HFP, or η^1 -phenylcarbene- η^5 -cyclopentadienyl-
dicarbonyliron triflate, (Fp[phenylcarbene]TFA). Reaction
of Fp[cycloheptatrienyli-
dene]HFP with lithium aluminum
hydride or methyllithium generated neutral cycloheptatriene
complexes. Oxidation of Fp[cycloheptatrienyli-
dene]HFP with
dimethylsulfoxide produced tropone.

The spectral data of Fp[4,5-benzocycloheptatrienyli-
dene]-
HFP indicates that the amount of positive charge on the
carbene ligand is almost equal to that on the carbene ligand
of Fp[cycloheptatrienyli-
dene]HFP. However, ^{13}C nmr data
indicates that more positive charge is located on the carbene
carbon of Fp[4,5-benzocycloheptatrienyli-
dene]HFP than Fp[cyclo-
heptatrienyli-
dene]HFP. As with Fp[cycloheptatrienyli-
dene]HFP,

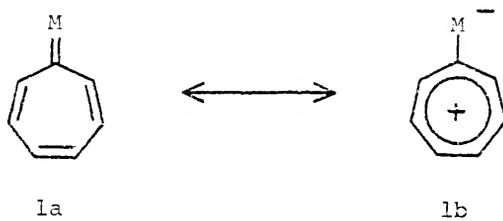
Fp[4,5-benzocycloheptatrienyli-
dene]HFP is susceptible to
attack by nucleophiles. Reaction of Fp[4,5-benzocyclo-
heptatrienyli-
dene]HFP with methyllithium or lithium
aluminum deuteride led to two neutral complexes.

The spectral data of Fp[3,4-benzocycloheptatrienyli-
dene]HFP suggest that there is less metal to ligand back
donation than with Fp[cycloheptatrienyli-
dene]HFP. Further-
more, ^{13}C nmr data indicate the amount of positive charge
residing on the carbene carbon of Fp[3,4-benzocyclohepta-
trienyli-
dene]HFP is less than that of Fp[cycloheptatrienyli-
dene]HFP and Fp[4,5-benzocycloheptatrienyli-
dene]HFP. From
an x-ray structural determination performed by Davis, the
carbene ligand of Fp[3,4-benzocycloheptatrienyli-
dene]HFP
appears planar with some bond alternation.

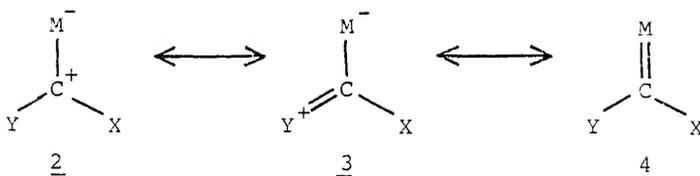
Attempts to prepare a 3,4-5,6-dibenzocycloheptatri-
enyli-
dene complex of iron were unsuccessful. Two potential
carbene precursors, 6-(cyclopentadienyli-
ron-
dicarbonyl)-5H-
dibenzo[a,c]cycloheptene and 6-(cyclopentadienyli-
ron-
dicarbonyl)-5-methoxy-5H-dibenzo[a,c]cycloheptene, were
prepared. However, generation of a dibenzocyclohepta-
trienyli-
dene complex from either was unsuccessful.

CHAPTER I
INTRODUCTION

The synthesis of aromatic carbene complexes of transition metals has for some time been restricted due to a lack of general synthetic methods.^{1, 2} In fact, no carbocyclic 6 pi electron or larger aromatic carbene complex has ever been reported. The synthesis of a cycloheptatrienyldiene transition metal complex (i.e. 1) and higher (4n+2) pi electron electron homologs would not only fill a void in the literature but would also provide a new class of transition metal carbene complexes from which physical and chemical properties could be obtained.

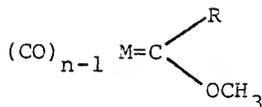
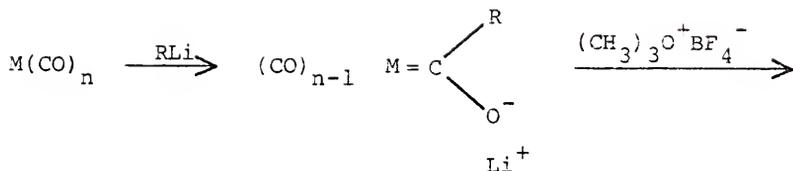


In general, carbene complexes are carbene species that are coordinated to a transition metal and, on the whole, can be formulated using the three extreme resonance forms 2 through 4.² These three forms represent the vacant p_z carbene orbital interacting (1) with no atom, (2) within

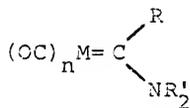
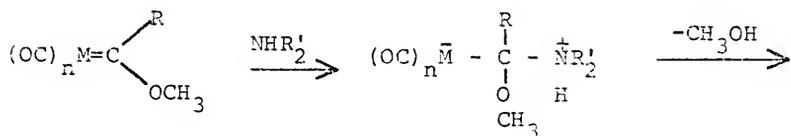


the ligand, and (3) with a metal orbital. Qualitatively, the difference in orbital energies between the d metal orbitals and the ligand orbitals causes the carbene p_z orbital to interact more within the ligand.² This means that with aromatic carbocyclic carbene complexes, metal back donation (as represented by 4) should decrease to some extent by delocalization of the $(4n+2)$ electrons within the pi system of the ligand. Thus aromatic carbene complexes are classified as those complexes which possess an intraligand $(4n+2)$ pi electron configuration.

Carbene complexes have been generated using a wide range of synthetic methods.^{1, 2} An extensive review will not be given even though several methods will be brought forth. The synthetic procedure most widely used was developed by Fisher and Maasböl³ and has been utilized in the synthesis of a large variety of heteroatom stabilized carbene complexes.^{1, 2} Their method involved the attack on a carbonyl ligand by an organolithium reagent. Alkylation of this intermediate, which was usually negatively charged, then led to a carbene complex (e.g. 5).

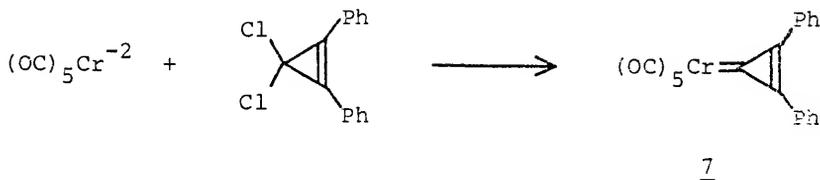
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A variety of complexes containing nitrogen as the stabilizing heteroatom have been synthesized by nucleophilic attack with a primary or secondary amine on the carbene carbon in oxygen stabilized complexes. Loss of alcohol thus led to complexes such as 6.⁴

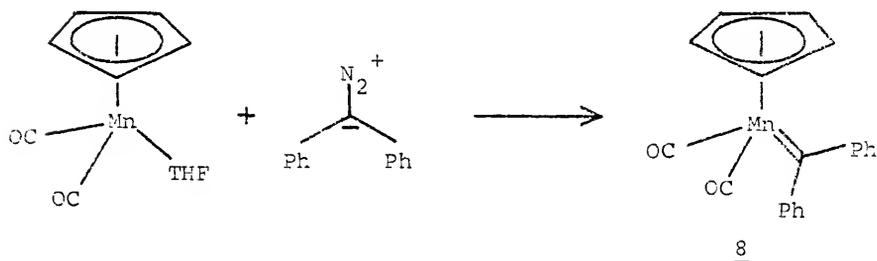
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Also, in recent years, a few non-heteroatom stabilized complexes have been generated from salt-like precursors. Ofele has used metal carbonyl dianions to synthesize the

only reported carbocyclic aromatic carbene complexes.^{5, 6} By displacing two chloride ions from 1,2-diphenyldichlorocyclopropene, the synthesis of the 2 pi electron diphenylcyclopropenylidene complex 7 was successful.

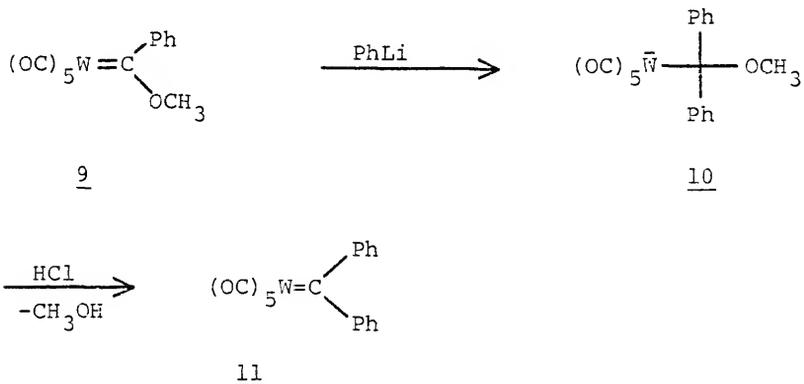


Herrmann has developed another synthetic procedure using a diazo precursor and a labile transition metal ligand. Their interaction resulted in loss of nitrogen and generation of the desired complexes. In this manner he successfully generated the diphenyl carbene complex 8.⁷



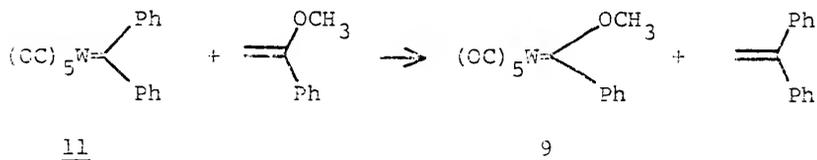
More recently, Casey et al.⁸ brought some innovative new approaches to the synthesis of non-heteroatom stabilized carbene complexes. By utilizing the electrophilicity of a phenylmethoxy carbene coordinated to pentacarbonyl tungsten, 9, he was able to generate three new non-heteroatom stabilized

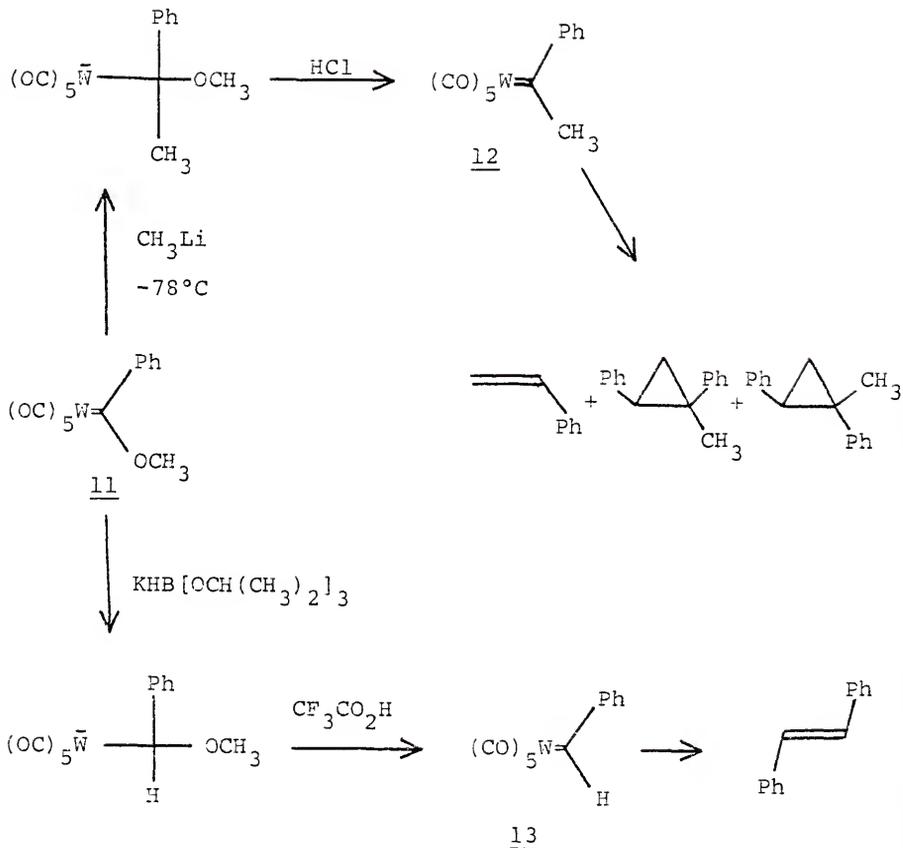
carbene complexes. Via attack with phenyllithium, the stable anionic intermediate 10 was generated. By addition of ethereal hydrogen chloride, protonation of the methoxy substituent resulted in loss of methanol giving the desired diphenyl carbene complex 11.



Two less stable complexes, 12⁹ and 13,¹⁰ were generated in a like manner. Although not observed by spectroscopic measurements, their decomposition products pointed to their respective intermediacy.

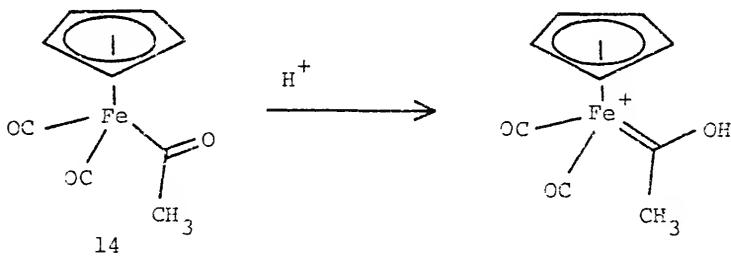
Casey and Burkhardt¹¹ found that the diphenyl carbene complex 11 underwent methathesis type reactions. When treated with 1-methoxy-1-phenylethene, 11 generated the methoxyphenylcarbene complex 9 via a metathesis mechanism.



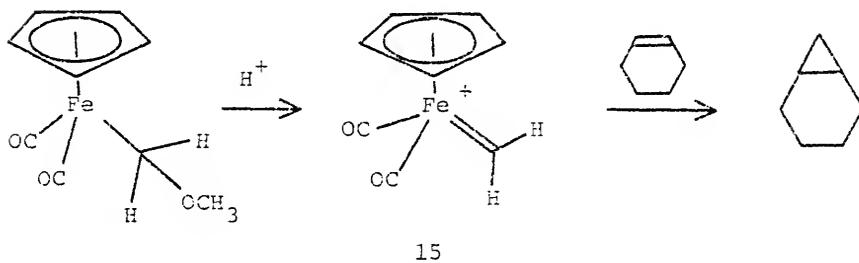


It should be mentioned that Schrock¹² has synthesized some unique tantalum carbene complexes. Additionally, Fisher et al.¹³ have had great success in generating carbene complexes from alkyne transition metal complexes.

Transition metal carbene complexes of cyclopentadienyl-dicarbonyliron (Fp) have also recently been under investigation. The simplest preparation of these was via protonation of an acyl complex 14.¹⁴

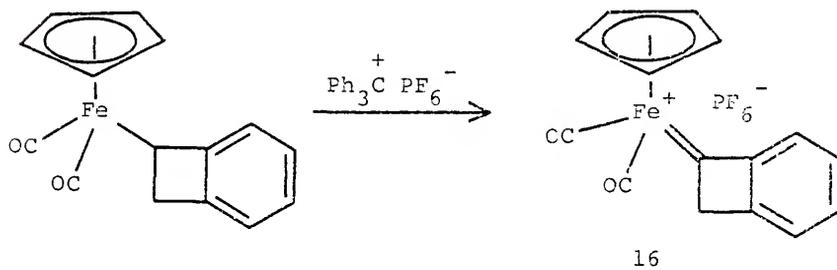


By utilizing methanol as a leaving group, the methylene complex of Fp, 15, was generated.^{15, 16} Although not isolated, its intermediacy was inferred via a reaction with cyclohexene which gave norcaradiene.

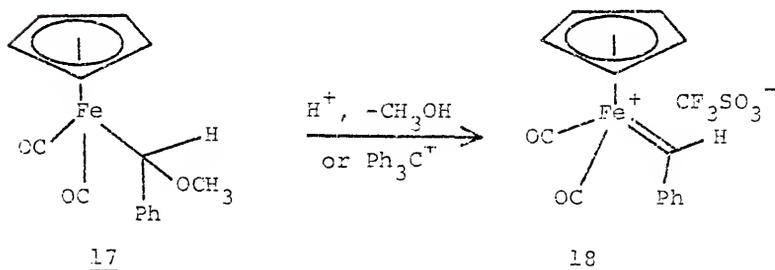


Also, two carbene complexes of Fp have been reported. By alpha hydride abstraction, Giering et al. synthesized

η^1 -benzocyclobutenylidene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate (Fp[benzocyclobutenylidene]HFP) (16).¹⁷



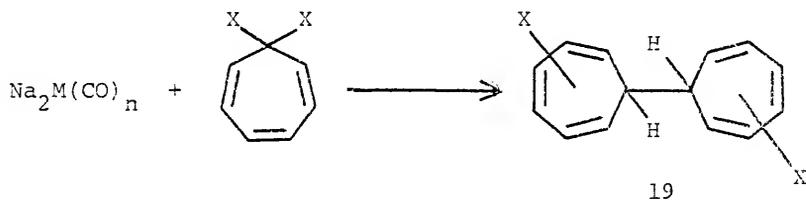
η^1 -Phenylcarbene- η^5 -cyclopentadienyldicarbonyliron triflate (Fp[phenylcarbene]TFA) (18)¹⁸ was prepared in a manner analogous to that used for the methylene complex 15. By treatment of a methoxybenzyl complex, 17, with acid or the triphenylcarbenium ion, generation of the phenyl carbene complex was possible.



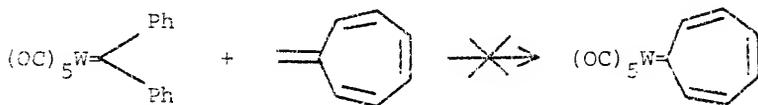
In regard to the generation of 6 pi electron or larger aromatic carbocyclic carbene complexes, there have been

several synthetic procedures attempted that held good potential for preparing a cycloheptatrienyliidene complex. However, as discussed below, all of these attempts proved futile.

After the system outlined by Öfele *vide supra*, DeJohn et al.¹⁹ employed dianion transition metal carbonyls (i.e. $\text{Na}_2\text{Cr}(\text{CO})_5$ and $\text{Na}_2\text{Fe}(\text{CO})_4$) in reactions with dichloro-, dibromo-, or 7,7-dimethoxycycloheptatriene. However, these attempts resulted in the reduction of the tropyli ring, yielding a mixture of substituted bitropyls 19.



Reactions of tropylium salts with $\text{NaFe}(\text{CO})_4\text{H}$,²⁰ modeled after another reaction scheme reported by Öfele²¹ also gave reduction of the tropyli ring. Furthermore, reaction of heptafulvalene with diphenylcarbene(pentacarbonyl)-tungsten(0) (11), modeled after Casey and Burkhardt's reaction using 1-methoxy-1-phenylethene¹¹ *vide supra*, gave no sign of a carbene complex or diphenylethylene.^{20, 22}

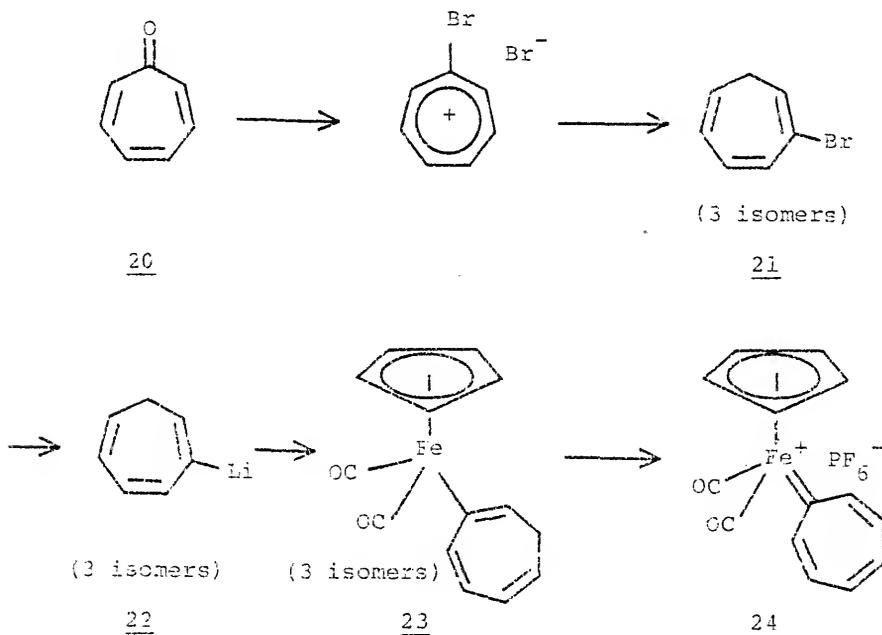


Decomposition of the sodium salt of tropone tosylhydrazide in hopes of trapping the presumed diazo intermediate with methylcyclopentadienyldicarbonyl (THF)manganese *vide supra* was also attempted. However, this also resulted in failure.

