

SYNTHESIS AND X-RAY STRUCTURE OF  
IRON STABILIZED STRAINED CYCLIC ALLENES.  
VALENCE ISOMERIZATION BETWEEN LINEAR PERPENDICULAR  
AND BENT PLANAR ALLENE

BY

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL  
OF THE UNIVERSITY OF FLORIDA IN  
PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1987

To my mother and  
in memory of my father

## ACKNOWLEDGEMENTS

I would like to thank Dr. W.M. Jones for providing an atmosphere conducive to my personal and intellectual growth during my stay. He has kept me entertained with a fun and exciting problem and his guidance and encouragement are crucial toward the successful completion of this study. He has attracted many fine individuals who are a pleasure to work with. I would also like to thank Dr. Palenik and Dr. Koziol for the X-ray crystal structure of my iron stabilized cyclic allene. The witty, sarcastic and sometimes acrimonious remarks of Mr. Nicholas Conti made me laugh at even the worst of my scientific blunders. The most special thanks go to Miss Margaret Easley; a soprano, a pianist, an artist and a dear friend. I have spent many happy moments with her engaged in intriguing conversations spanning an extremely wide range of topics. She introduced me to opera and classical music and therefore made an everlasting impact on my life. Her friendship is greatly appreciated and she will always be remembered with fondness.

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Abstract of Dissertation Presented to the Graduate  
School of the University of Florida in Partial  
Fulfillment of the Requirements  
for the Degree of Doctor of Philosophy

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May 1987

Chairman: William M. Jones  
Major Department: Chemistry

The synthesis and isolation of strained organic molecules has been an area of active research for over forty years. Strained cyclic allenes are of no exception and have been studied both theoretically and experimentally. Calculations have shown that strained cyclic allenes down to 1,2-cyclopentadiene remained twisted and chiral but with a 2-5 kcal/mole barrier for racemization. Experimentally, 1,2-cyclohexadiene was found to be chiral but with a very low barrier for racemization.

Extended Huckel molecular orbital (EHMO) calculations have shown that the racemization barrier of the twisted 1,2-cycloheptadiene via its bent planar allyl cation is

lowered considerably upon complexation with a transition metal.

We have synthesized and studied the racemization process of dicarbonyl( $h^5$ -cyclopentadienyl)iron(II) [Fp] and carbonyl( $h^5$ -cyclopentadienyl)triphenylphosphineiron(II) [Fpp] complexed 1,2-cycloheptadiene.

Although we have failed to observe the racemization of Fp complexed 1,2-cycloheptadiene directly, we have experimental evidence which indicates that the bent planar allyl cation was formed either via methoxy abstraction from the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp leading to the formation of  $h^2$ -1,2-cycloheptadiene Fp or from the isomerization of  $h^2$ -1,2-cycloheptadiene Fp itself. We have also determined that the allene to allyl cation isomerization must be at least 14.7 kcal/mole.

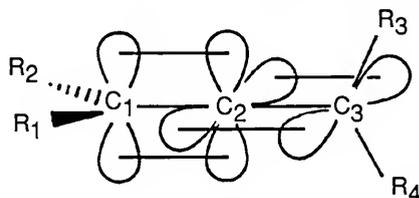
The Fpp complexed 1,2-cycloheptadiene was synthesized as enantiomeric pairs of diastereomers. Its fluxional barrier for 1,2-Fpp shift is between 15 kcal/mole and 18 kcal/mole. An enriched mixture of one diastereomer slowly equilibrates at room temperature to its thermodynamic mixture. The iron center here is stereochemically rigid and epimerization through dissociation and reassociation of the triphenylphosphine ligand does not occur. We infer from our observation that the thermal equilibration occurs via the allyl cation. Methoxy abstraction from the  $h^1$ -(7-methoxy)cycloheptadien-1-yl Fpp proceeds via the allyl cation as in the case with  $h^1$ -(7-methoxy)cycloheptadien-1-yl Fp.

We also report the first X-ray crystal structure of the  $h^2$ -1,2-cycloheptadiene Fpp cation.

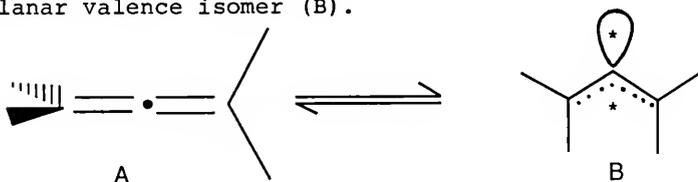
Finally, we were able to synthesize and isolate the  $h^2$ -1,2-cyclohexadiene Fpp complex as a thermally unstable solid. This solid reacted with ethanol, in a manner typical of most metal olefin complexes, to give  $h^1$ -(6-ethoxy)cyclohexen-1-yl Fpp.

CHAPTER I  
INTRODUCTION

Allenes are a class of organic compounds which contain two cumulated double bonds arranged in an orthogonal geometry. Acyclic allene has a linear structure and the planes defined by  $R_1R_2C_1$  and  $R_3R_4C_3$  are mutually perpendicular.



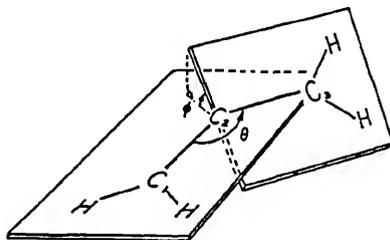
One of the most fascinating problems both experimentalists and theoreticians have been concerned with regarding the allene structure is the energy gap separating the ground state linear perpendicular allene (A) from its excited bent planar valence isomer (B).



Equally interesting is the extent to which this energy gap can be lessened and perhaps be inverted such that the bent planar allene becomes the ground state.

One can approach this problem by either increasing the ground state energy of the linear perpendicular allene or decreasing the excited state energy of the bent planar allene or both.

Incorporating a linear perpendicular allenic unit into a small ring will deform this allenic unit in two ways in order to facilitate ring closure and reduce ring strain. The allene will bend at the  $C_2$  carbon about an axis perpendicular to the  $R_1R_2C$  plane as defined by  $\theta$ . The allene will also twist about the  $R_1R_2C_1$  and the  $R_3R_4C_3$  planes as defined by  $\phi$ .

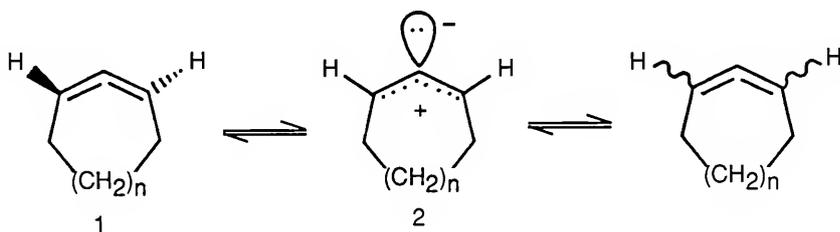


This combined effect raises the ground state energy of the allenic unit and is reflected by its kinetic instability. 1,2-Cyclononadiene<sup>1</sup> is a distillable liquid while 1,2-cyclooctadiene<sup>2</sup> dimerizes within hours at room temperature. 1,2-Cycloheptadiene<sup>1</sup> and 1,2-cyclohexadiene<sup>3</sup> have only a fleeting existence and can only be trapped chemically or, in the second case, by trapping in an argon matrix.

Although cyclic allenes lack an asymmetric carbon, they are chiral molecules with a  $C_2$  point group. Their R and S configuration, using 1,2-cycloheptadiene as an example, are shown below.<sup>4</sup>



In order for one enantiomer to convert to the other, the allenic pi-bonds of that enantiomer must be rotated out of orthogonality, passing through a planar state to the other enantiomer. The smaller the ring size of the cyclic allene the greater the allene is bent and twisted towards its planar isomer. When ring constraints force the pi-bonds of an optically active cyclic allene (1) to rotate out of orthogonality and become planar (2), optical activity is lost.



Racemization of an optically active cyclic allene is sufficient proof that a planar intermediate is accessible. The energy barrier for racemization can be measured via the loss of optical activity and represents the minimum energy separating the two forms of the allene, (A) and (B).

Numerous calculations have been performed over the last 20 years on 1,2-propadiene and 1,2-cyclohexadiene, the

archetype cyclic allene, in order to estimate this barrier for racemization and to address the electronic nature of the bent planar allene. The ground state geometry for 1,2-cyclononadiene, 1,2-cyclooctadiene and 1,2-cycloheptadiene are accepted generally as slightly bent and twisted towards planarity. The results from the latest MNDO calculations<sup>5</sup> are given in Table 1.