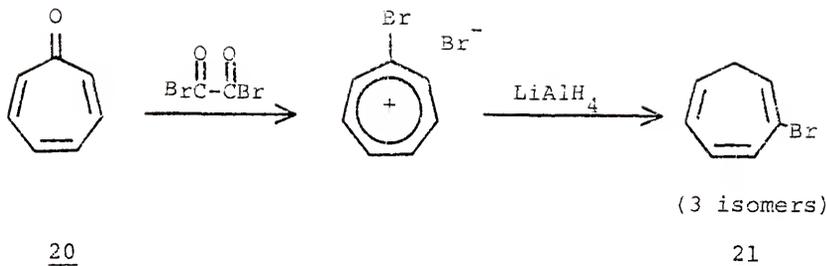
Therefore, the primary objective of this research was to synthesize and explore the chemistry of a transition metal complex of cycloheptatrienyliene. If such a complex could be synthesized, it would be the first example of a cycloheptatrienyliene complex and an unsubstituted carbocyclic aromatic carbene complex.

CHAPTER II
RESULTS AND DISCUSSION

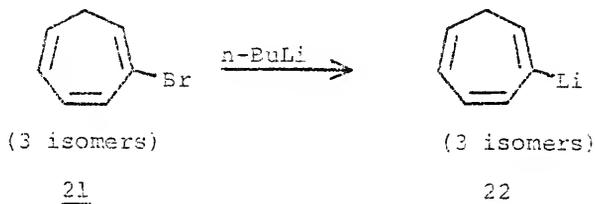
The synthesis of the first transition metal complex of cycloheptatrienyliene was successfully accomplished via the synthetic route shown below.²² A detailed look at this synthesis follows.



The preparation of 1-, 2-, and 3-bromocycloheptatrienes (21) from tropone (20) was previously reported.^{23, 24} Treatment of tropone with oxalyl bromide gave bromotropylium bromide. Reduction of the dibromide with lithium aluminum hydride gave the isomeric mixture of bromocycloheptatrienes, 21, as reported.

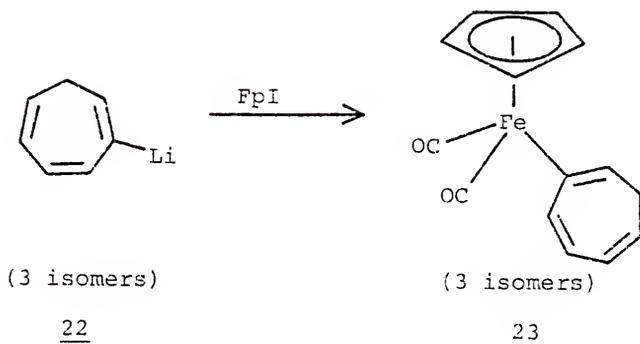


The next step, the generation of the cycloheptatrienyllithiums, 22, held the key to the successful complexing of a cycloheptatriene moiety to a transition metal. Even though their generation had not been reported, this type of exchange reaction with vinyl bromides and iodides is well known.²⁵ It was found that by treating the bromocycloheptatrienes with *n*-butyllithium, the exchange reaction occurred readily, giving a dark green colored solution.

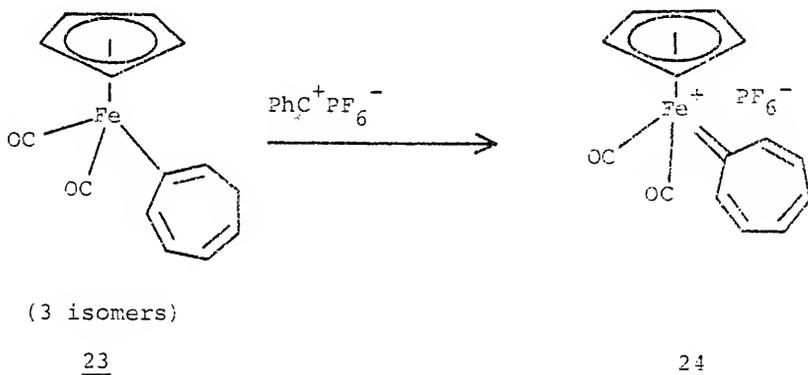


The reaction of transition metal halides with alkyl and aryl Grignard and lithium reagents is well documented.²⁶⁻³¹ Treatment of the cycloheptatrienyllithiums 22 with cyclopentadienylirondicarbonyl iodide (FpI) resulted in the generation of the 1-, 2-, and 3-(cyclopentadienylirondicarbonyl)-cycloheptatrienes {Fp[cycloheptatriene]} (23; 26-29); as a

yellow, air sensitive oil. The ^1H nmr spectrum of the mixture is given in Figure 1.



With the isolation of 23 in hand, hydride abstraction from the cycloheptatriene ligands with triphenylcarbenium hexafluorophosphate gave 24 (90%), a solid whose elemental analysis is consistent with a $\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_7\text{H}_6)\text{PF}_6$ formula. The ^1H nmr spectrum of 24 is given in Figure 2.



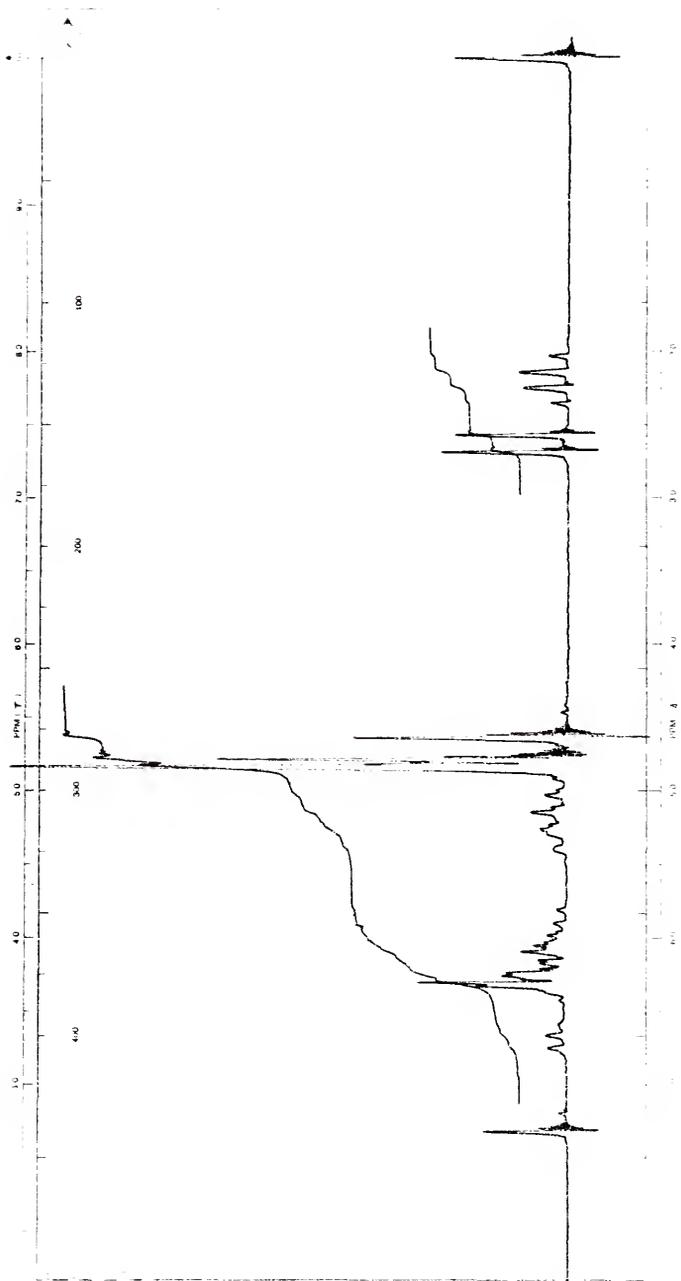


Figure 1. ^1H NMR Spectrum of 1-, 2-, and 3-(cyclopentadienylironcarbonyl)cycloheptatrienes (23).

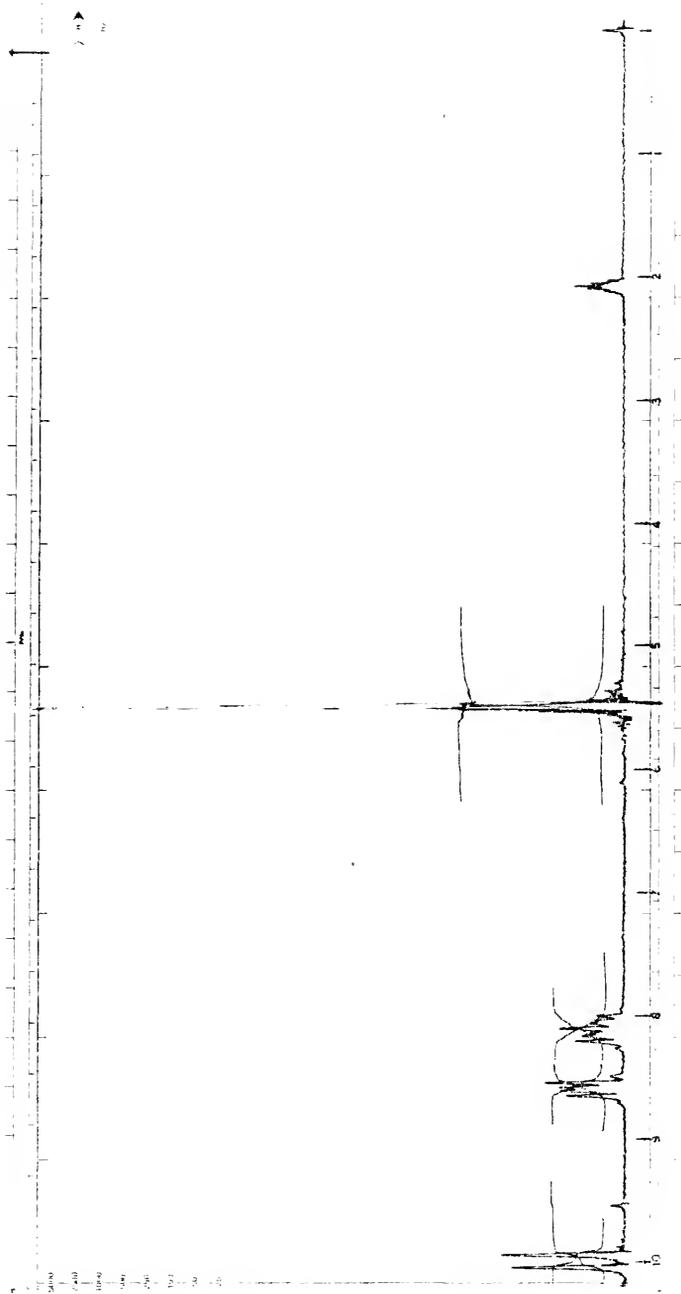
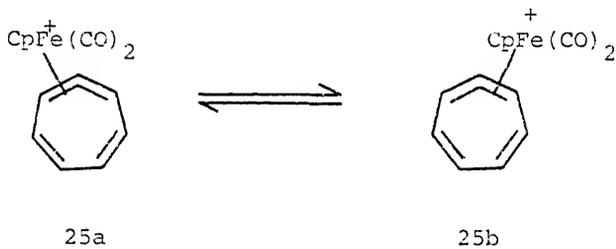


Figure 2. ^1H nmr Spectrum of h^1 -Cycloheptatrienylylidene- h^5 -cyclopentadienyldicarbonyl-iron Hexafluorophosphate (24).

Proof of the carbene structure of 24 lies in its spectral data. As is seen in the ^1H nmr spectrum, the doublet at $\delta 10.01$ and the multiplets at $\delta 8.48-8.74$ and $7.94-8.3$ appear at fairly low field. The ir spectrum exhibits two carbonyl stretching frequencies at 2045 and 1996 cm^{-1} . Both the ^1H nmr and ir absorptions are indicative of the inherent symmetry within the complex.

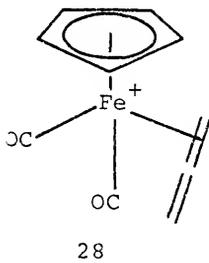
However, at the time of its generation, it was thought that the ligand could be complexed in the form of an allene (e.g. 25) rather than a carbene. This was considered because



(1) Cycloheptatrienyliidene (26) exhibits properties consistent with a cycloheptatetraene intermediate (27)^{32, 33} and (2) there are numerous examples of Fp allene complexes.³⁴



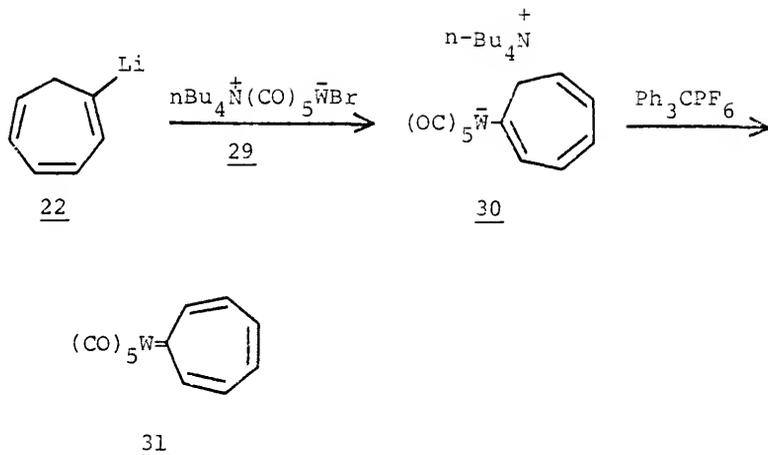
However, from the ^1H nmr, this allene structure may be ruled out on the basis of the low field proton resonances. Whereas $\text{Cp}(\text{CO})_2\text{Fe}^+(\text{allene})$ (28) shows resonances at $\delta 6.59$, 6.25, and 3.3,³⁴ the proton resonances at the C-2 and C7



positions in 24 appear at much lower field ($\delta 10.01$). From this, it is seen that an allene structure is unlikely and the preferred structure is the carbene complex 24.

η^1 -Cycloheptatrienyldiene- η^5 -cyclopentadienyldicarbonyl-iron hexafluorophosphate ($\text{Fp}[\text{cycloheptatrienyldiene}]\text{HFP}$) (24) is a stable yellow-orange solid with a fairly high decomposition point (180.5 - 181.5°C). It forms plates when recrystallized from methylene chloride. Moreover, it is stable to air as a solid and can be stored for months as a solid in a dark bottle, in the presence of air, without decomposition. Even after refluxing in dichloroethane (b.p. 83°C) for 6 hours, the salt was reisolated with no apparent decomposition.

To test the generality of this method with other transition metals, a neutral cycloheptatrienyldiene complex was prepared by Kawada.²² This synthetic route is shown below.

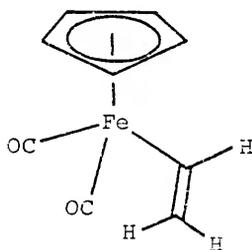


Reaction of the cycloheptatrienyllithiums (enriched in the 1-isomer) 22 with tetra-butylammonium bromopentacarbonyl-tungstate (29) gave the negative cycloheptatriene complex 30. Hydride abstraction from 30 with triphenylcarbenium hexafluorophosphate then gave cycloheptatrienyliidene(pentacarbonyl)tungsten (31).

The spectra of $\text{Fp}[\text{cycloheptatrienyliidene}]\text{HFP}$ (24) and cycloheptatrienyliidene(pentacarbonyl)tungsten (31) give some insight into their bonding. As can be seen in Figure 2, the proton resonances of the carbene ligand in $\text{Fp}[\text{cycloheptatrienyliidene}]\text{HFP}$ appear at low field. Because the complex is a salt, the question may be asked, "Do these chemical shifts primarily arise from the inherent positive charge of the complex?" This may be answered by comparison of its spectrum with the neutral tungsten cycloheptatrienyliidene complex 31. Whereas 24 shows resonances at $\delta 10.01$, $8.48\text{--}8.74$, and $7.94\text{--}8.3$, the neutral tungsten complex's resonances

appear at only slightly higher field (δ 9.96, 8.1, and 7.7) and are identical in shape to those of the iron complex. It would appear from this data that almost equivalent amounts of positive charge lie in their ligands.

The ir spectral data of both the iron and tungsten complexes indicate that more positive charge is localized on the carbene ligands than is the case with other known carbene complexes. For example, the carbonyl stretching frequencies of $\text{Fp}[\text{cycloheptatrienyldiene}]\text{HFP}$ at 2045 and 1996 cm^{-1} are substantially lower than those of $\text{Fp}[\text{benzocyclobutenyldiene}]\text{HFP}$ (16)¹⁷ at 2065 and 2020 cm^{-1} . A lower carbonyl frequency has been interpreted in terms of less electron density on the metal³⁵ and hence less back donation from the metal to the carbene ligand.¹³ However, comparison of the two absorptions of either vinylcyclopentadienylnoncarbonyl ($\text{Fp}[\text{vinyl}]$) (32)³⁶ or $\text{Fp}[\text{cycloheptatriene}]$ (23) that appear at 2020 and 1950 cm^{-1} , suggests qualitatively that the carbene ligand in $\text{Fp}[\text{cycloheptatrienyldiene}]\text{HFP}$ does accept a substantial degree of back donation.



The similarity of the ^1H nmr spectra of the iron and tungsten cycloheptatrienylydene complexes suggests that the character of the carbene ligands and hence the amount of back donation afforded to the two ligands is roughly equivalent. Due to the fact that tungsten has both cis and trans carbonyl ligands with respect to the carbene ligands, some semi-quantitative calculations can be made. By using a method outlined by Cotton and Kraihanzel,³⁷ the carbonyl stretching force constants k_1 and k_2 in m dyn/A may be calculated. Furthermore, Darensbourg and Darensbourg³⁸ have utilized k_1 and k_2 in a semi-quantitative method for calculating relative amounts of back donation to carbene ligands. Using $(\text{CO})_5^{\text{WNH}}(\text{C}_6\text{H}_{11})$ as a standard, the values shown in Table 1 can be calculated. A larger value for π represents greater back donation into the carbene ligand.

Table 1. Carbonyl Stretching Force Constants in m dyn/A and π Parameters for Some $\text{LW}(\text{CO})_5$ Complexes

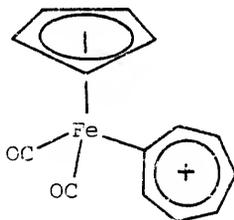
Compound	k_1	k_2	Δk_1	Δk_2	π	Ref.
$(\text{CO})_5^{\text{WNH}}(\text{C}_6\text{H}_{11})$	15.07	15.75	0	0	0	38
$(\text{CO})_5^{\text{WC}}\text{H}_6$ (31)	15.34	15.72	0.27	-0.03	0.30	22
$(\text{CO})_5^{\text{WC}}(\text{Ph})\text{OCH}_3$ (9)	15.71	15.90	0.64	0.15	0.49	8
$(\text{CO})_5^{\text{WC}}(\text{Ph})_2$ (11)	15.87	16.08	0.80	0.33	0.47	8

From the values of π it is seen that although the amount of back donation to the carbene ligand in cycloheptatrienylydene(pentacarbonyl)tungsten is substantial, it is

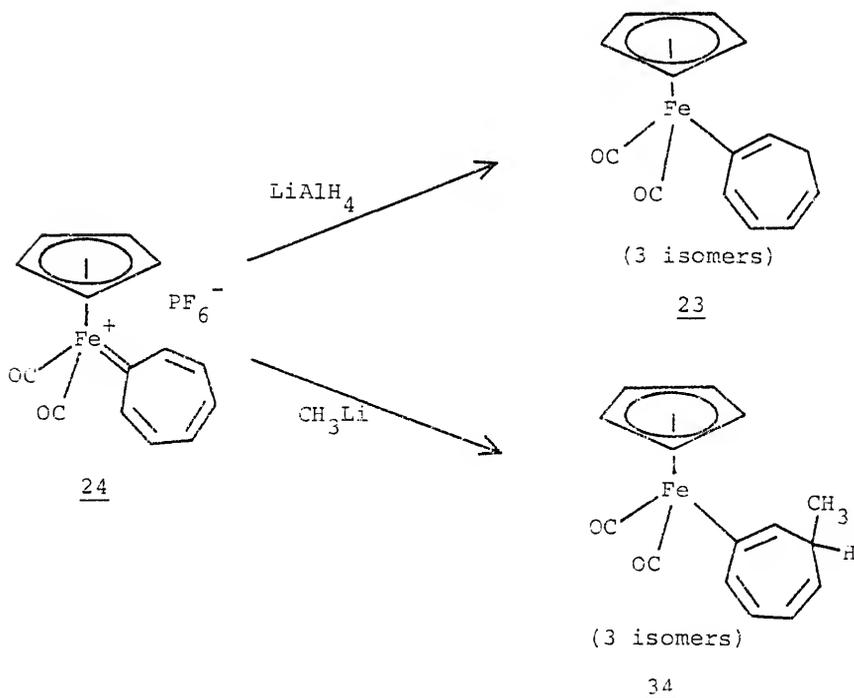
not as great as in the diphenylcarbene and phenylmethoxy-carbene tungsten complexes, 11 and 9, respectively. It should be noted that this agrees well with the suggested amount of back donation for Fp[cycloheptatrienyldiene]HFP vide supra.