Allenic geometries for this series of three cyclic allenes clearly show the effect of ring strain on the allenic unit. An X-ray crystal structure is available for a phenylurethane derivative of 1,2-cyclononadiene<sup>6</sup> and agrees closely with the calculated results.

Historically, there have been considerable doubts as to the ground state structure of 1,2-cyclohexadiene. Moore and Moser<sup>7</sup> predicted the singlet diradical as the ground state. INDO calculations by Dillon and Underwood<sup>8</sup> suggested that the triplet diradical might be lower in energy. Recent SCF calculations of Johnson favor a chiral allenic ground state structure for 1,2-cyclohexadiene.<sup>5</sup> The calculations further predict a chiral ground state structure for 1,2-cyclopentadiene but with a 2-5 kcal/mole barrier for racemization.

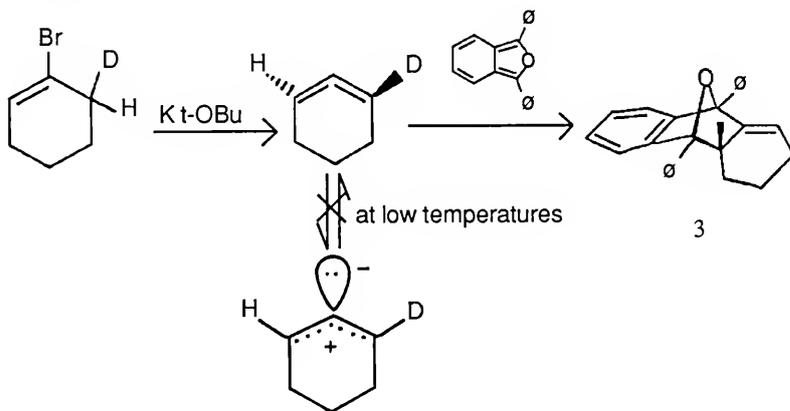
Mechanistic studies of 1,2-cyclohexadiene by Bottini et al.<sup>9</sup> suggested that 1,2-cyclohexadiene has an allenic structure but rapidly racemizes to a singlet diradical form. He also showed some chemistry arising from the zwitterionic form of 1,2-cyclohexadiene.

Table 1. Geometries of cyclic allenes calculated by MNDO.

	$C_1-C_2-C_3$	out of plane H bend <sup>a</sup>
1,2-cyclononadiene	170.4°	33.7°
1,2-cyclooctadiene	161.5°	31.0°
1,2-cycloheptadiene	153.4°	27.6°

<sup>a</sup>defined as the angle made by the C-H bond with the  $C_1-C_2-C_3$  plane containing the  $C_2$  axis, e.g., 45° for 1,2 propadiene.

Optically active 1,2-cyclohexadiene, synthesized via asymmetric dehydrobromination of resolved 1-bromocyclohexene-6d<sub>1</sub> with potassium tert-butoxide, was trapped in situ with diphenylisobenzofuran.<sup>10</sup> The adduct (3) is optically active when the reaction is done at low temperatures but optically inactive above +80°C suggesting that racemization of the cyclic allene is competitive with cycloaddition and the inversion barrier is low.



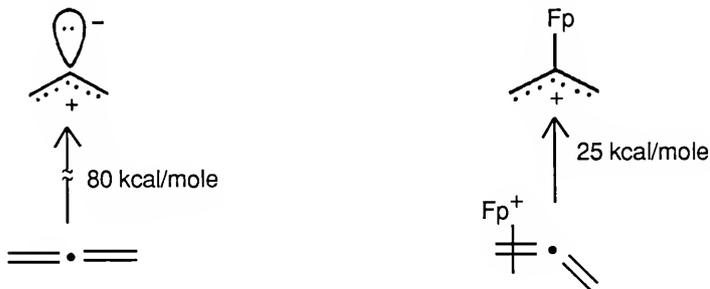
The adduct from reaction of 1,2-cycloheptadiene and diphenylisobenzofuran remained optically active under similar reaction conditions. The allene subunit in this larger ring has maintained its orthogonality.