The ^{13}C nmr spectrum of Fp[cycloheptatrienyldiene]HFP exhibits a resonance for C-1 at $\delta 242.3$. This lies in the high field range of known carbene complexes³⁹ and is 100 ppm higher field than that of Fp[phenylcarbene]TFA (18) at $\delta 342.4$.¹⁸ This suggests that there is less positive charge residing on the carbene carbon of Fp[cycloheptatrienyldiene]-HFP than Fp[phenylcarbene]TFA.

In summary, it is apparent that there is more positive charge on the ligand of Fp[cycloheptatrienyldiene]HFP (24) than Fp[benzocyclobutenyldiene]HFP (16). Furthermore, the positive charge in the carbene ligand of Fp[cycloheptatrienyldiene]HFP is more highly delocalized than in Fp[phenylcarbene]-TFA (18) indicating the importance of resonance forms represented by 33. Also the ^1H nmr and ir spectra of cycloheptatrienyldiene(pentacarbonyl)tungsten suggests similarities in the amount of back donation and positive charge afforded to the carbene ligand.

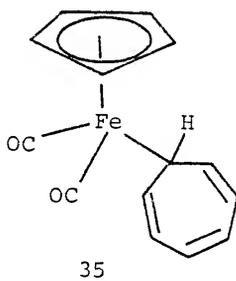
33

It was reported that $\text{Fp}[\text{benzocyclobutenylidene}]\text{HFP}$ (16) reacts with nucleophiles.¹⁷ Similarly, it was found that $\text{Fp}[\text{cycloheptatrienylidene}]\text{HFP}$ (24) also reacts quite rapidly with nucleophiles. For example, reaction with lithium aluminum hydride resulted in the regeneration of 1-, 2-, and 3-(cyclopentadienylirondicarbonyl)cycloheptatrienes (23; 67%). Furthermore, $\text{Fp}[\text{cycloheptatrienylidene}]\text{HFP}$ reacted with methyllithium to give 1-, 2-, and 3-(cyclopentadienylirondicarbonyl)-7-methylcycloheptatrienes (34). It is interesting to note that in contrast to the reactions

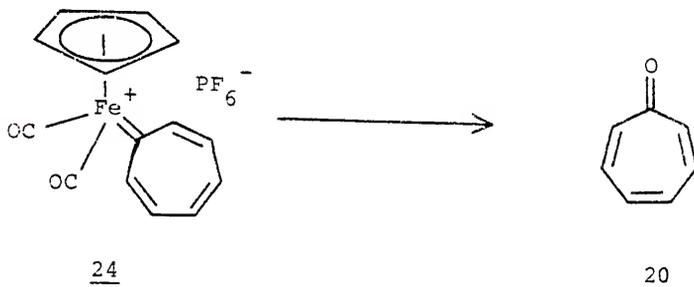


of $\text{Fp}[\text{benzocyclobutenylidene}]\text{HFP}$ (16), these nucleophiles gave no evidence of attack at the carbene carbon. For

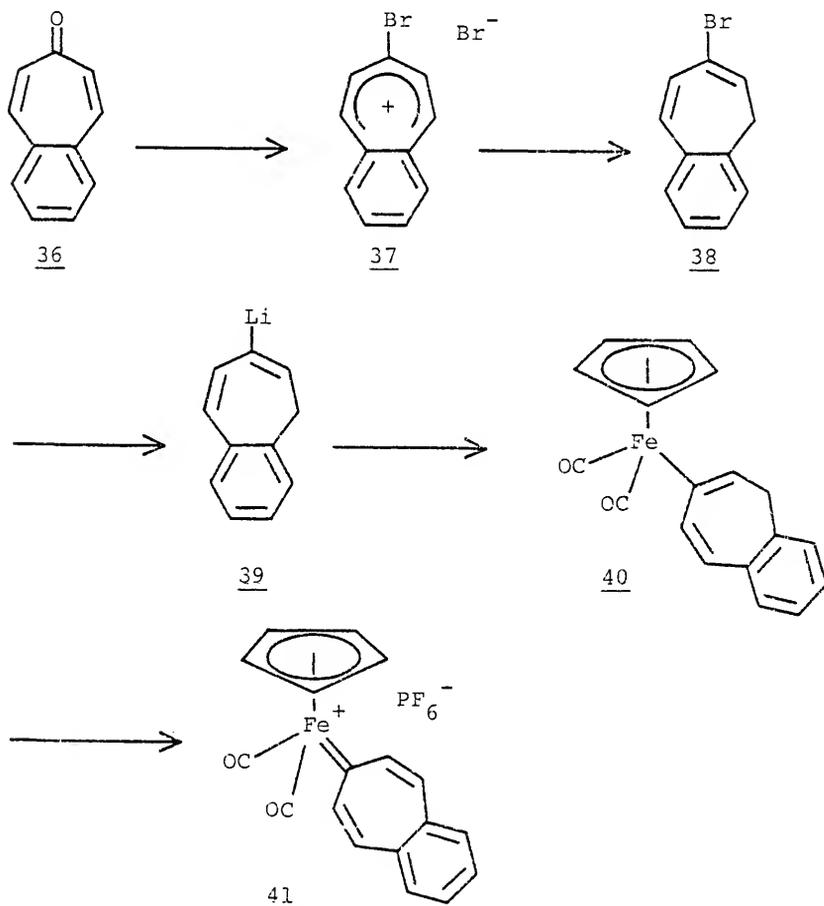
instance, the reaction with lithium aluminum hydride, gave no sign of products that would be expected from the cycloheptatriene complex 35.⁴⁰ However, in the future perhaps a study should be done with more selective reducing reagents.



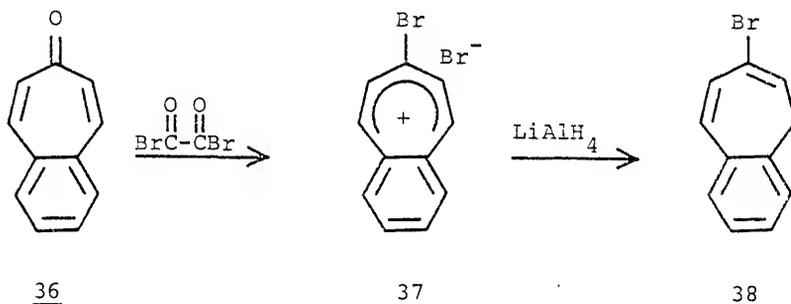
Carbene complexes are also known to undergo oxidative cleavage when treated with dimethylsulfoxide. For instance, diphenylcarbene(pentacarbonyl)tungsten was oxidized to benzophenone.⁸ $\text{Fp}[\text{cycloheptatrienyliidene}]\text{HFP}$ also readily undergoes oxidative cleavage with this reagent. After being stirred overnight in dimethylsulfoxide, $\text{Fp}[\text{cycloheptatrienyliidene}]\text{HFP}$ gave tropone (20; 17%).



To test the generality of this synthetic method for preparing aromatic carbene complexes, the synthesis of a 4,5-benzocycloheptatrienylidene complex was attempted. In fact, this test proved to be quite rewarding. The synthesis of η^1 -4,5-benzocycloheptatrienylidene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate (Fe[4,5-benzocycloheptatrienylidene]HFP) (41) is outlined below. A detailed look at this synthesis follows.



The preparation of 4,5-benzotropone (36) has been reported by Paquette and Ewing.⁴¹ Even though the synthesis of 1,2-benzo-5-bromocycloheptatriene (38) had not been reported at the time of its preparation in this laboratory, Föhlisch et al. reported an almost identical procedure at a later date.⁴² Treatment of 4,5-benzotropone (36) with oxalyl bromide gave 1,2-benzo-5-bromotropylium bromide (37) in the form of a red solid. Treatment of a solution of this bromide with lithium aluminum hydride readily gave 38 in 65% yield.



Treatment of 38 with an equivalent amount of n-butyllithium gave a dark evergreen colored solution. Addition of this newly generated lithium reagent 39 to cyclopentadienylirondicarbonyl iodide (FpI) gave 1,2-benzo-5-(cyclopentadienylirondicarbonyl)cycloheptatriene (40; 26%) as a yellow, air sensitive solid. Its ^1H nmr spectrum is given in Figure 3.

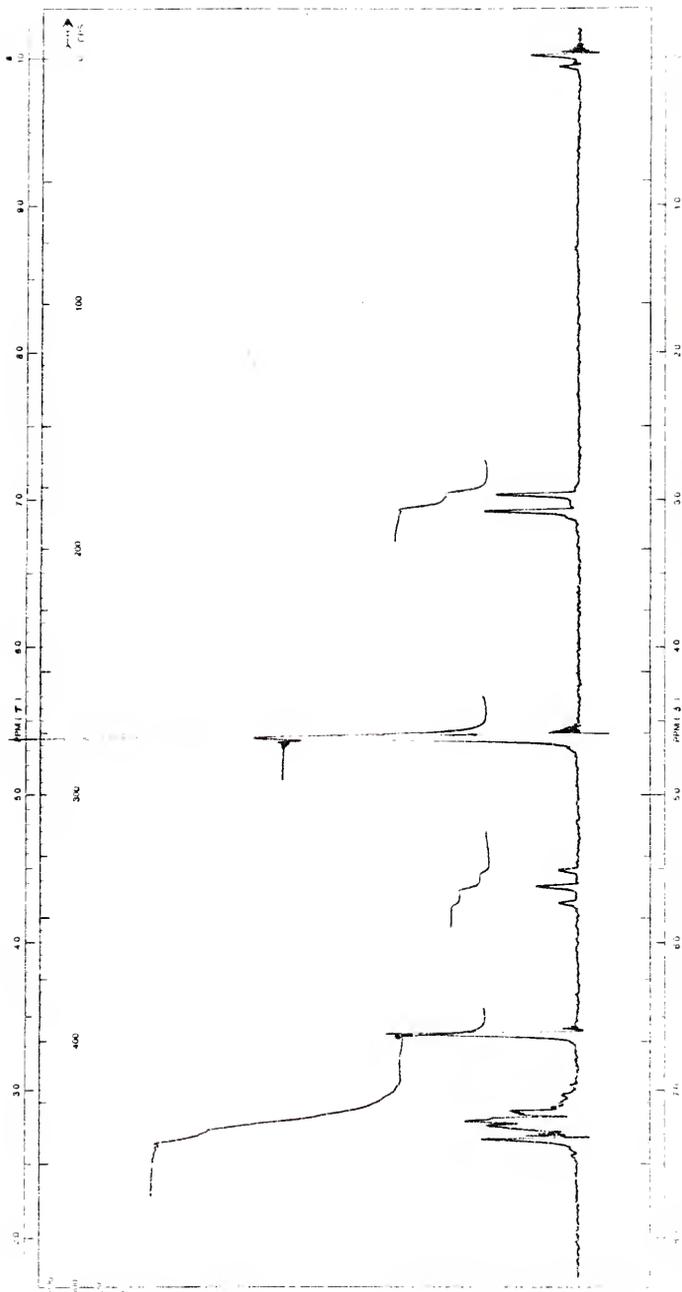
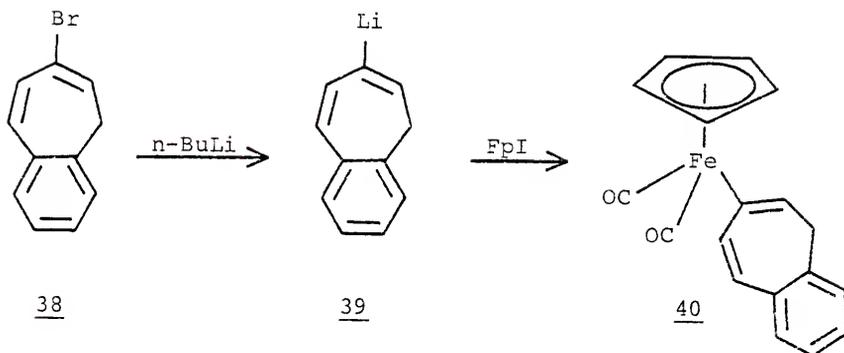
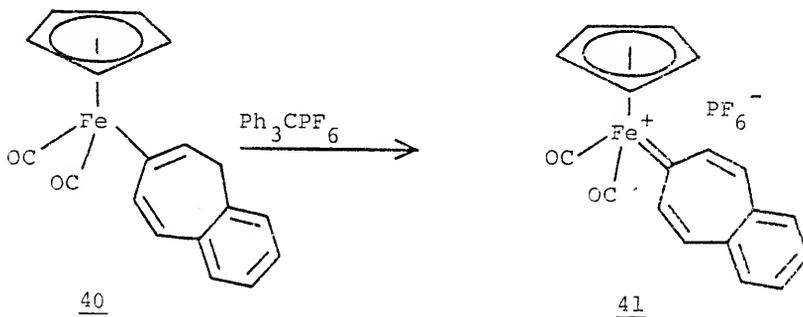


Figure 3. ^1H NMR Spectrum of 1,2-Benzo-5-(cyclopentadienylironcarbonyl)cycloheptatriene (40).



When a methylene chloride solution of 40 was treated with triphenylcarbenium hexafluorophosphate, it rapidly turned from yellow to red. Workup of the reaction solution gave 41, (93%), a fire-brick red solid, whose elemental analysis is consistent with a $\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_{11}\text{H}_8)\text{PF}_6$ formula. Its ^1H nmr spectrum is given in Figure 4.



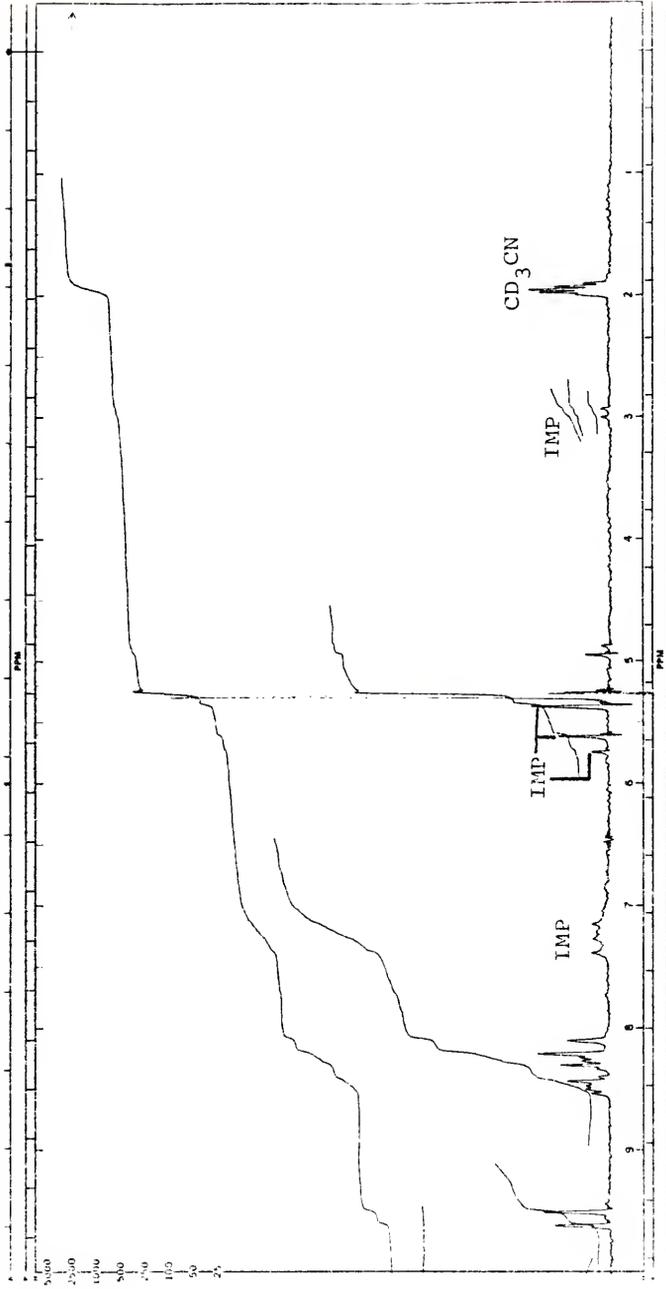
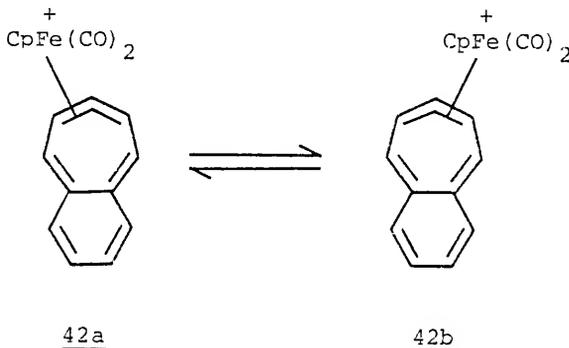


Figure 4. ^1H NMR Spectrum of h^1 -4,5-benzocycloheptatrienylidene- h^5 -cyclopentadienyl-dicarbonyliron Hexafluorophosphate (36).

The structure of formula $\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_{11}\text{H}_8)\text{PF}_6$ could be consistent (as in the case of $\text{Fp}[\text{cycloheptatrienyliidene}]\text{HFP}$) with either a carbene complex or an allene complex (i.e. 42). However, as before, the allene structure may be ruled out



on the basis of the low field proton resonances of the ligand. Whereas $\text{Cp}(\text{CO})_2\text{Fe}^+(\text{allene})$ shows resonances at $\delta 6.59$, 6.25 , and 3.3 ,³⁴ the proton resonances of C-2, 3, 10, and 11 in $\text{Fp}[4,5\text{-benzocycloheptatrienyliidene}]\text{HFP}$ (41) appear at $\delta 9.58$ and 8.26 . From this it is clear that the allene structure is unlikely and the preferred structure is the carbene complex 41.

Complex 41 is an air stable solid with a decomposition point of $177\text{--}178^\circ\text{C}$. Furthermore, even after being stored as a solid for four months in a dark bottle, it showed no sign of decomposition.

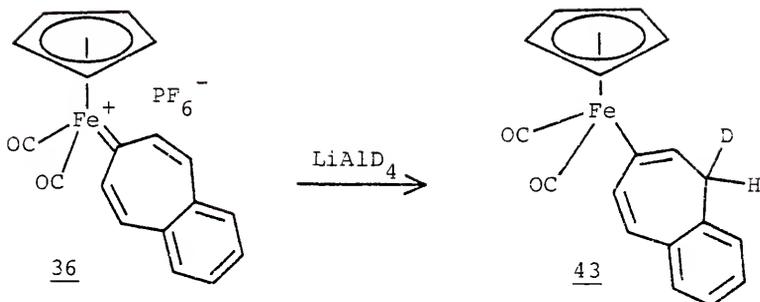
As seen in $\text{Fp}[\text{cycloheptatrienyliidene}]\text{HFP}$, the proton resonances of 41 are also significantly shifted downfield.

Whereas $\text{Fp}[\text{cycloheptatrienyli-}d\text{ene}]\text{HfP}$ shows resonances at $\delta 10.01$, $8.48\text{--}8.74$, and $7.94\text{--}8.3$, the resonances of 41 appear at $\delta 9.58$ and 8.26 (for C-2, 3, 10, and 11). Interestingly, in the fused benzene ring the proton shifts at $\delta 8.58$ to 8.08 are downfield from most organic aromatic resonances. This indicates that the positive charge is delocalized throughout the pi system.