We have now extended our studies from the free strained cyclic allenes to the transition metal complexed strained cyclic allenes. We are interested in the effect the transition metal has on the allenic unit, in particular with

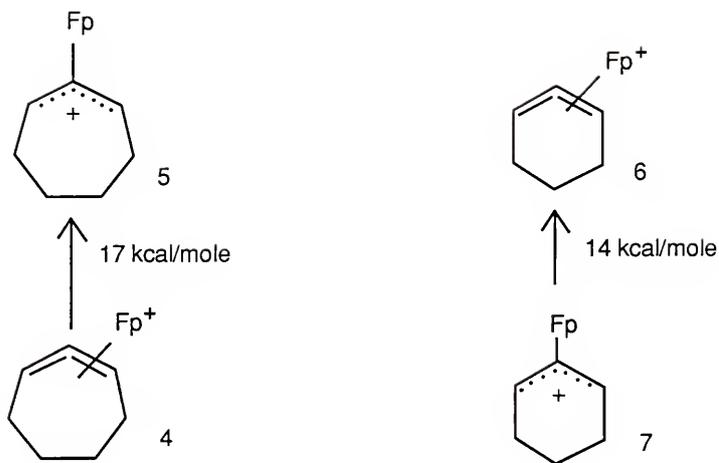
regard to the isomerization of the allene unit from its linear perpendicular form to its bent planar isomer.

EHMO calculations<sup>11</sup> predict that the energy gap separating the linear perpendicular allene from its bent planar isomer is lessened considerably when the allene is complexed onto the (Cp)Fe(CO)<sub>2</sub> [Fp] cationic fragment. Here lies the impetus to study Fp complexed allenes.

1,2-Propadiene lies about 80 kcal/mole below that of its bent planar isomer according to EHMO. The relative energy between 1,2-propadiene and its bent planar isomer is only 25 kcal/mole when both are bound to the Fp fragment.



Similarly, Fp bound 1,2-cycloheptadiene (4) is calculated to be only 17 kcal/mole below its bent planar form (5). Furthermore, EHMO predicts the Fp bound bent planar 1,2-cyclohexadiene (7) is actually 14 kcal/mole more stable than the allene form (6).

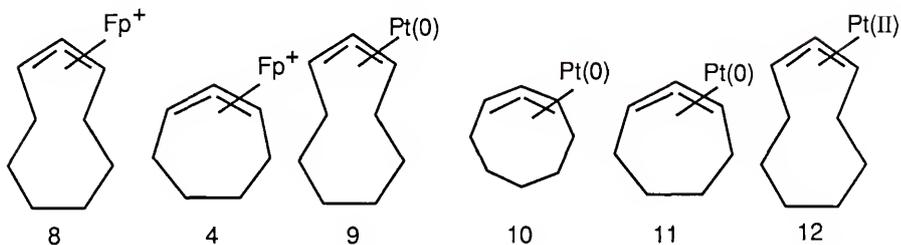


Although energies derived from EHMO should not be accepted as absolute values, one does see a trend favoring a bent planar allenic ground state as one proceeds towards Fp complexed allene with the allene incorporated into a smaller ring. This decrease in relative energy between the linear perpendicular allene and its bent planar isomer is largely due to the greater stabilizing interaction between the Fp-LUMO and the bent planar allenic HOMO.

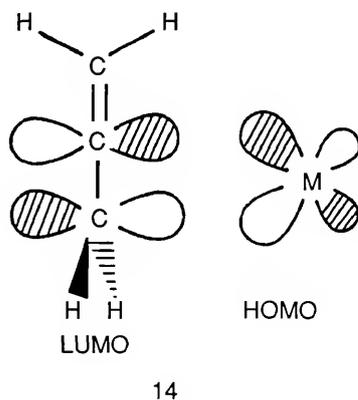
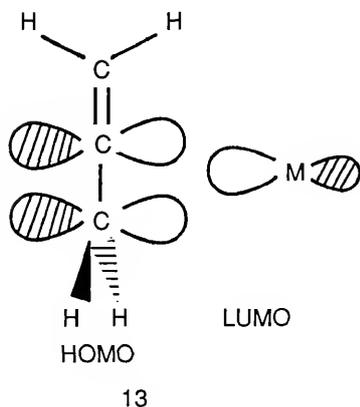
We decided to choose the Fp complexed 1,2-cycloheptadiene as the starting point of our work.

Transition metal complexes of acyclic allenes are well known and have been reviewed extensively.<sup>12</sup> However cyclic counterparts are limited to Fp complexes of 1,2-cyclononadiene<sup>13</sup> (8) and 1,2-cycloheptadiene<sup>14</sup> (4),  $(\text{PPh}_3)_2\text{Pt}(0)$  complexes<sup>15</sup> of 1,2-cyclononadiene (9), 1,2-cyclooctadiene

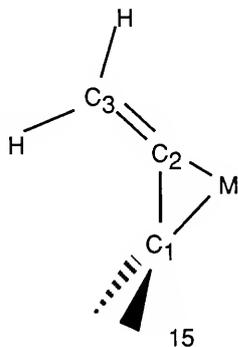
(10) and 1,2-cycloheptadiene (11) and (Am)(Cl)<sub>2</sub>Pt(II) complex of 1,2-cyclononadiene<sup>16</sup> (12).



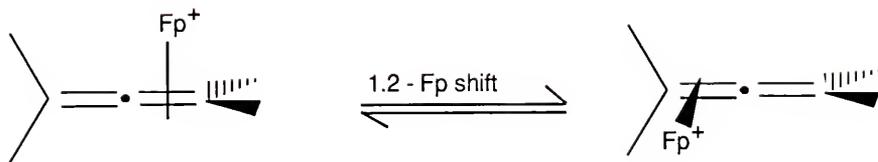
The bonding between the metal fragment and the allene can be described using the Dewar-Chatt-Duncanson model.<sup>17</sup> The bond is formed by the interaction of the HOMO of one of the allene double bonds with an empty acceptor on the metal (13). The filled metal d-orbital in turn back bonds with the LUMO of the same double bond (14).



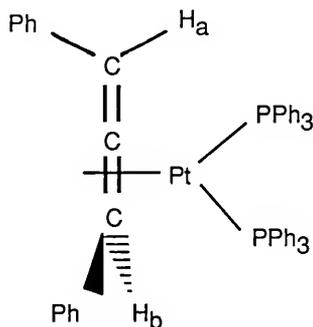
This back bonding causes substituents on the complexed double bond to bend away from the metal, the degree of which is directly related to the extent of this back bonding. The metal to olefin pi-bond is often looked upon as a metallo-cyclopropane.<sup>18</sup> The metal is not positioned symmetrically about the C<sub>1</sub> and C<sub>2</sub> carbons of the allene. The metal is closer to the C<sub>2</sub> carbon because of its greater s character compared to the C<sub>1</sub> carbon (15).



Allene complexes of metals, like olefin complexes of metals, rotate about the metal to olefin pi-bond. In addition to this rotational motion, allene complexes of most metals also exhibit fluxional behavior whereby the complexed metal fragment moves from one double bond of the allene to the adjacent double bond. Such fluxional behavior of acyclic allenes complexed to Fp was studied extensively by Rosenblum et al.<sup>13</sup> and was shown to be nondissociative (i.e. intramolecular).



Unlike the Fp complexed allenes, not all platinum complexed allenes are fluxional. The Pt(0) complex of 1,3-diphenylpropadiene (16) is not fluxional.<sup>19</sup>  $H_a$  and  $H_b$  remain distinct in the  $^1H$  NMR even at high temperatures.

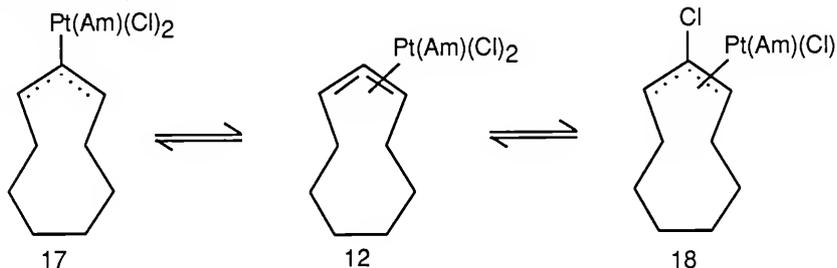


16

The Pt(II) complex of tetramethylallene however is fluxional with the metal moving back and forth between the two allenic double bonds.<sup>20</sup>

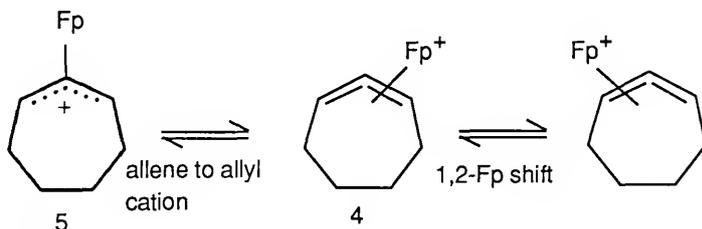
1,2-Fp shifts do not involve a bent planar intermediate. Optical rotation of an optically active 1,2-cyclo-nonadiene complexed onto Fp remained unchanged<sup>13</sup> up to

+80°C. A racemate would result if a bent planar intermediate were involved. In contrast, the optical activity of the Pt(II) complex of 1,2-cyclononadiene (12) diminishes with time. The 1,2-cyclononadiene is believed to racemize via a  $h^3$ -allyl Pt intermediate (18) and not the bent planar allene<sup>16</sup> (17).