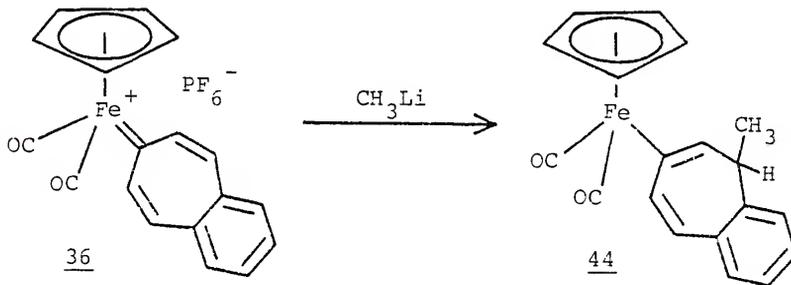
In the ir spectrum, the carbonyl stretching frequencies of $\text{Fp}[4,5\text{-benzocycloheptatrienyli-}d\text{ene}]\text{HfP}$ at 2045 and 2000 cm^{-1} are very close to those observed for $\text{Fp}[\text{cycloheptatrienyli-}d\text{ene}]\text{HfP}$ at 2045 and 1996 cm^{-1} . This suggests almost identical back bonding to the carbene ligands.^{13, 35} Thus the amount of positive charge on each carbene ligand is roughly equivalent.

Perhaps the most intriguing data are seen in the ^{13}C nmr spectrum. Whereas the $\text{Fp}[\text{cycloheptatrienyli-}d\text{ene}]\text{HfP}$ shows its C-1 resonance at $\delta 242.3$, the resonance of $\text{Fp}[4,5\text{-benzocycloheptatrienyli-}d\text{ene}]\text{HfP}$ appears at $\delta 265.9$. This suggests that there is more positive charge on the carbene carbon of $\text{Fp}[4,5\text{-benzocycloheptatrienyli-}d\text{ene}]\text{HfP}$ than that of $\text{Fp}[\text{cycloheptatrienyli-}d\text{ene}]\text{HfP}$.

As with $\text{Fp}[\text{cycloheptatrienyli-}d\text{ene}]\text{HfP}$, $\text{Fp}[4,5\text{-benzocycloheptatrienyli-}d\text{ene}]\text{HfP}$ also undergoes reduction. Treatment of the complex with lithium aluminum deuteride generated 1,2-benzo-5-(cyclopentadienyli-}r\text{ondicarbonyl})-7-deuterocycloheptatriene (43; 62%).

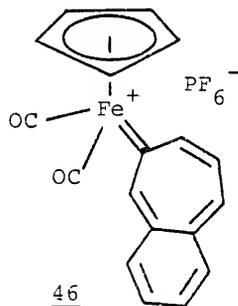
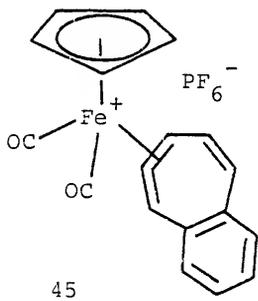


Furthermore, nucleophilic attack with methyllithium generated the methyl substituted complex 44 in 38% yield.



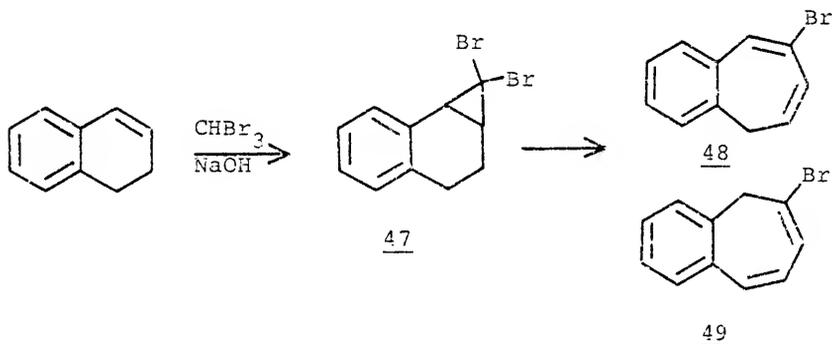
As indicated above, in principle, it is possible that the complex of cycloheptatrienylidene could exist as either a carbene or an allene species. In the case of $\text{Fp}[\text{cycloheptatrienylidene}]\text{HFP}$ and $\text{Fp}[4,5\text{-benzocycloheptatrienylidene}]\text{HFP}$, there can be little question but that the carbene form is the dominant and perhaps exclusive form.

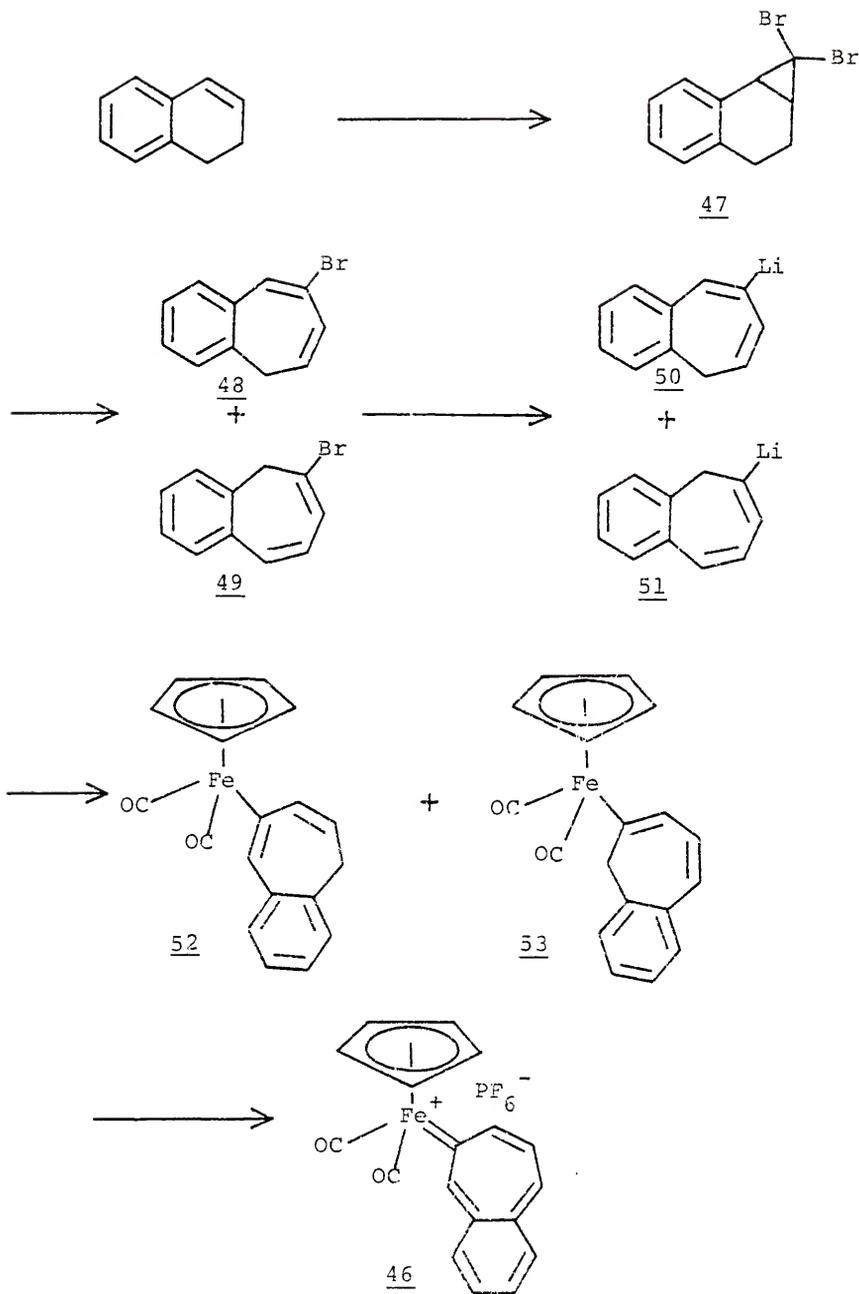
With an eye toward biasing the ligand in the direction of an allene form, it was thought that 3,4-benzo-annulation might favor an allene complex 45 over the carbene complex 46.



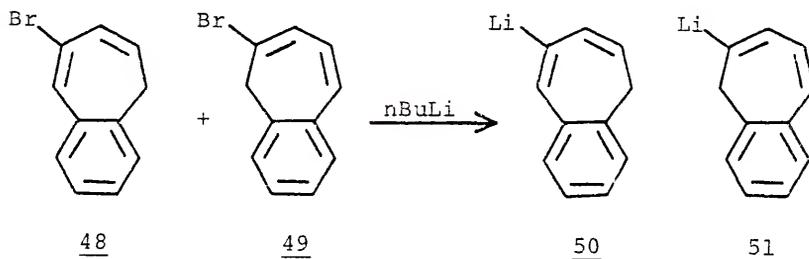
The synthesis of a 3,4-benzo-annulated system is outlined on page 33. A detailed discussion of this synthesis follows.

Addition of dibromocarbene to 1,2-dihydronaphthalene⁴³ generated the dibromocyclopropane 47. This dibromo compound was thermally unstable and upon distillation spontaneously eliminated hydrogen bromide with a concomitant ring expansion to give the mixture of isomeric bromides 48 and 49.

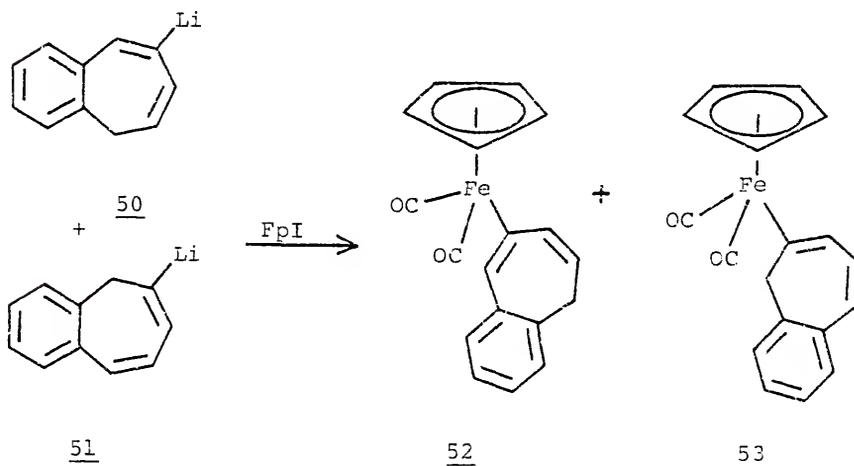




The preparation of 1,2-benzo-4- and 1,2-benzo-6-lithiocycloheptatrienes (50 and 51, respectively) was accomplished by treating these bromides with *n*-butyllithium.



The solution of 50 and 51 was then added to a solution of cyclopentadienyliron dicarbonyl iodide (FpI) giving an isomeric mixture of 1,2-benzo-4- and 1,2-benzo-6-(cyclopentadienyliron dicarbonyl)cycloheptatrienes (52 and 53, respectively). The ^1H nmr spectrum of the mixture is given in Figure 5.



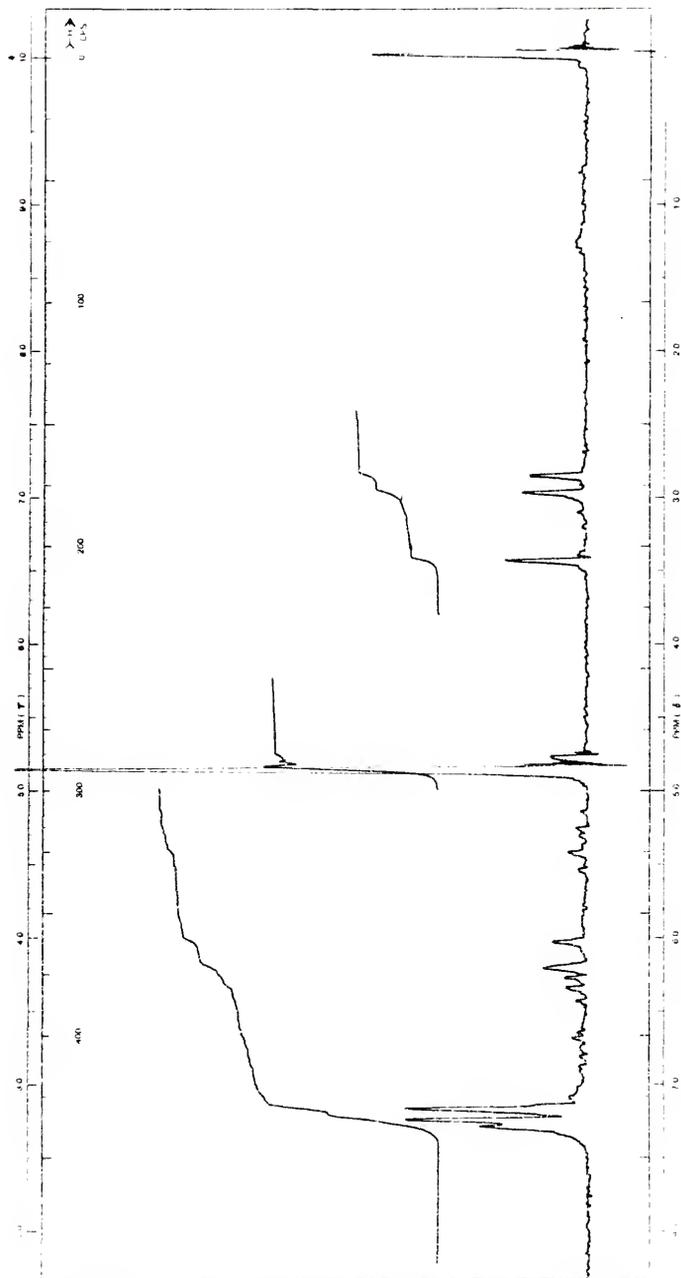
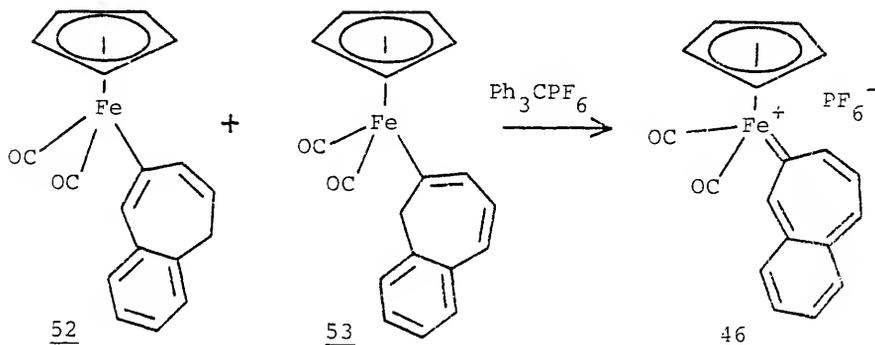


Figure 5. ^1H NMR Spectrum of 1,2-Benzo-4- and 1,2-Benzo-6-(cyclopentadienyl)iron-dicarbonylcycloheptatrienes (52, 53).

The generation of a brick red solid whose elemental analysis is consistent with $\text{Cp}(\text{CO})_2\text{Fe}(\text{C}_{11}\text{H}_8)\text{PF}_6$ was smoothly accomplished via treatment of 52 and 53 with triphenylcarbenium hexafluorophosphate. The ^1H nmr spectrum of 46 is shown in Figure 6.



Surprisingly, from the ^1H nmr spectrum, an allene structure may be ruled out on the basis of the low field resonances that this material exhibits. Whereas $\text{Cp}(\text{CO})_2\text{Fe}^+$ (allene) shows resonances at δ 6.59, 6.25, and 3.3,³⁴ the resonances of 46 appear at much lower field (δ 10.4, 9.92, 9.93, 8.5, and 3.16). Therefore, even 3,4-benzo-annulation of a cycloheptatrienyliene complex failed to favor an allene complex and instead gave η^1 -3,4-benzocycloheptatrienyliene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate ($\text{Fp}[3,4\text{-benzocycloheptatrienyliene}]\text{HFP}$) (46).

This compound gives dark violet crystals from methylene chloride and has a rather high decomposition point (176-177°C). Moreover, 46 as a solid is perfectly stable to air. However,

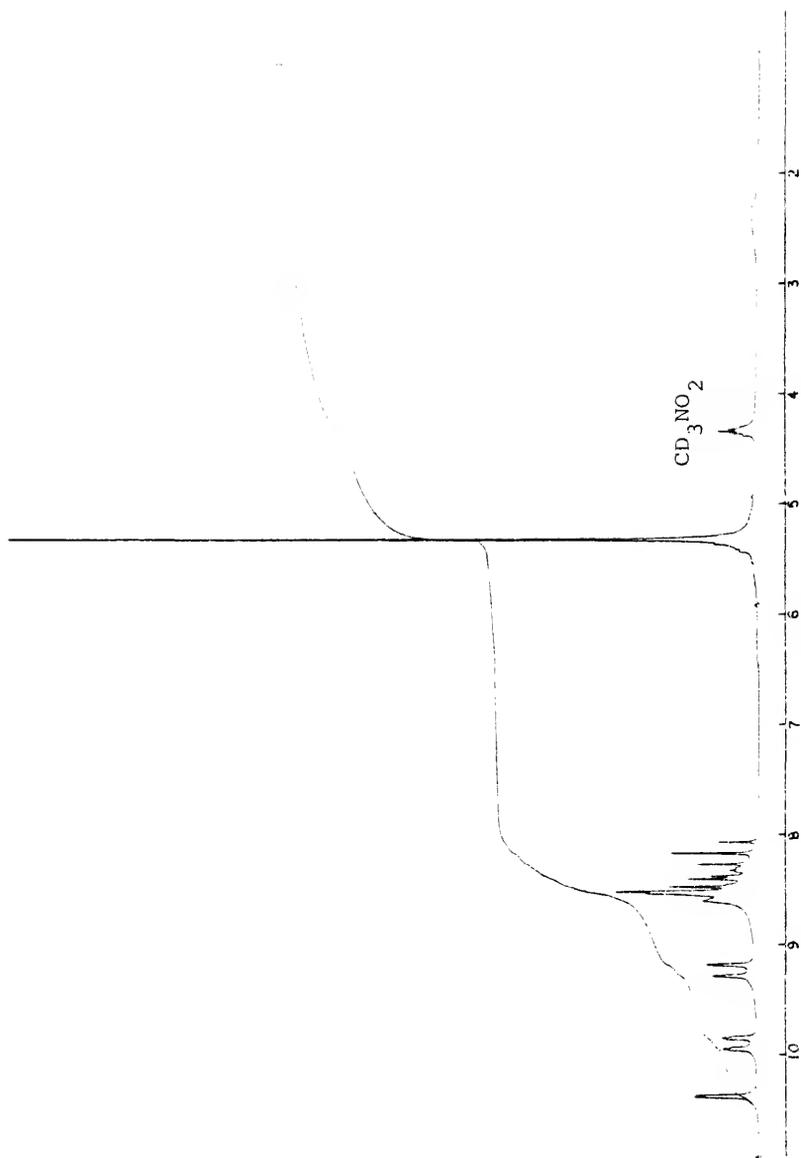


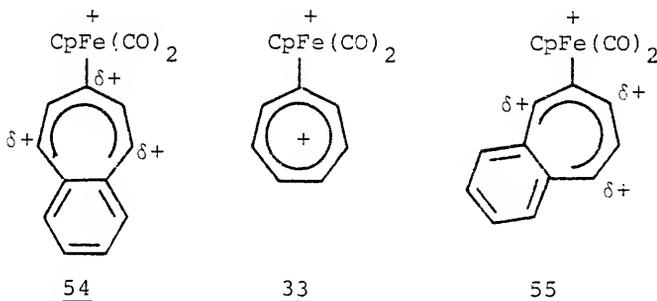
Figure 6. ^1H NMR Spectrum of $h^1-3,4$ -Benzocycloheptatrienyliidene- h^5 -cyclopentadienyldicarbonyliron Hexafluorophosphate (46).

in contrast to $\text{Fp}[\text{cycloheptatrienylidene}]\text{HFP}$, 46 does slightly decompose after storing several months in a dark bottle. The most interesting characteristic of 46 is its unusual ^1H nmr spectrum. As seen in Figure 6, its ^1H nmr spectrum exhibits the lowest field resonance (at $\delta 10.4$, C-2) of the aromatic carbenes. In fact, this resonance is 0.4 ppm lower field than that of $\text{Fp}[\text{cycloheptatrienylidene}]\text{HFP}$ at $\delta 10.01$. The fused benzene ring's proton resonances appear around $\delta 8.50$. These are only slightly different from the resonances of $\text{Fp}[4,5\text{-benzocycloheptatrienylidene}]\text{HFP}$ at $\delta 8.58\text{-}8.08$. This indicates qualitatively that the amounts of positive charge lying on the fused benzene rings of both complexes are roughly equivalent.