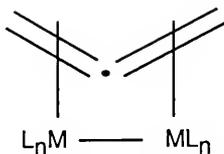


1,2-Cycloheptadiene complexed to Fp has a measured fluxional barrier of 13.9 kcal/mole and is the lowest barrier observed for Fp allene complexes.<sup>14</sup> Fluxional barriers for  $h^2$ -methylallene,  $h^2$ -1,1-dimethylallene and  $h^2$ -tetramethylallene Fp cationic complexes are 23.1 kcal/mole, 18.0 kcal/mole and 16.3 kcal/mole, respectively.<sup>13</sup>  $h^2$ -1,2-Cyclononadiene Fp has a fluxional barrier of 16.9 kcal/mole. Although the decrease in fluxional barrier with increasing methyl substitution is probably steric in origin, one could not help but to wonder if a bent planar allene intermediate were involved. The bent planar allene is an allyl cation and should be favored by electron donating methyl substituents. Moreover, if one assumes that the steric environment immediate to the Fp center is the same for 1,3-dimethylpropadiene, 1,2-cyclononadiene and

1,2-cycloheptadiene, bending and twisting the linear perpendicular allenic unit toward its bent planar form by tying it into a ring lowers the fluxional barrier. Therefore, it was not known at the time it was reported whether the fluxional barrier of 13.9 kcal/mole for  $h^2$ -1,2-cycloheptadiene Fp (4) represented a simple 1,2-Fp shift or that an allyl cation intermediate (5) was involved.



X-ray crystal data is available for many allene complexes of Rh, Pt and Pd.<sup>21</sup> In all cases the complexed double bond is longer than the uncomplexed double bond. The metal is unsymmetrically positioned about the bound double bond and is further away from the terminal carbon than the central carbon. The  $C_1-C_2-C_3$  bond angle falls within the range of  $158^\circ$  to  $142^\circ$ . The complexed allenes are not planar. Allene complexes of transition metal dimers (19) where each of the allene double bonds is bound to a different metal in the dimer are also known. The  $C_1-C_2-C_3$  angles of such complexes are, on the average, much smaller.<sup>22</sup>



19

The only X-ray structure of an iron allene complex is the  $h^2$ -tetramethylallene Fp.<sup>23</sup> The complexed allene is oriented parallel to the cyclopentadienyl ring as expected. The bond length of the uncomplexed double bond is  $1.335\text{\AA}$  and the complexed double bond is  $1.367\text{\AA}$ . The complexed double bond is longer as a result of back bonding from the Fp to the  $\pi^*$  of the allene double bond. The iron is asymmetrically placed about the double bond and is closer to the central carbon ( $2.063\text{\AA}$ ) than the outer carbon ( $2.237\text{\AA}$ ). The  $C_1-C_2-C_3$  bond angle is  $145.7^\circ$  but the allene is still orthogonal.

There have been no X-ray data reported on any metal complexed cyclic allenes to date although such compounds are well known. It would be interesting to compare the X-ray structure of  $h^2$ -1,2-cycloheptadiene Fp with  $h^2$ -tetramethylallene Fp. Of particular importance is how the ring affects the allene  $C_1-C_2-C_3$  bond angle and how far the allene is away from orthogonality.

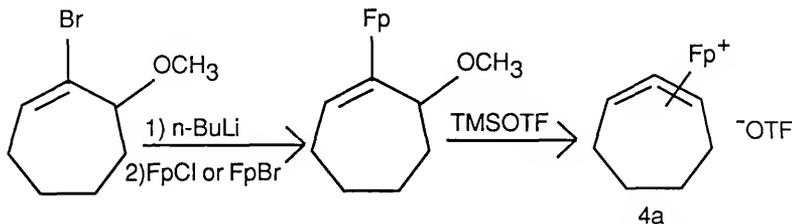
The objective of this study was to determine whether a 1,2-Fp shift between the double bond of the cyclic allene

involves a bent planar intermediate and, if not, to determine if the latter is accessible. It was also to provide the first X-ray structure of a metal complexed cyclic allene.