However, the carbonyl stretching frequencies in the ir spectrum do point to a difference. Whereas $\text{Fp}[3,4\text{-benzocycloheptatrienylidene}]\text{HFP}$ shows absorptions at 2037 and 1992 cm^{-1} , the absorptions of $\text{Fp}[4,5\text{-benzocycloheptatrienylidene}]\text{HFP}$ appear at 2045 and 2000 cm^{-1} . This difference is significant and suggests that there could be less back bonding to the carbene ligand in $\text{Fp}[3,4\text{-benzocycloheptatrienylidene}]\text{HFP}$ than in $\text{Fp}[4,5\text{-benzocycloheptatrienylidene}]\text{HFP}$.¹³

The C-1 ^{13}C nmr chemical shift of $\text{Fp}[3,4\text{-benzocycloheptatrienylidene}]\text{HFP}$ is also significantly different from 36. As mentioned earlier, the resonance of $\text{Fp}[4,5\text{-benzocycloheptatrienylidene}]\text{HFP}$ at $\delta 265.9$ lies significantly lower field than that of $\text{Fp}[\text{cycloheptatrienylidene}]$ at $\delta 242.3$. Conversely, the resonance of $\text{Fp}[3,4\text{-benzocycloheptatrienylidene}]\text{HFP}$ is higher field at $\delta 201$. It is interesting to

note that these shifts correspond to what classical resonance theory predicts for three compounds whose resonance forms may be represented by 54, 33, and 55.



An x-ray structural determination of $\text{Fp}[3,4\text{-benzocycloheptatrienyli-}dene]\text{HFP}$ was performed by Davis.⁴⁴ The computer drawing shown in Figure 7 shows a fairly planar carbene ligand. It is interesting to note that the smallest angle in the seven membered ring is the $\text{C}(2)\text{-C}(1)\text{-C}(11)$ angle and the longest bond is the $\text{C}(3)\text{-C}(8)$ bond. Furthermore, some degree of bond alternation is present. A full tabulation of bond angles and distances is given in Table 2.

From classical resonance theory, annelation of a second benzene ring in the 5,6-position of 3,4-benzocycloheptatrienyli-*dene* should further enhance a cycloheptatriene form. This also is consistent with INDO calculations.⁴⁵ The synthesis of $\eta^1\text{-}3,4\text{-}5,6\text{-dibenzocycloheptatrienyli-}dene\text{-}\eta^5\text{-cyclopentadienyldicarbonyliron hexafluorophosphate}$ (56) (or the

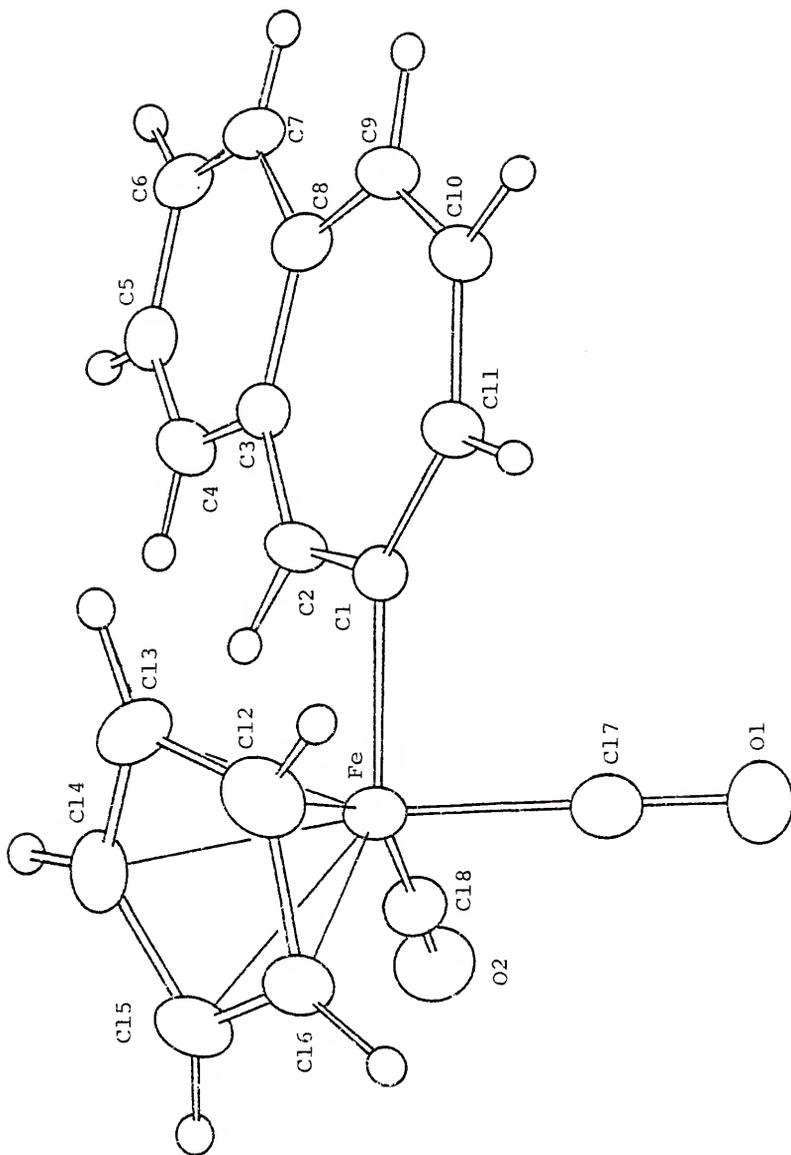
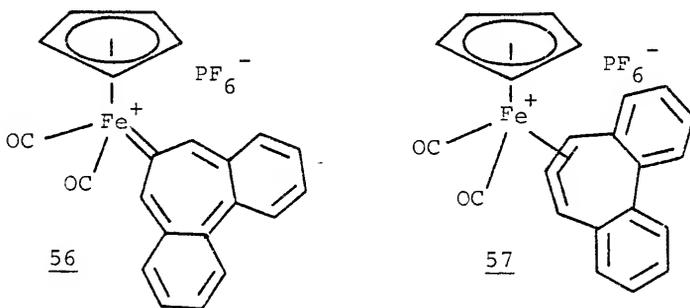


Figure 7. Computer Drawing of $h^1-3,4$ -Benzocycloheptatrienyliene- h^5 -cyclopentadienyldicarbonyliron Hexafluorophosphate (46).

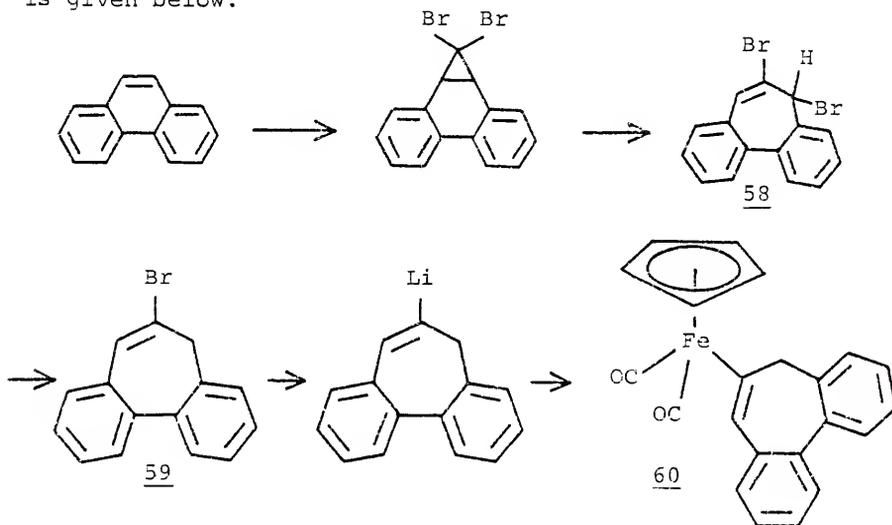
Table 2. Bond Lengths and Bond Angles for η^1 -Benzocycloheptatrienyliidene- η^5 -cyclopentadienyldicarbonyliron Hexafluorophosphate (46).

a. Bond Lengths, Å			
Fe-C(1)	1.996	C(7)-C(8)	1.429
Fe-C(17)	1.769	C(8)-C(9)	1.400
Fe-C(18)	1.766	C(10)-C(11)	1.388
C(1)-C(2)	1.395	C(12)-C(13)	1.387
C(1)-C(11)	1.407	C(12)-C(16)	1.418
C(2)-C(3)	1.416	C(13)-C(14)	1.412
C(3)-C(4)	1.429	C(14)-C(15)	1.402
C(3)-C(8)	1.435	C(15)-C(16)	1.403
C(4)-C(5)	1.358	C(17)-O(1)	1.140
C(5)-C(6)	1.402	C(18)-O(2)	1.138
C(6)-C(7)	1.346		
Fe-C(cp)	2.099, 2.101, 2.103, 2.098, 2.106		
b. Bond Angles, deg.			
Fe-C(1)-C(2)	119	C(4)-C(5)-C(6)	120
Fe-C(1)-C(11)	118	C(5)-C(6)-C(7)	120
C(1)-Fe-C(17)	93	C(6)-C(7)-C(8)	122
C(1)-Fe-C(18)	93	C(7)-C(8)-C(9)	116
C(1)-C(2)-C(3)	134	C(8)-C(9)-C(10)	130
C(1)-C(11)-C(10)	131	C(9)-C(10)-C(11)	130
C(2)-C(1)-C(11)	123	C(12)-C(13)-C(14)	109
C(2)-C(3)-C(4)	116	C(12)-C(16)-C(15)	107
C(2)-C(3)-C(8)	127	C(13)-C(12)-C(16)	108
C(3)-C(4)-C(5)	122	C(13)-C(14)-C(15)	107
C(3)-C(8)-C(7)	118	C(14)-C(15)-C(16)	109
C(3)-C(8)-C(9)	125	C(17)-Fe-C(18)	95
C(4)-C(3)-C(8)	118		

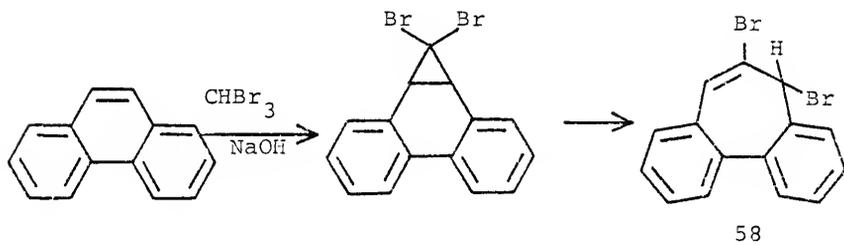
allene complex 57) was therefore attempted. If a carbene → allene isomerization could be effected in an unsaturated seven membered cyclic system (with iron as the metal), it was thought that this system offered the best chance for success.



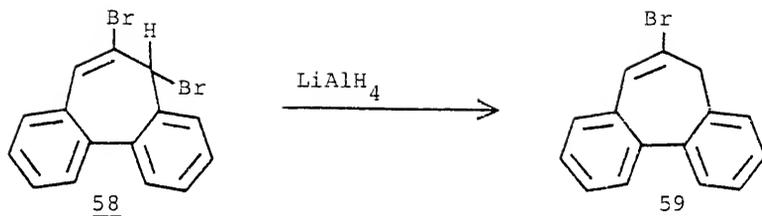
The synthetic route for the generation of 5-(cyclopentadienylirondicarbonyl)-5H-dibenzo[*a, e*]cycloheptene (60), a potential precursor for a carbene (or allene) complex, is given below.



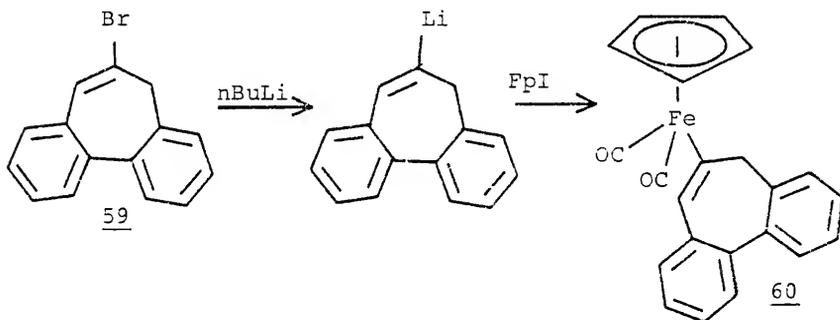
The preparation of 5,6-dibromo - 5H - dibenzo[*a,c*]cycloheptene (58) was accomplished through a dibromocarbene addition to phenanthrene followed by a ring expansion. Due to the difficulty encountered in separating the product from phenanthrene, a large excess of bromoform and base was used so as to completely eliminate the phenanthrene. However, difficulty in separating a polymeric material from the product still resulted in fairly low yields of pure material. Work up of the reaction mixture and fractional recrystallization from benzene gave the ring expanded dibromide 58 (12.4%) suitable for further use.



Reduction of the dibromide 58 gave the desired bromide 59. However, the reduction with lithium aluminum hydride must be done at low temperature ($\sim 78^\circ\text{C}$) with subsequent slow warming to room temperature to maximize yields. Reduction at a higher temperature led to 1,2-3,4-dibenzocycloheptatriene.



Treatment of 6-bromo-5H-dibenzo[*a,c*]cycloheptene (59) with *n*-butyllithium gave an aqua-green solution. Addition of this to cyclopentadienyliron dicarbonyl iodide (FpI) gave in 31% yield 6-(cyclopentadienyliron dicarbonyl)-5H-dibenzo[*a,c*]cycloheptene (60). Its ^1H nmr spectrum is given in Figure 8.



The attempted synthesis of the carbene complex (or allene complex) from 60 was unsuccessful. In a typical reaction, triphenylcarbenium hexafluorophosphate was introduced into a cold (-35°C) methylene chloride solution of 60. Even after five days of stirring at low temperature, the starting complex was recovered. Triphenylmethane or carbene complex was not detected.

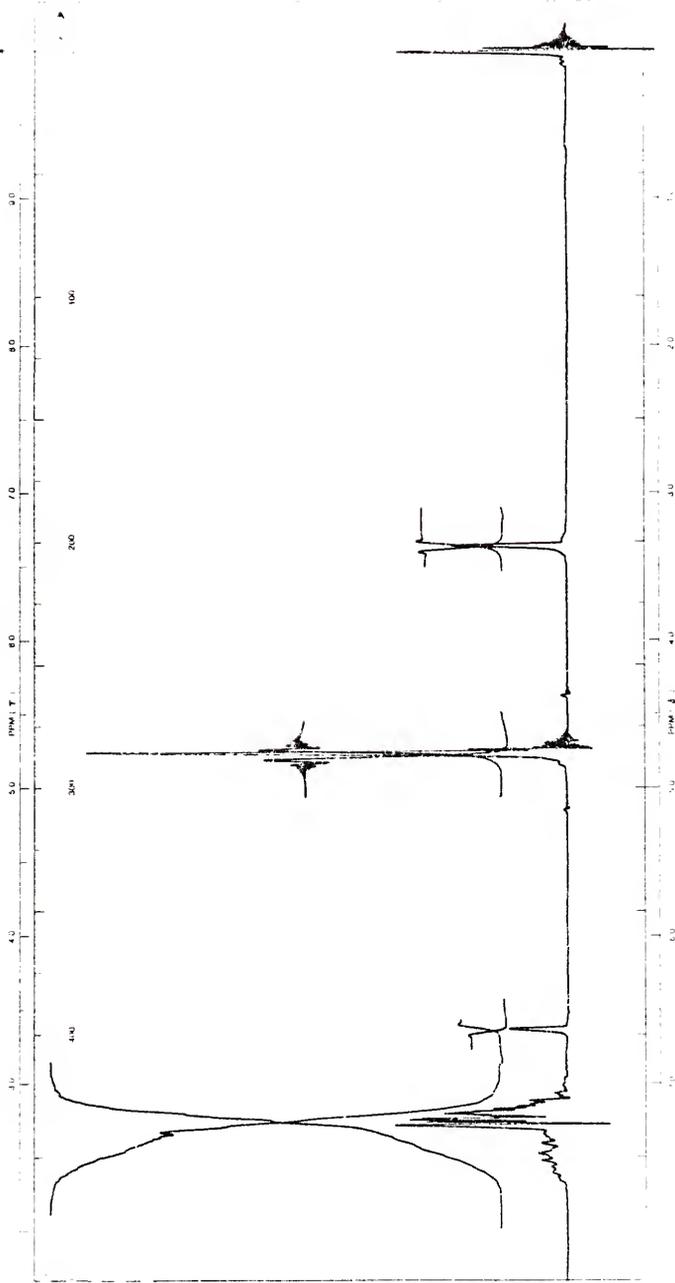
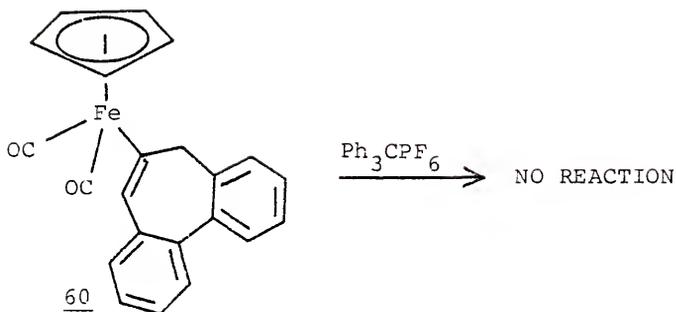
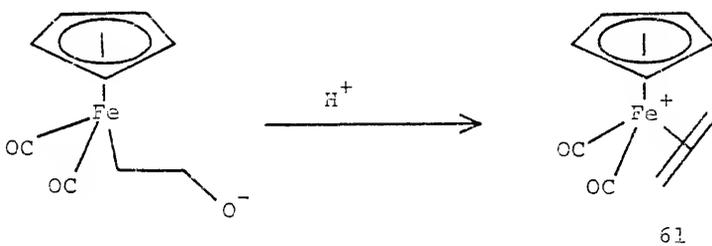
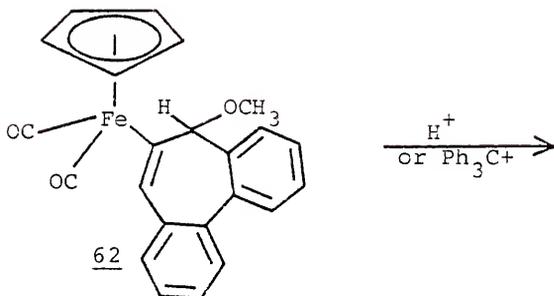


Figure 8. ^1H nmr Spectrum of 6-(Cyclopentadienyli ron di carbonyl) -5H-dibenzo [a, c] -cycloheptene (60).

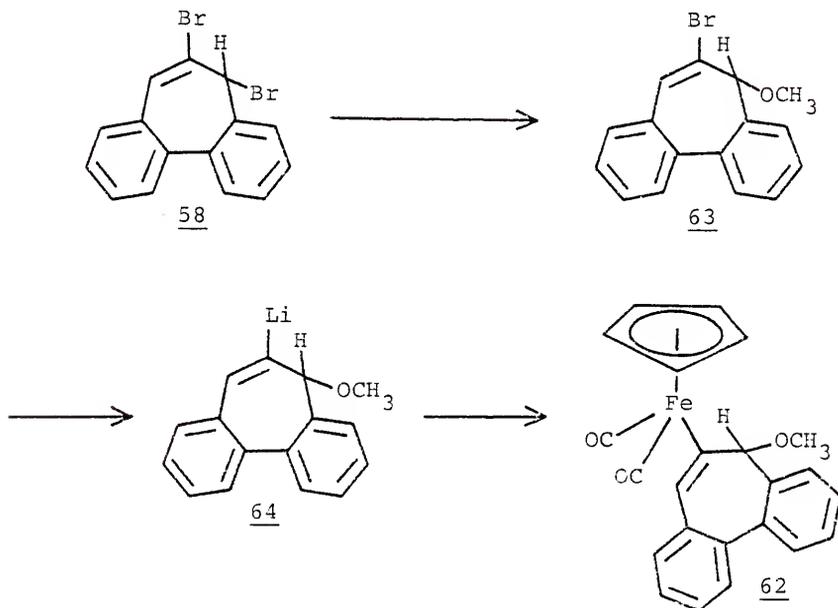


Since all attempts to generate the carbene (or allene) complex by hydride abstraction were unsuccessful, a second preparative method was attempted. From Brookhart's successful alpha methoxy abstraction with triphenylcarbenium ion in the generation of the phenyl carbene complex 18, vide supra, and the fact that olefin complexes (e.g. 61) are formed with relative ease via treatment of beta oxides with acid,⁴⁶ it was thought that a compound such as 6-(cyclopentadienylirondicarbonyl)-5-methoxy-5H-dibenzo[*a,e*]cycloheptene (62) might be the key to the synthesis of the desired carbene (or allene) complex.