CHAPTER II

DICARBONYL ( $h^5$ -CYCLOPENTADIENYL) IRON (II) COMPLEXED  
1,2-CYCLOHEPTADIENE

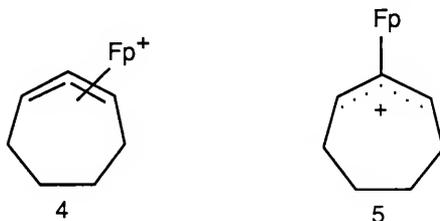
The  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp was synthesized in moderate yields by reacting the 1-lithio-7-methoxycycloheptene with either Fp chloride or Fp bromide. Treating a methylene chloride solution of the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp with trimethylsilyl trifluoromethanesulfonate followed by precipitation with diethyl ether yielded the desired  $h^2$ -1,2-cycloheptadiene Fp cation complex (4a) as an air and thermally sensitive yellow solid.



Attempts to synthesize the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp by this route failed with Fp iodide. It is critical that the 1-bromo-7-methoxycycloheptene be in a slight excess relative to n-butyllithium when generating the 1-lithio-7-methoxycycloheptene in order to ensure a maximum yield of the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp. Synthesis

of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp by this method was far superior to a longer and lower yield route used previously.<sup>14</sup>

The yellow colored methylene chloride solution of the  $h^2$ -1,2-cycloheptadiene Fp trifluoromethanesulfonate (4a) turned red within 30 mins at room temperature. In contrast, the  $h^2$ -1,2-cyclononadiene Fp tetrafluoroborate (8) is not only air stable as a solid but a methylene chloride solution of it is also stable for over 14 hrs at +83°C. Although the extreme thermal instability of the  $h^2$ -1,2-cycloheptadiene Fp (4a) in methylene chloride is an inconvenience, it may signal a different pathway for the fluxional process; a pathway that is different from that of the  $h^2$ -1,2-cyclononadiene Fp (8) and perhaps involves the bent planar allene (allyl cation) intermediate from which decomposition may occur. We will now refer to (4) as the allene form and (5) as the allyl cationic form.



$^1H$  NMR was used to follow the decomposition of the  $h^2$ -1,2-cycloheptadiene Fp (4a) in a methylene chloride solution at +40°C. Decomposition was complete within 3 hrs and Fp trifluoromethanesulfonate and 1,3-cycloheptadiene

were the only major decomposition products observed. The former was identified by comparing its  $^1\text{H}$  NMR with that of Fp trifluoromethanesulfonate synthesized independently from Fp chloride and silver trifluoromethanesulfonate and the latter with an authentic sample of 1,3-cycloheptadiene. The decomposition mixture was red in color. The result of this experiment is in agreement with that by Manganiello<sup>14</sup>. Neither cycloheptene nor the 1,2-cycloheptadiene dimer were observed in the  $^1\text{H}$  NMR.

According to the  $^1\text{H}$  NMR, the decomposition of the  $\text{h}^2$ -1,2-cycloheptadiene Fp (4a) to Fp trifluoromethanesulfonate and 1,3-cycloheptadiene proceeded via a short lived, thermally unstable intermediate. This intermediate had a singlet at 5.58 ppm, Fig. 1. Its concentration increased rapidly up to a certain point and then decreased to the baseline with a concurrent increase in the concentration of both Fp trifluoromethanesulfonate and 1,3-cycloheptadiene, Fig. 2. Based upon this observation, the thermally labile intermediate was suspected to be the  $\text{h}^2$ -1,3-cycloheptadiene Fp cation complex. The singlet at 5.58 ppm is certainly within the range for cyclopentadienyl hydrogen resonances of cationic Fp-olefin complexes. The  $\text{h}^2$ -1,3-cycloheptadiene Fp could not be synthesized via a common thermal exchange reaction between 1,3-cycloheptadiene and the  $\text{h}^2$ -propene Fp cation,<sup>24</sup> which lends further evidence for its thermal lability.