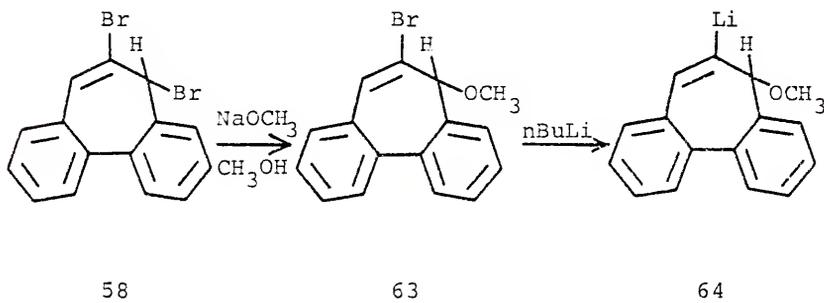




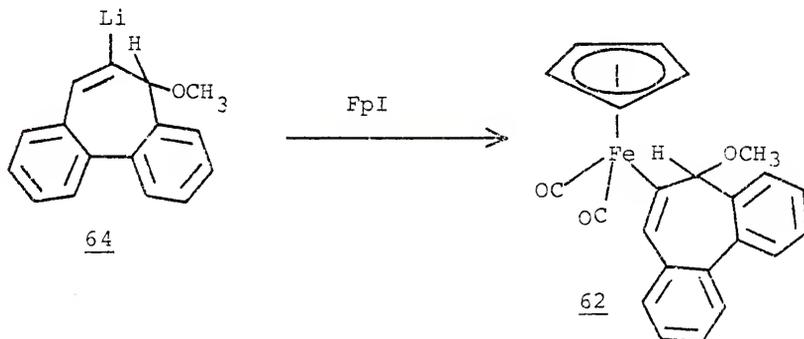
The preparative route to this second potential carbene precursor is shown below. A detailed discussion of its synthesis follows.



Treatment of 5,6-dibromo-5H-dibenzo[*a,c*]cycloheptene (58) with sodium methoxide in refluxing methanol readily afforded 6-bromo-5-methoxy-5H-dibenzo[*a,c*]cycloheptene (63; 91%). Treatment of a solution of 63 with *n*-butyllithium gave the 6-lithio-5-methoxy-5H-dibenzo[*a,c*]cycloheptene (64).



Addition of 64 to cyclopentadienyliron dicarbonyl iodide (FpI) gave 6-(cyclopentadienyliron dicarbonyl)-5-methoxy-5H-dibenzo[*a,c*]cycloheptene (62; 19%) as a yellow, air sensitive oil. Its ¹H nmr spectrum is given in Figure 9.



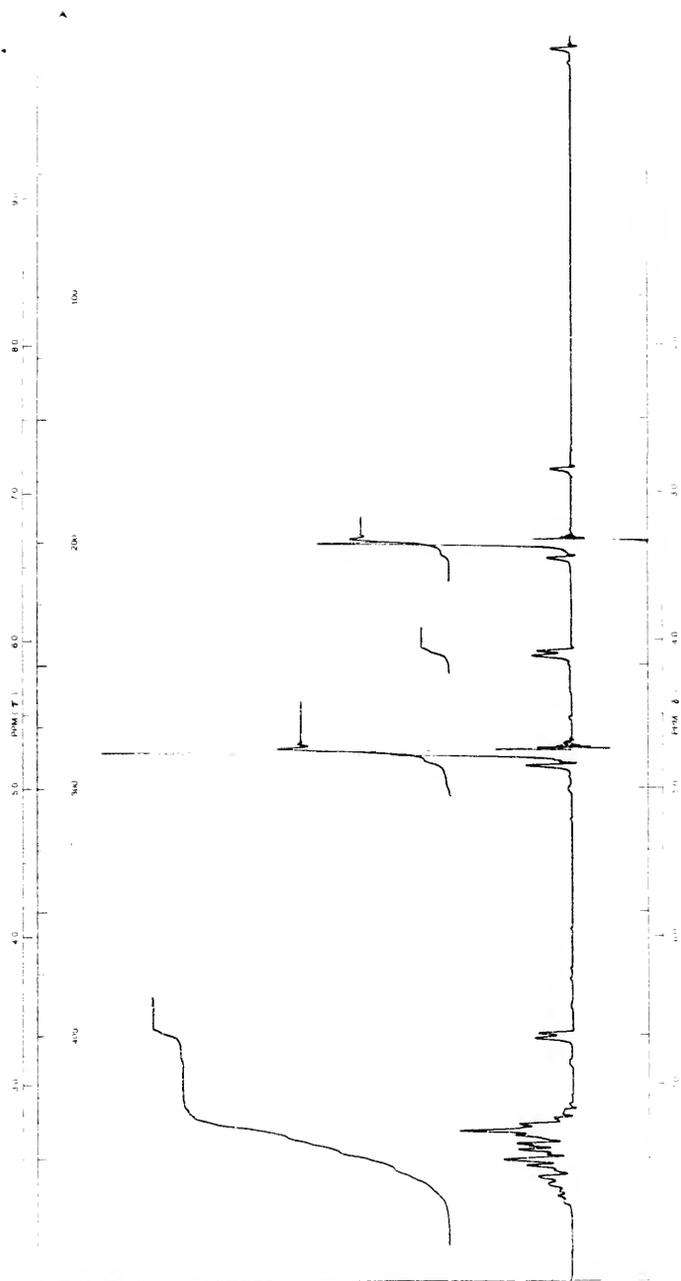
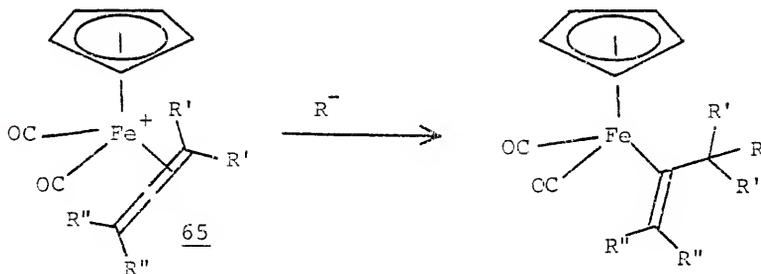


Figure 9. ^1H nmr Spectrum of 6-(Cyclopentadienylirondicarbonyl)-5-methoxy-5H-dibenzo-[a,c]cycloheptene (62).

Treatment of 62 with triphenylcarbenium hexafluorophosphate resulted in the generation of a yellow solid 66 that precipitated out of solution upon addition of ethyl ether at low temperature. Triphenylmethylmethyl ether was present whereas the starting complex was not present in the filtrate (by ^1H nmr). A low temperature ^1H nmr spectrum (0°C , CD_3NO_2) of the yellow solid 66 shows a complex pattern (Figure 10). Upon warming to room temperature in the nmr tube, the spectrum dramatically changes (Figure 11). The ir spectrum (KBr) of the yellow solid 66 shows the presence of carbonyl stretching and hexafluorophosphate bands (Figure 12).

It has been shown that nucleophilic attack on Fp carbene¹⁷ or allene (e.g. 65)⁴⁷ complexes leads to neutral sigma complexes. Therefore if a carbene (or allene)



complex had been generated, the reaction with a nucleophile should lead back to a neutral species that could be stable in solution. Reaction of the yellow solid 66 with sodium methoxide in methanol led to two identifiable products, triphenylmethylmethyl ether and 1,2-3,4-dibenzocycloheptatriene. However, no neutral transition metal complex

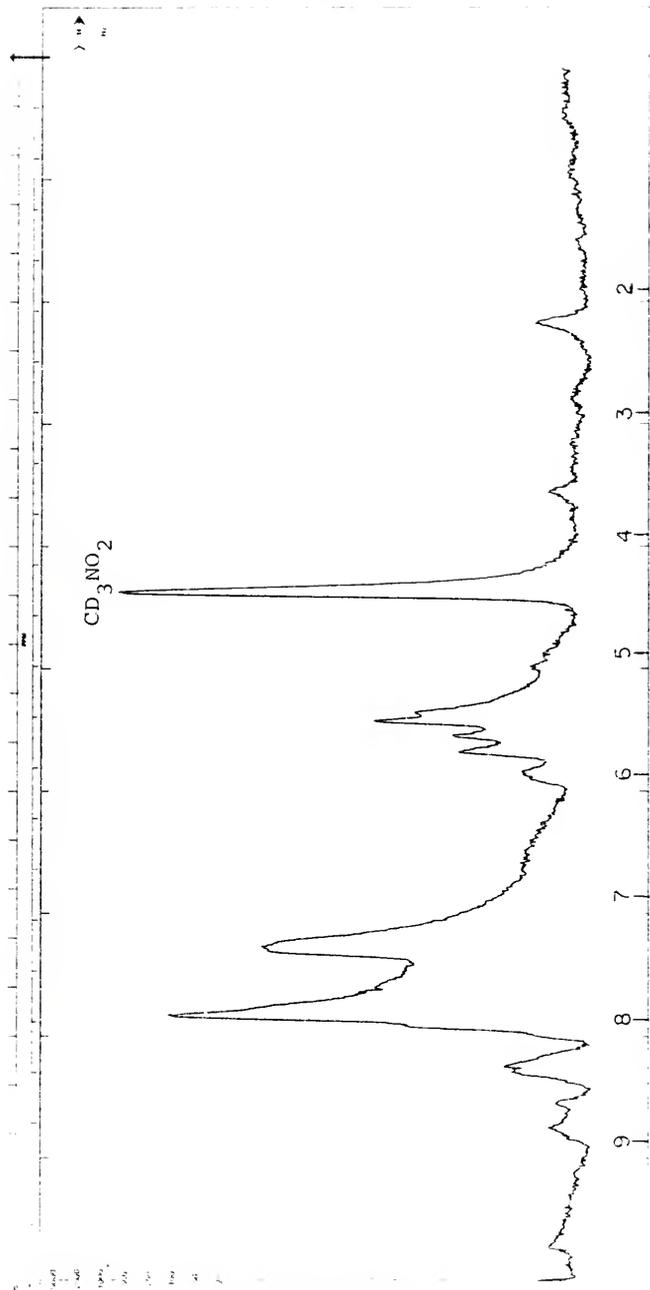


Figure 10. Low Temperature ^1H nmr Spectrum (CD_3NO_2) of Yellow Solid (66).

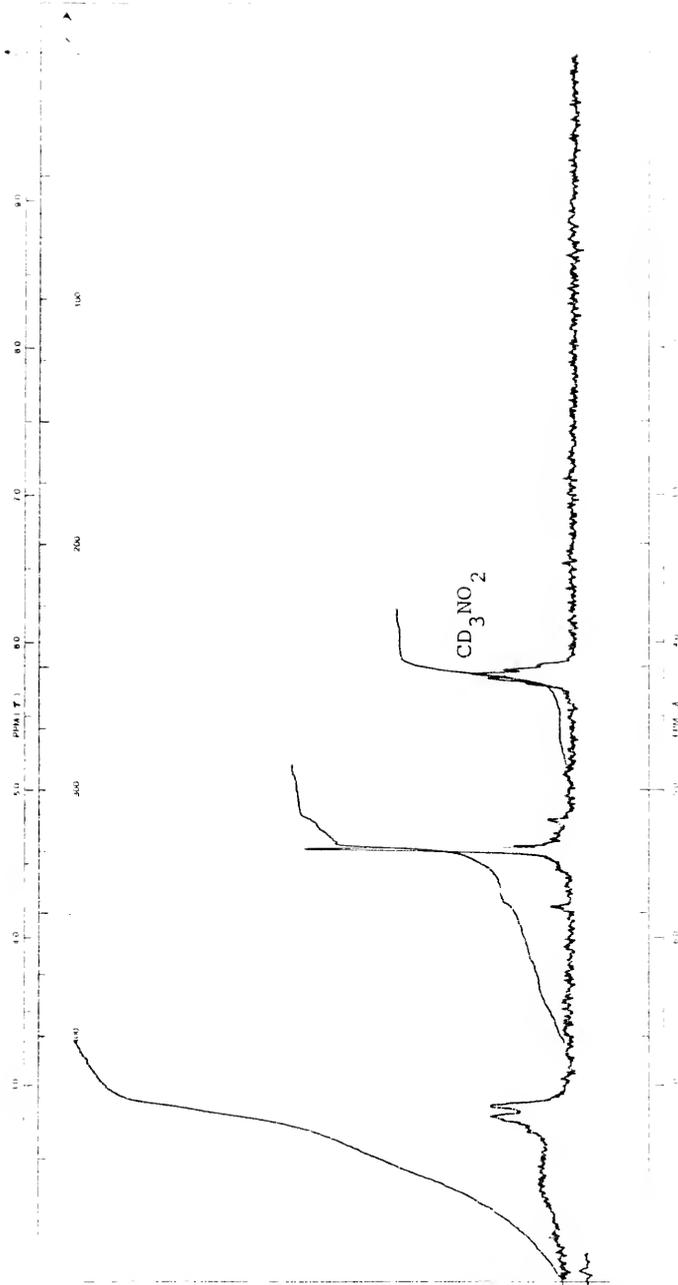


Figure 11. Room Temperature ^1H nmr Spectrum (CD_3NO_2) of Yellow Solid (66).

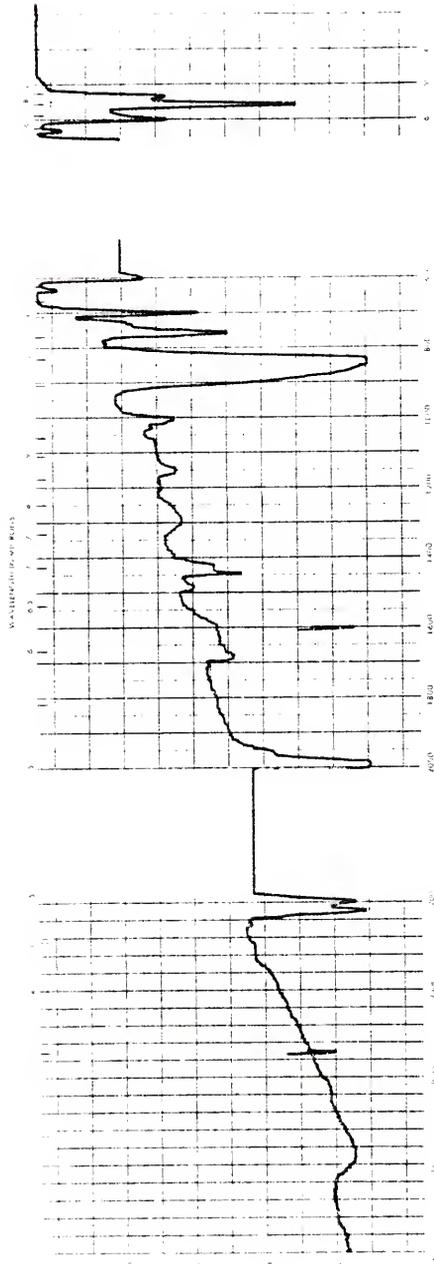
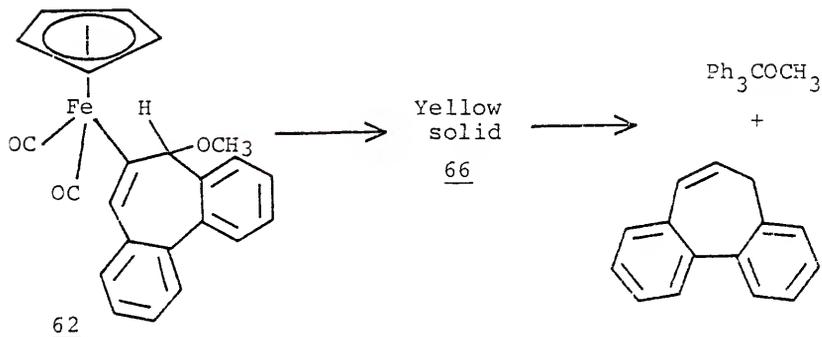
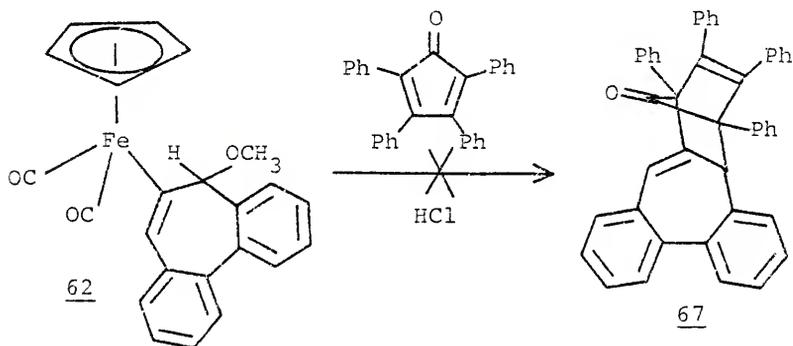


Figure 12. Ir Spectrum (KBr) of Yellow Solid (66).

was detected. Therefore, speculation as to the structure of this yellow solid is almost impossible at this time.



In the event that a labile carbene (or allene) ligand was formed (as in the case of $\text{Cp}(\text{CO})_2\text{Fe}^+(\text{methylene})$ (15)^{15, 16} vide supra), 62 was treated with acid in the presence of a trap. However, the expected tetracyclone adduct 67 was not detected.



A collection of selected spectral data of some Fp complexes is given in Table 3. In summary, it can be seen

Table 3. Summary of Selected Spectral Data of Some Fp Complexes

Compound	ir(CO) cm^{-1}	^{13}C nmr (C_{carb})	Ref.
Fp[benzocyclobutenylidene]HFP (<u>16</u>)	2065, 2020	--	17
Fp[phenylcarbene]TFA (<u>18</u>)	--	342.4	18
Fp[cycloheptatrienyliidene HFP (<u>24</u>)	2045, 1996	242.3	22
Fp[4,5-benzocycloheptatrienyliidene]HFP (<u>41</u>)	2045, 2000	265.9	--
Fp[3,4-benzocycloheptatrienyliidene]HFP (<u>46</u>)	2037, 1992	201	--
Fp[vinyl] (<u>32</u>)	2020, 1950	--	36
Fp[cycloheptatriene] (<u>23</u>)	2020, 1950	--	--

that the amount of back donation afforded to the carbene ligands in 24, 41, and 56 is less than that in Fp[benzocyclobutenylidene]HFP (16). However, comparison of the carbonyl stretching frequencies of the aromatic carbene complexes with those of Fp[vinyl] and Fp[cycloheptatriene] suggests that there is still substantial back bonding present in 24, 41, and 46. The ^{13}C nmr data indicate that the amount of positive charge on the carbene carbons of 24, 41, and 46 is less than that of Fp[phenylcarbene] vide supra.

In conclusion, the synthesis of three aromatic carbene complexes of iron strongly suggests the general applicability of this synthetic method to other aromatic carbene ligands. In addition, the synthesis of a tungsten cycloheptatrienylidene complex by the same procedure indicates that this synthetic method need not be limited to only one particular transition metal or one particular charge type.

CHAPTER III EXPERIMENTAL

General. All melting points were obtained on a Thomas Hoover melting point apparatus and are uncorrected. All 60 MHz nuclear magnetic resonance data were obtained on a Varian A-60A or Jeol PMX 60 spectrometer and are reported in units of δ from tetramethylsilane which was used as an internal standard. All 100 MHz nuclear magnetic resonance data were obtained on a Varian XL 100 or Jeol FX 100 spectrometer and are reported in the same manner. Infrared data were obtained on a Beckman IR 10 spectrophotometer, Perkin-Elmer 137 spectrophotometer, or a single beam Perkin Elmer E-14 spectrophotometer. Combustion analyses were performed by Atlantic Microlab Inc., Atlanta, Georgia. Mass spectra were obtained on an AEI MS 30 spectrometer.

Unless otherwise noted, solvents used were reagent grade except tetrahydrofuran and methylene chloride. The tetrahydrofuran was purified by distillation over sodium-potassium alloy as described by Ward.⁴⁸ Reagent grade methylene chloride was distilled from P_2O_5 under nitrogen and used immediately.

The alumina used (except where noted otherwise) was Fisher certified neutral alumina, Brockman Activity 1, to which 3% w/w water was added. It was purged several times with nitrogen and allowed to stand for two or more days.

The silica gel used was prepared by Baker and was 60-300 mesh. All reactions were performed under either a nitrogen or an argon atmosphere. All organometallic compounds were prepared using a Schlenk type apparatus and kept under nitrogen or argon at all times except where noted otherwise.

Cyclopentadienyliron dicarbonyl iodide. This material was obtained from Alfa Products.

Preparation of tropone (20). This compound was prepared by a modified procedure of Radlich⁴⁹ from cycloheptatriene. Instead of allowing the reaction mixture to stand overnight, it was stirred with a mechanical stirrer in a Morton flask. This improved the yield to 37% (reported yield 25%).

Preparation of bromotropylium bromide. This material was prepared according to the method of Föhlisch et al.²³

Preparation of 1-, 2-, and 3-bromocycloheptatrienes (21). This isomeric mixture was prepared according to the method described by Föhlisch and Haug.²⁴

Preparation of 1-, 2-, and 3-lithiocycloheptatrienes (22). To a cold (dry ice and isopropanol) addition funnel, 16.5 ml (26.4 mmoles, 1.6 molar solution in hexane) of n-butyllithium was added dropwise with a syringe to a stirred solution of 4.32 g (26.4 mmoles) 1-, 2-, and 3-bromocycloheptatrienes in 30 ml of tetrahydrofuran. The dark green solution was allowed to stir for 30 minutes and was used immediately.

Preparation of 1-, 2-, and 2-(cyclopentadienyliron dicarbonyl)cycloheptatrienes (23). A cold solution of 26.4 mmoles) 1-, 2-, and 3-lithiocycloheptatrienes in

tetrahydrofuran was added to a rapidly stirred solution of 8.2 g (26.9 mmoles) cyclopentadienylirondicarbonyl iodide in 20 ml of tetrahydrofuran cooled by a dry ice-isopropanol bath. The reaction mixture was stirred for 45 minutes. It was then warmed to room temperature and stirred an additional 20 minutes. To the reaction mixture, a small amount of alumina was added and the tetrahydrofuran was removed *in vacuo*. The reaction products coated on the alumina were chromatographed on alumina using pentane as the eluent. Two simultaneously eluted bright yellow bands were collected. Removal of the solvent *in vacuo* (rotary evaporator) gave 2.02 g (29%) of a yellow, air sensitive oil.

The spectral data were as follows: ^1H nmr (CDCl_3), Figure 1, δ 2.15, 2.25, 2.62, (2H, t, t, d, satd. CH), 4.65, 4.79, 4.84 (5H, s, s, s, Cp), 4.98-5.50, 5.78-6.83 (5H, br m, br m, vinyl); ir (neat) 3020, 2020, 1950, 1495, 1430, 1015, 830, 725 cm^{-1} ; ms m/e 268.01841 (calcd. 268.01860).

Preparation of h^1 -cycloheptatrienyliidene- h^5 -cyclopentadienyldicarbonyliron hexafluorophosphate (24). A solution of 2.02 g (7.55 mmoles) of 1-, 2-, and 3-(cyclopentadienylirondicarbonyl)cycloheptatrienes in 10 ml of methylene chloride was cooled in a dry ice and isopropanol bath. To the stirred solution, 2.93 g (7.55 mmoles) of triphenylcarbenium hexafluorophosphate in 30 ml of methylene chloride was added with a syringe. The reaction mixture was stirred for 30 minutes and then was allowed to warm to room temperature. Immediately after 30 minutes of additional stirring, ca. 20 ml

of methylene chloride was rapidly removed *in vacuo* and ca. 60 ml of ethyl ether (freshly opened can) was rapidly added via syringe to precipitate the complex. The solid was immediately collected on a medium grade glass frit and was washed with several 15 ml portions of ethyl ether. The remaining solvent was removed *in vacuo*. This yielded 2.8 g (90%) of a yellow-orange, air stable solid. Recrystallization from methylene chloride gave orange-yellow plates, m.p. 180.0-180.5°C (dec.).

The spectral data were as follows: ^1H nmr (0°C, acetone d_6), Figure 2, δ 10.01 (2H, d, $J=10.0$, H-2, 7), 8.48-8.74 (2H, m, H-4, 5), 7.94-8.30 (2H, m, H-3, 6); 5.50 (5H, s, Cp); decouples ^{13}C nmr (0°C, acetone d_6) δ 242.3 (C-1), 212.8 (CO), 170.0, 148.3, 138.2 (C-2, C-3, C-4), 88.3 (Cp); ir (CH_2Cl_2) 2045, 1996 cm^{-1} (KBr) 3130, 2040, 1980, 1460, 1005, 830, 730, 590, 555 cm^{-1} ; UV-visible (acetonitrile): λ_{max} (log ϵ)-205 (4.41), 220 (sh), 340 (sh), 405 (3.60).

Analysis calculated for $\text{C}_{14}\text{H}_{11}\text{F}_6\text{FeO}_2\text{P}$: C, 40.81; H, 2.69. Found: C, 40.55; H, 2.71.

Reaction of η^1 -cycloheptatrienylylidene- η^5 -cyclopentadienyl-dicarbonyliron hexafluorophosphate with lithium aluminum hydride. Powdered lithium aluminum hydride (12.9 mg (0.340 mmoles)) was added to 0.201 g (0.489 mmoles) of η^1 -cycloheptatrienylylidene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate in 15 ml of tetrahydrofuran. After a few minutes of stirring, alumina was added and the tetrahydrofuran was rapidly removed *in vacuo*. The product was chromatographed

on alumina. Pentane eluted a yellow band which was taken to dryness *in vacuo* (rotary evaporator) and yielded 88 mg (67%) of pure 1-, 2-, and 3-(cyclopentadienylirondicarbonyl) cycloheptatrienes (23) which were identified by ^1H nmr. No organic products were detected.

Reaction of η^1 -cycloheptatrienyliene- η^5 -cyclopentadienyl-dicarbonyliron hexafluorophosphate with methyllithium. To a stirred solution of 0.113 g (0.274 mmoles) η^1 -cycloheptatrienyliene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate in 10 ml of tetrahydrofuran was added 0.15 ml of methyllithium (0.31 mmoles, 2.05 molar solution in ethyl ether) via syringe. After 20 minutes of stirring, alumina was added and the solvent was rapidly removed *in vacuo*. Column chromatography on alumina (with pentane and then a 5% v/v benzene-pentane mixture as eluents) produced a yellow band which yielded 10.2 mg (13.2%) of a yellow oil 34 after removal of the solvent *in vacuo* (rotary evaporator). The proton spectrum matched that of the cycloheptatriene complexes with the exception of the methyl signals appearing at $\delta 0.8, 1.2$ (3H, d, complex m). The saturated cycloheptatriene hydrogens were at too low intensity to be distinguished. The mass spectrum gave m/e 282 (M^+), 254 ($M^+-\text{CO}$), 226 ($M^+-2\text{CO}$), base peak at 56.

Oxidation of η^1 -cycloheptatrienyliene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate with dimethylsulfoxide. To 0.210 g (0.509 mmoles) of η^1 -cycloheptatrienyliene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate in a schlenk tube, 10 ml of dimethylsulfoxide was

added via syringe. After stirring overnight, water was added and the solution neutralized. Workup included extraction with two 250 ml portions of methylene chloride and drying with anhydrous magnesium sulfate. After removal of the solvent *in vacuo* (rotary evaporator), tropone was separated by a preparatory thin layer plate (silica gel using ethyl ether as the eluent) that had been spotted with an original sample of tropone. Collection of the corresponding band, extraction with methylene chloride and concentration of the product *in vacuo* (rotary evaporator) gave 9.0 mg (17%) of tropone that was identified by ir and ^1H nmr spectra.

Preparation of 4,5-benzotropone (36). This material was prepared according to the method of Paquette and Ewing.⁴¹

Preparation of 1,2-benzo-5-bromotropylium bromide (37). This material was prepared according to the method of Föhlisch et al. and used immediately.⁴²

Preparation of 1,2-benzo-5-bromocycloheptatriene (38). This material was prepared by a procedure similar to that described by Föhlisch et al.⁴² with the following modifications. Before the addition of lithium aluminum hydride to 1,2-benzo-5-bromotropylium bromide, all solvent was removed *in vacuo* and the bromide salt was taken up in pure tetrahydrofuran. The lithium aluminum hydride was then added over a 60 minute time period to the cold (0°C) solution. After slow addition of water, the solution was filtered, extracted with methylene chloride (reagent grade), dried

with anhydrous magnesium sulfate and concentrated *in vacuo* (rotary evaporator). Column chromatography on silica gel (pentane) gave 4.39 g (65%) of a white solid. The spectral data matched those of reported spectra.

Preparation of 1,2-benzo-5-lithiocycloheptatriene (39).

To an addition funnel cooled with a dry ice-isopropanol mixture, 10.1 ml (16.1 mmoles, 1.6 molar solution in hexane) of n-butyl lithium was added dropwise with a syringe to a stirred solution of 3.85 g (17.4 mmoles) 1,2-benzo-5-bromocycloheptatriene in 25 ml of tetrahydrofuran. The evergreen colored solution was allowed to stir for 30 minutes and was used immediately.

Preparation of 1,2-benzo-5-(cyclopentadienylirondicarbonyl)cycloheptatriene (40). A cold solution of 1,2-benzo-5-lithiocycloheptatriene (17.4 mmoles) in 25 ml of tetrahydrofuran was rapidly added to a stirred solution of 6.1 g (20 moles) cyclopentadienylirondicarbonyl iodide in 20 ml of tetrahydrofuran cooled by dry ice-isopropanol. The cold reaction mixture was stirred for 30 minutes. A small amount of alumina was added to the reaction mixture and the tetrahydrofuran was removed *in vacuo*. The reaction products coated on the alumina were chromatographed on alumina using 600 ml of pentane and then a benzene-pentane mixture as eluents (gradually increasing the benzene content to a 20% v/v benzene-pentane mixture). After two faint yellow bands were discarded, the bright yellow band was collected. Removal of the solvent *in vacuo* gave 1.36 g (26%) of a yellow, air sensitive solid, m.p. 114.5-115.5°C (dec.).

The spectral data were as follows: ^1H nmr (CDCl_3), Figure 3, δ 3.0 (2H, d, $J=7\text{Hz}$, satd. CH), 4.6 (5H, s, Cp), 5.63 (1H, t, $J=7\text{Hz}$, vinyl), 6.62 (2H, s, vinyl), 7.2 (4.5H, br m, benzylic); ir (KBr) 3120, 3000, 2380, 2020, 1955, 1930, 1490, 1430, 945, 835, 790, 755, 740, 640, 590, 570 cm^{-1} ; ms m/e 318 (M^+), 290 (M^+-CO), 262 ($\text{M}^+=2\text{CO}$).

Analysis calculated for $\text{C}_{18}\text{H}_{14}\text{FeO}_2$: C, 67.95; H, 4.44.
Found: C, 67.99; H, 4.47.

Preparation of η^1 -4,5-benzocycloheptatrienylidene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate (4l).

A solution of 1.19 g (3.73 mmoles) of 1,2-benzo-5-(cyclopentadienyliron dicarbonyl)cycloheptatriene in 3 ml of methylene chloride was cooled in a dry ice-isopropanol bath. To the stirred solution, 1.45 g (3.73 mmoles) of triphenylcarbenium hexafluorophosphate in 15 ml of methylene chloride was added with a syringe over 10 minutes. The red mixture was stirred for 30 minutes. It was then warmed to room temperature. Some of the solvent (ca. 8 ml) was removed *in vacuo* and ca. 60 ml of ethyl ether (freshly opened can) was added to precipitate the complex. The complex was collected on a medium grade glass frit and was washed with several 30 ml portions of ethyl ether. The remaining solvent was removed *in vacuo*. This yielded 1.6 g (93%) of a fire brick red solid. Recrystallization from methylene chloride gave red-brown plates, m.p. 177-178°C (dec.).

The spectral data were as follows: ^1H nmr (0°C, acetonitrile d_3), Figure 4, δ 9.58 (2H, d, $J=11\text{Hz}$), 8.26, 8.58-8.08

(6H, d, $J=11\text{Hz}$, m, A_2B_2), 5.3 (5H, s, Cp); decoupled ^{13}C nmr (0°C , nitromethane d_3) δ 265.9 (C-1), 212.7 (CO), 158.5, 141.6, 140.3, 137.8, 137.1 (C-2 through C-11), 89.5 (Cp); ir (CH_2Cl_2) 2045, 2000 cm^{-1} , (KBr) 2030, 1990, 1510, 1470, 965, 840, 560 cm^{-1} ; UV-visible (CH_2Cl_2): λ_{max} (log ϵ) = 500 (3.47), 468 (3.52) 330 (sh), 315 (sh), 282 (sh), 272 (4.21), 233 (4.20).

Analysis calculated for $\text{C}_{18}\text{H}_{13}\text{F}_6\text{FeO}_2\text{P}$: C, 46.79, H, 2.84.
Found: C, 46.78; H, 2.86.

Reaction of h^1 -4,5-benzocycloheptatrienylydene- h^5 -cyclopentadienyldicarbonyliron hexafluorophosphate with lithium aluminum deuteride. Powdered lithium aluminum deuteride (0.016 g, 0.38 mmoles) was added to a cold (dry ice-isopropanol) solution of 0.200 g (0.432 mmoles) h^1 -4,5-benzocycloheptatrienylydene- h^5 -cyclopentadienyldicarbonyliron hexafluorophosphate in 5 ml of tetrahydrofuran. The remaining reducing reagent was washed out of the solid addition flask with ca. 5 ml of tetrahydrofuran. The solution was stirred 10 minutes and then it was warmed to room temperature. Upon warming, the solution turned from red to yellow. The solvent was removed *in vacuo* during which the products were coated on alumina. Rapid column chromatography on alumina (pentane) and collection of the yellow band followed by removal of the solvent *in vacuo* yielded 0.0850 g (62%) 1,2-benzo-5-(cyclopentadienyliron dicarbonyl)-7-deuterocycloheptatriene (43). The ^1H nmr was identical to that of 1,2-benzo-5-(cyclopentadienyliron dicarbonyl)cycloheptatriene (40) except for the doublet at δ 5.63 and

the broad doublet at δ 3.0 (1H); ms m/e 291.04630 (calcd. 291.0540).

Reaction of $\overset{1}{h}$ -4,5-benzocycloheptatrienyliidene- $\overset{5}{h}$ -cyclopentadienyldicarbonyliron hexafluorophosphate with methyllithium. Methyllithium (0.25 ml; 0.51 mmoles of a 2.05 molar solution in ethyl ether) was syringed over a 2 minute time period into a cold (dry ice-isopropanol) solution of 0.240 g (0.518 mmoles) of $\overset{1}{h}$ -4,5-benzocycloheptatrienyliidene- $\overset{5}{h}$ -cyclopentadienyldicarbonyliron hexafluorophosphate in 10 ml of tetrahydrofuran. The color of the solution changed from red to yellow almost immediately. After stirring for 15 minutes, the solution was warmed to room temperature (whereby the color turned darker). A small amount of alumina was added and solvent was removed *in vacuo*. Column chromatography of the coated alumina with alumina (pentane) and collection of the yellow band yielded 65 mg (38%) of 1,2-benzo-5-(cyclopentadienyliironedicarbonyl)-7-methylcycloheptatriene (44).

The spectral data were as follows: ^1H nmr (CDCl_3) δ 1.5 (3H, d, J=7Hz), 2.75 (1H, m, satd CH), 4.5 (5H, s, Cp), 5.25 (1H, d, J=7Hz, vinyl), 6.7 (2H, s, vinyl), 7.25 (4H, m, arom.).

Preparation of 1-bromo-1,2,3,4-tetrahydronaphthalene.⁴³

A solution of 404 g (3.06 moles) tetralin and 500 ml of carbon tetrachloride were heated to reflux. Using an addition funnel, 443 g (2.77 moles) of bromine was added over a 3.5 hour period. The mixture was allowed to stand at room temperature overnight. The solvent was removed

in vacuo (rotary evaporator). The residue, 636.1 g, was used as is in the next step.

Preparation of 1,2-dihydronaphthalene.⁴³ An aqueous sodium hydroxide solution (160 g NaOH in 500 ml of H₂O) was brought to reflux. The above bromide was added over a two hour period. After an additional 0.5 hour of reflux, the mixture was allowed to stand at room temperature overnight.

The mixture was twice extracted with 200 ml portions of petroleum ether. The organic extracts were dried over anhydrous magnesium sulfate and the solvent was removed *in vacuo* (rotary evaporator). The residue was vacuum distilled. This distillate was a mixture of dihydronaphthalene, tetralin, and naphthalene. The amount of the dihydronaphthalene (0.610 moles) was determined by nmr integration.

Preparation of 1,2-benzo-4- and 1,2-benzo-6-bromocycloheptatrienes (48, 49). A mixture of naphthalene, tetrahydronaphthalene, dihydronaphthalene (0.610 moles in a 218 g mixture), benzyltriethylammonium chloride (0.8 g), and bromoform 459.4 g (1.8 moles) was mechanically stirred and cooled with a water bath. To this mixture, 500 g of 50% w/w aqueous sodium hydroxide was added dropwise. After 24 hours of stirring, 500 ml of H₂O was added and the organic layer was washed twice with 250 ml portions of water. After drying with anhydrous magnesium sulfate, the organic layer was filtered through celite. The bromoform was removed by vacuum distillation (10 mm, 32°C to 3.5 mm, 60°C).

The residue was taken up in 500 ml of pentane and filtered to remove the brown polymer. The organic products were concentrated *in vacuo* (rotary evaporator).

Distillation of this residue (1.5 mm, 60°C) removed the tetrahydronaphthalene. Three distillations (3 mm, 140°C; 2.75 mm, 92-118°C; and finally with a Nester Faust spinning band column at 0.25 mm, 90-100°C) resulted in loss in hydrogen bromide and gave a mixture of the two bromides (51.9 g; 38%) that was suitable for further use.

The spectral data were as follows: ^1H nmr (CDCl_3) δ 3.08, 3.52 (2H, d, $J=7\text{Hz}$, s, satd. CH), 5.45-6.5 (2H, m, vinyl), 6.9-7.55 (4.5H, m, vinyl and arom.); ir (neat) 3000, 1601, 1480, 1440, 1420, 1340, 1190, 1110, 1030, 980, 860, 780, 755 cm^{-1} ; ms m/e 219.98953 (calcd. 219.98850).

Preparation of 1,2-benzo-4- and 1,2-benzo-6-lithiocycloheptatrienes (50, 51). To an addition funnel cooled with a dry ice-isopropanol mixture and containing a stirred solution of 5.22 g (23.6 mmoles) 1,2-benzo-4-, and 1,2-benzo-6-bromocycloheptatrienes in 32 ml of tetrahydrofuran, was added 14.5 ml (2.32 mmoles, 1.6 molar solution in hexane) of n-butyllithium dropwise with a syringe. The green solution was stirred for 30 minutes and used immediately.

Preparation of 1,2-benzo-4- and 1,2-benzo-6-(cyclopentadienyliron dicarbonyl)cycloheptatrienes (52, 53). A cold solution of (2.32 mmoles) 1,2-benzo-4- and 1,2-benzo-6-lithiocycloheptatrienes in 32 ml of tetrahydrofuran was added rapidly to a stirred solution of 7.2 g (2.4 mmoles)

cyclopentadienylirondicarbonyl iodide in 20 ml of tetrahydrofuran cooled with dry ice-isopropanol. The cold reaction mixture was stirred for 45 minutes and then warmed to room temperature. At this time, 40 ml of alumina was added to the reaction mixture and the tetrahydrofuran was removed *in vacuo*. The reaction products coated on the alumina were chromatographed on alumina using pentane and then a benzene-pentane mixture (gradually increasing the benzene content to 15% v/v benzene-pentane). The yellow band was collected. Removal of the solvent *in vacuo* (rotary evaporator) gave 2.74 g (37%) of a yellow, air sensitive oil.

The spectral data were as follows: ^1H nmr (CDCl_3), Figure 5, δ 2.9, 3.45 (2H, d, s, satd. CH), 4.9 (5H, s, Cp), 5.35, 6.2, 6.7, 7.2 (8H, complex multiplets, vinyl and aromatics); ir (neat) 3020, 2010, 1950, 1775, 1525, 1480, 1430, 1020, 910, 830, 730 cm^{-1} ; ms m/e 318.03302 (calcd. 318.03410).

Preparation of η^1 -3,4-benzocycloheptatrienyliidene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate (46).
 A solution of 2.74 g (8.60 mmoles) of 1,2-benzo-4- and 1,2-benzo-6-(cyclopentadienylirondicarbonyl)cycloheptatrienes in 15 ml of methylene chloride was cooled in a dry ice-isopropanol bath. To the stirred solution, 3.34 g (8.60 mmoles) of triphenylcarbenium hexafluorophosphate in *ca.* 30 ml of methylene chloride was added dropwise with a syringe. The reaction mixture was stirred for one hour. It was then warmed to room temperature. Partial rapid

removal of the methylene chloride (ca. 30 ml) *in vacuo* followed by rapid addition of ethyl ether (ca. 60 ml) aided the precipitation of the complex. The solid was immediately collected on a medium grade glass frit and was washed with several 10 ml portions of ethyl ether. The residual solvent was removed *in vacuo*. This yielded 3.5 g (88%) of a brick red solid. Recrystallization from methylene chloride gave violet needles, m.p. 176-177°C (dec.).

The spectral data were as follows: ^1H nmr (8°C, nitromethane d_3), Figure 6, δ 10.4 (1H, d, $J=2\text{Hz}$) 9.92 (1H, d, $J=10.6\text{Hz}$), 9.23 (1H, d of m, $J=10.6, 0.5\text{Hz}$), 8.50, 8.16 (5H, m, t, $J=10.6\text{Hz}$); decoupled ^{13}C nmr (0°C, nitromethane d_3), δ 215 (CO), 201 (C-1), 176, 174, 155, 145, 139, 138, 138, 137, 136, 133 (C-2 through C-11), 89 (Cp); ir (CH_2Cl_2) 2037, 1992 cm^{-1} , (KBr) 3140, 2025, 1975, 1420, 840, 595, 560 cm^{-1} ; UV-visible (CH_2Cl_2): λ_{max} (log ϵ) = 380 (3.52), 313 (sh), 280 (4.36), 232 (4.28).

Analysis calculated for $\text{C}_{18}\text{H}_{13}\text{F}_6\text{FeO}_2\text{P}$: C, 46.79; H, 2.84. Found: C, 46.68; H, 2.86.

Preparation of 5,6-dibromo-5H-dibenzo[α, ϵ]cycloheptene (58). To a mechanically stirred mixture of 50 g (0.280 mole) phenanthrene, 890 g (3.52 moles) bromoform, 1.9 g triethylbenzylammonium chloride and 5 ml of ethanol, 500 g w/w NaOH (aq) solution (6.25 moles) was added dropwise during 20 minutes. After addition, a water bath was employed to cool the slightly exothermic reaction.

After stirring overnight, 500 ml of water and 500 ml of methylene chloride (reagent grade) was added to the reaction mixture. The organic layer was washed twice with 500 ml portions of water and then was dried with anhydrous magnesium sulfate. The methylene chloride was removed *in vacuo* (rotary evaporator). The remaining brown residue was transferred to a one liter flask. With rapid stirring (mechanical stirrer), 750 ml of pentane was added and an organic tar oiled out. This tar was saved for further purification (next paragraph). The pentane and bromoform mixture was decanted through a medium sintered glass funnel and the pentane removed *in vacuo* (rotary evaporator). The bromoform was distilled under high vacuum (0.025 mm, water bath employed should not exceed 60°C) and the residue was transferred to a petri dish to evaporate traces of bromoform *vide infra*.

The remaining tar in the one liter flask was taken up in 200 ml of methylene chloride (technical grade). Once again it was rapidly stirred with a mechanical stirrer. Once dissolved, *ca.* 600 ml of pentane was added with stirring and a brown solid precipitated out (containing a polymeric material). This was filtered on a medium sintered glass funnel and the filtrate was concentrated *in vacuo* (rotary evaporator). This brown tar was combined with the material isolated above in the petri dish.

After the brown oil was stirred in the petri dish for four days under a stream of nitrogen gas, it was transferred

to a 250 ml erlenmeyer flask and taken up in a minimum amount of hot benzene. Fractional recrystallization from benzene gave 12.2 g (12.4%) of product suitable for use (m.p. 138.5-141.0°C).

An analytical sample could be obtained by further fractional recrystallization from benzene, m.p. 140.5-141.5°C.

The spectral data were as follows: ^1H nmr (CDCl_3) δ 5.95 (1H, d, $J = 2\text{Hz}$, satd. CH), 7.45 (9H, m, aromatic and vinyl); ir (KBr) 3000, 1620, 1470, 1430, 1200, 1150, 1010, 890, 860, 840, 810, 760, 750, 725 cm^{-1} ; ms m/e ($\text{M}^+ - \text{Br}$) 270.99283 (calcd. 270.99450).

Analysis calculated for $\text{C}_{15}\text{H}_{10}\text{Br}_2$: C, 51.47; H, 2.88.
Found: C, 51.52; H, 2.92.

Preparation of 6-bromo-5H-dibenzo[α , ϵ]cycloheptene (59).

Powdered lithium aluminum hydride (0.155 g, 4.08 mmoles) was added in small portions to a cold (dry ice-isopropanol) solution of 5,6-dibromo-5H-dibenzo[α , ϵ]cycloheptene in 25 ml of tetrahydrofuran. The reaction mixture was stirred for three hours and then allowed to slowly warm to room temperature (the dry ice-isopropanol bath should be allowed to warm up with the flask). At this time, water was added and the organic products were extracted with ethyl ether and dried with anhydrous magnesium sulfate. Chromatography with silica gel (pentane) gave 1.13 g (47%) of a clear oil.

The spectral data were as follows: ^1H nmr (CDCl_3) δ 3.48 (2H, s, satd. CH), 6.83 (1H, s, vinyl), 7.4 (8H, m, arom.);

ir (neat) 3060, 1630, 1480, 1450, 1440, 1210, 1110, 855, 750, 730 cm^{-1} ; ms m/e 270.00354 (calcd. 270.00430).

Analysis calculated for $\text{C}_{15}\text{H}_{11}\text{Br}$: C, 66.44; H, 4.09.
Found: C, 66.57; H, 4.13.

Preparation of 6-lithio-5H-dibenzo[α , ϵ]cycloheptene.

To an addition funnel cooled with dry ice-isopropanol, 3.3 ml (5.28 mmoles, 1.6 molar solution in hexane) of n-butyllithium was added dropwise with a syringe to a stirred solution of 1.42 g (5.26 mmoles) 6-bromo-5H-dibenzo[α , ϵ]cycloheptene in *ca.* 40 ml of tetrahydrofuran. The aqua-green solution was stirred for 30 minutes and was used immediately.

Preparation of 6-cyclopentadienylirondicarbonyl)-5H-dibenzo[α , ϵ]cycloheptene (60). The cold solution of 6-lithio-5H-dibenzo[α , ϵ]cycloheptene (5.27 mmoles) in tetrahydrofuran was added to a cold (dry ice-isopropanol), rapidly stirred solution of 1.6 g (5.26 mmoles) cyclopentadienylirondicarbonyl iodide in *ca.* 20 ml of tetrahydrofuran. The reaction mixture was stirred for 45 minutes whereupon it was then warmed to room temperature. A small amount of alumina was then added and the solvent was removed *in vacuo*. The reaction products coated on the alumina were chromatographed on alumina using pentane eluent first, followed by a benzene-pentane mixture (gradually increasing the benzene content to a 25% v/v benzene-pentane mixture). A yellow band was collected. Removal of the solvent *in vacuo* gave 0.604 g (31%) of a yellow, air sensitive glass.

The spectral data were as follows: ^1H nmr, Figure 8, δ 3.38 (2H, s, satd. CH), 4.82 (5H, s, Cp), 6.65 (1H, s, vinyl), 7.4 (9H, m, arom.); ir (neat) 3060, 2020, 1950, 1775, 1570, 1480, 1430, 1100, 990, 825, 750 cm^{-1} ; ms m/e (M^+) 340.05700 (calcd. 340.0550), ($\text{M}^+ - \text{CO}$) 312.05969 (calcd. 312.06000).

Attempted synthesis of η^1 -3,4-5,6-dibenzocycloheptatrienylidene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate (56) from 6-(cyclopentadienyliron dicarbonyl)-5H-dibenzo[*a,c*]cycloheptene (60). Via syringe, 1.10 g (2.84 mmoles) of triphenylcarbenium hexafluorophosphate in 25 ml of methylene chloride was added dropwise to a cooled (-35°C) solution of 1.06 g (2.87 mmoles) 6-(cyclopentadienyliron dicarbonyl)-5H-dibenzo[*a,c*]cycloheptene in 20 ml of methylene chloride. After five days of stirring at -35°C , ethyl ether was added until a yellow salt precipitated (presumably triphenylcarbenium hexafluorophosphate). The unreacted starting complex was identified from the filtrate by ^1H nmr. No triphenylmethane was detected by ^1H nmr.

Preparation of 6-bromo-5-methoxy-5H-dibenzo[*a,c*]cycloheptene (63). 6,7-Dibromo-5H-dibenzo[*a,c*]cycloheptene (1.9 g, 5.43 mmoles) was dissolved in 20 ml of methanol (dried by distillation from magnesium). To this, 0.3 g (5.55 mmoles) of sodium methoxide was added. The solution was stirred and refluxed for one hour. The reaction solution was extracted with ethyl ether and washed several times with water. This yielded 1.49 g (91%) of a clear oil which was used without further purification.

The spectral data were as follows: ^1H nmr (CDCl_3) δ 3.33 (3H, s, methyl), 4.52 (1H, br s, satd. CH), 7.00 (1H, s, vinyl), 7.5 (8.5H, m, arom.); ir (neat) 3060, 2940, 2840, 1620, 1480, 1445, 1350, 1205, 1135, 1120, 1090, 750, 730 cm^{-1} ; ms m/e 300.01212 (calcd. 300.01490).

Preparation of 6-lithio-5-methoxy-5H-dibenzo[α , e]cycloheptene (64). To a stirred cold (dry ice-isopropanol) solution of 1.89 g (6.29 μmoles) 6-bromo-5-methoxy-5H-dibenzo[α , e]cycloheptene in 15 ml of tetrahydrofuran, 3.9 ml (6.24 μmoles , 1.6 molar solution in hexane) of n-butyl-lithium was added dropwise with a syringe. This reaction mixture was stirred for 30 minutes and was used immediately.

Preparation of 6-(cyclopentadienylirondicarbonyl)-5-methoxy-5H-dibenzo[α , e]cycloheptene (62). Cyclopentadienyl-irondicarbonyl iodide (2.3 g, 7.57 μmoles) in 20 ml of tetrahydrofuran was added dropwise with a syringe to a cold (dry ice-isopropanol) solution of 6-lithio-5-methoxy-5H-dibenzo[α , e]cycloheptene (6.29 μmoles) in 15 ml of tetrahydrofuran. This solution was stirred at -78°C for 30 minutes. It was then warmed and stirred for an equal amount of time at room temperature. The addition of a small amount of Woelm alumina (Brockmann activity grade II, neutral) was followed by removal of the solvent *in vacuo*. The products on the coated alumina were chromatographed on Woelm alumina (activity grade II neutral alumina that had been stored under N_2 for a few days). The column was eluted first with pentane and then the eluent's polarity was gradually increased

with benzene (up to a 25% v/v benzene-pentane mixture). Collection of all but the first portion of the bright yellow band gave 0.473 g (19%) of an air sensitive oil.

The spectral data were as follows: ^1H nmr (CDCl_3), Figure 9, δ 3.33 (3H, s, methyl), 4.08 (1H, d, $J=2\text{Hz}$, satd. CH), 4.75 (5H, s, Cp), 6.68 (2H, d, $J=2\text{Hz}$, vinyl), 7.45 (10H, m, arom.); ir (neat) 3100, 3050, 2940, 2000, 1950, 1470, 1430, 1110, 905, 730 cm^{-1} ; ms m/e 370.0683 (calcd. 370.06540).

Attempted Synthesis of h^1 -3,4-5,6-dibenzocycloheptatrienylidene- h^5 -cyclopentadienyldicarbonyliron hexafluorophosphate (56) from 6-(cyclopentadienyliron dicarbonyl)-5-methoxy-5H-dibenzo[α,ϵ]cycloheptene (62). Via syringe, 0.400 g (1.03×10^{-3} moles) of triphenylcarbenium hexafluorophosphate in ca. 6 ml of methylene chloride was added dropwise over a 10 minute period to a cold (dry ice-isopropanol) stirred solution of 0.426 g (1.06×10^{-3} moles) 6-(cyclopentadienyliron dicarbonyl)-5-methoxy-5H-dibenzo[α,ϵ]cycloheptene in 7 ml of methylene chloride. After stirring for 30 minutes, the solution was warmed up to room temperature over a 15 minute time period. It was then cooled down again (dry ice-isopropanol) and 50 ml of cold (dry ice-isopropanol) ethyl ether (freshly opened can) was syringed into the reaction mixture. The yellow solid 66 that precipitated was collected on a medium grade glass frit and washed with several 10-30 ml portions of cold ethyl ether.

The filtrate was collected and the solvent removed *in vacuo* (rotary evaporator). Triphenylmethylmethyl ether was present in the filtrate (identified by ^1H nmr).

The yellow, extremely air sensitive solid 66 quickly reacted with any nmr solvent (acetone, nitromethane, and acetonitrile) at room temperature. However, at 0°C (CD₃NO₂) ¹H nmr resonances appear as shown in Figure 10. Its ir spectra (KBr) is given in Figure 12. Upon warming in the nmr probe, the solid gave the spectrum shown in Figure 11.

Reaction of yellow solid 66 with sodium methoxide.

To a cold solution (dry ice-isopropanol) of 0.185 g of yellow solid 66 in 5 ml of methylene chloride, 17.8 mg (0.330 mmoles) of sodium methoxide was added with a solid addition funnel. The remaining solid was washed into the reaction mixture with ca. 5 ml of methylene chloride. After warming to room temperature and stirring for five minutes, no visible color change occurred and undissolved sodium methoxide remained. At this time, 4 ml of methanol was added via syringe. The solution's color changed from dark to light red. After an additional five minutes of stirring, the solvent was removed *in vacuo*. Methylene chloride (10 ml) was then added, the solution was cooled again (dry ice-isopropanol) and 50 ml of ethyl ether was added. The solution was filtered and the filtrate concentrated *in vacuo* (rotary evaporator). Column chromatography of the filtrate products with silica gel (pentane) gave dibenzocycloheptatriene and triphenylmethylmethyl ether.

Reaction of 6-(cyclopentadienylirondicarbonyl)-5-methoxy-5H-dibenzo[a,c]cycloheptene with hydrogen chloride in the presence of tetracyclone. Gaseous hydrogen chloride was

bubbled for one hour into a cold (dry ice - isopropanol) stirred solution of 79.2 mg (0.199 mmole) 6-(cyclopentadienylirondicarbonyl)-5-methoxy[α, c]cyclohept-6-ene and 0.299 g (0.596 mmole) tetracyclone in 4 ml of methylene chloride. After 30 minutes of additional stirring, the reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. A small amount of silica gel was added and the solvent removed *in vacuo*. Column chromatography on silica gel (pentane) gave 2.6 mg of dibenzocycloheptatriene that was identified by ^1H nmr and mass spectrum.

REFERENCES

1. D.J. Cardin, B. Centikaya, and M.F. Lappert, *Chem. Rev.*, 72, 545 (1972).
2. F.A. Cotton and C.M. Lukehart, *Prog. Inorg. Chem.*, 16, 487 (1972).
3. E.O. Fisher and A. Massböl, *Angew. Chem., Int. Ed. Engl.*, 3, 580 (1964).
4. E.O. Fisher and U. Klabunde, *J. Am. Chem. Soc.*, 89, 7141 (1967).
5. K. Öfele, *Angew. Chem., Int. Ed. Engl.*, 8, 916 (1969).
6. K Öfele, *J. Organomet. Chem.*, 22, C9 (1970).
7. W.A. Herrmann, *Chem. Ber.*, 108, 486 (1975).
8. C.P. Casey, T.J. Burkhardt, C.A. Bunnell, and J.C. Calabrese, *J. Am. Chem. Soc.*, 99, 2127 (1977).
9. C.P. Casey, L.D. Albin, and T.J. Burkhardt, *ibid.*, 99, 2533 (1977).
10. C.P. Casey and S.W. Polichnowski, *ibid.*, 99, 6097 (1977).
11. C.P. Casey and T.J. Burkhardt, *ibid.*, 96, 7808 (1974).
12. R.R. Schrock, *ibid.*, 97 6577 (1975).
13. E.O. Fisher, R.L. Clough, G. Besl, and F.R. Kreissl, *Angew. Chem. Int. Ed. Engl.*, 15, 543 (1976).
14. C.H. Game, M. Green, J.R. Moss, and F.G.A. Stone, *J. Chem. Soc., Dalton*, 351 (1974).
15. P.W. Jolley and R. Pettit, *J. Am. Chem. Soc.*, 88, 5044 (1966).
16. M.L.H. Green, M. Ishaq, and R.N. Whiteley, *J. Chem. Soc., A*, 1508 (1967).
17. W.P. Giering, A. Sanders, L. Cohen, D. Kenedy, and C.V. Magatti, *J. Am. Chem. Soc.*, 95 5430 (1973).
18. M. Brookhart and G.O. Nelson, *ibid.*, 99, 6099 (1977).

19. D. DeJohn, C. Mayor, and J. Morris, University of Florida, unpublished results.
20. W.M. Jones and Y. Kawada, University of Florida, unpublished results.
21. K. Öfele, J. Organomet. Chem., 12, P42 (1968).
22. N.T. Allison, Y. Kawada, and W.M. Jones, J. Am. Chem. Soc., 100, 5224 (1978).
23. B. Föhlisch, P. Bürgele, and D. Krackenberger, Chem. Ber., 101, 2717 (1968).
24. B. Föhlisch and E. Haug, *ibid.*, 104, 2324 (1971)
25. B.J. Wakefield, "The Chemistry of Organolithium Compounds," Pergamon Press Ltd., Elmsford, N.Y., 1974.
26. B.F. Hullman and P.L. Pauson, Chem. and Ind., 653 (1955).
27. M.L.H. Green, M. Ishaq, and T. Mole, Z. Naturforschg., 206, 598 (1965).
28. M.L. Green and T. Mole, J. Organomet. Chem., 12, 404 (1968).
29. T.E. Piper and G. Wilkinson, J. Inorg. and Nucl. Chem., 3, 104 (1956).
30. L. Summers, R.H. Uloth, and A. Holms, J. Am. Chem. Soc., 77, 3604 (1955).
31. A. Eisenstadt, G. Scharf, and B. Fuchs, Tetrahedron Lett., 679 (1971).
32. W.M. Jones and U.H. Brinker, "Pericyclic Reactions," Vol. 1, A.P. Marchand and R.E. Henr. Ed., Academic Press, New York, N.Y., 1977, Ch. 3.
33. W.M. Jones, Accounts of Chemical Research, 10, 353 (1977).
34. M. Rosenblum, B. Foxmann, D. Marten, A. Rosan, and S. Raghu, J. Am. Chem. Soc., 99, 2160 (1977).
35. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd Ed., Interscience, New York, N.Y., 1972, p. 687.
36. R.B. King and M.B. Bisnette, J. Organomet. Chem., 2, 15 (1974).
37. F.A. Cotton and C.S. Kraihanzel, J. Am. Chem. Soc., 84, 4432 (1962).

38. M.Y. Darensbourg and D.J. Darensbourg, *Inorg. Chem.*, 9, 32 (1970).
39. M.H. Chisholm and S. Godleski, *Prog. Inorg. Chem.*, 20, 299 (1976).
40. C. Ciappenelli and M. Rosenblum, *J. Am. Chem. Soc.*, 91, 6876 (1969).
41. L.A. Paquette and G.D. Ewing, *J. Org. Chem.*, 40, 2965 (1975).
42. B. Föhlisch, C. Fisher, E. Widmann, and E. Wolf, *Tetrahedron*, 34, 533 (1978).
43. E.E. Waali, University of Wisconsin, Whitewater, personal communication, 1977.
44. R.E. Davis, University of Texas, Austin, personal communication, 1978.
45. R.L. Tyner, W.M. Jones, Y. Öhrn, and J.R. Sabin, *J. Am. Chem. Soc.*, 96, 3765 (1974).
46. A. Cutler, D. Ehnthdt, W.P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, and D. Wells, *ibid.*, 98, 3495 (1976).
47. D. Lennon, A.M. Rosan, and M. Rosenblum, *ibid.*, 99, 8426 (1977).
48. R.L. Ward, *ibid.*, 83, 1296 (1961).
49. P. Radlich, *J. Org. Chem.*, 29, 960 (1964).

BIOGRAPHICAL SKETCH

Neil Thomas Allison was born August 19, 1953, in Athens, Georgia. At the age of one, he and his parents moved to Macon, Georgia. He attended Lanier High School in Macon.

In September, 1971, he began undergraduate work at Georgia College in Milledgeville, Georgia. In 1972, he married the former Miss Amelia Ann Hancock.

While attending Georgia College, Mr. Allison received a Georgia College Alumni Scholarship and the Outstanding Chemistry Major Award. In June, 1975, he received the BS degree from Georgia College. Three months later, he began graduate work at the University of Florida in Gainesville, Florida.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



William M. Jones, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



John F. Helling
Associate Professor of Physical
Sciences and Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



William R. Dolbier, Jr.
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Martin T. Vala

Martin T. Vala
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Mark P. Hale, Jr.
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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