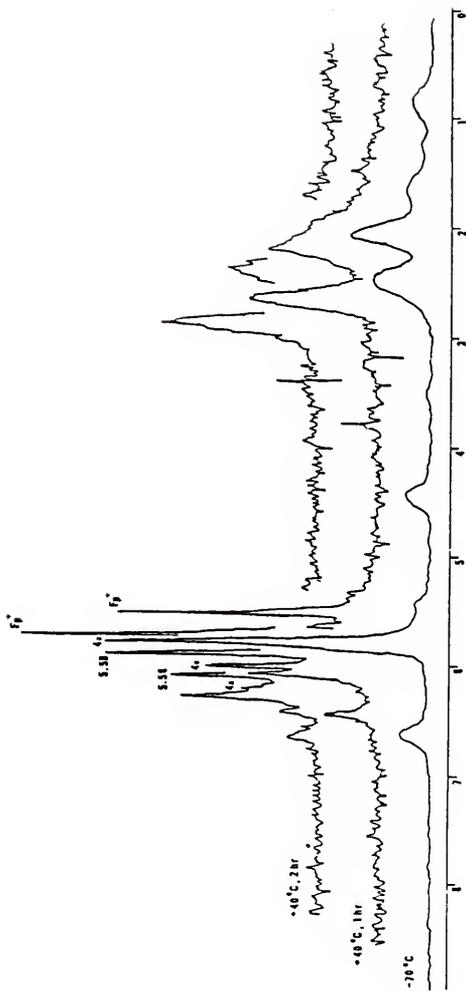


Fig. 1. Thermal decomposition of (4a) in  $CD_2Cl_2$ .

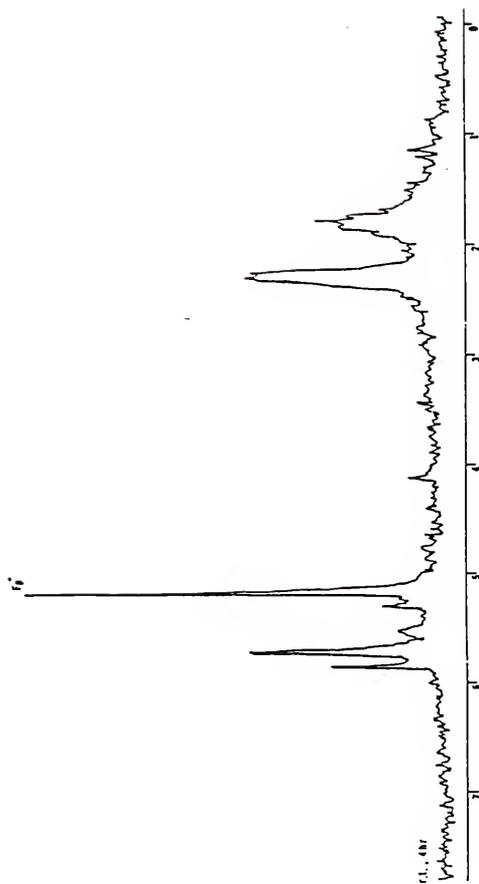
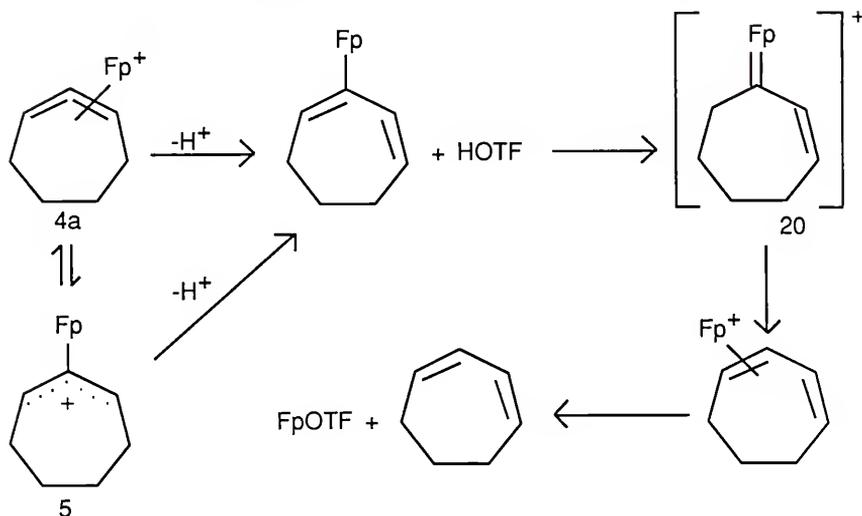


Fig. 2. Fp trifluoromethanesulfonate and 1,3-cycloheptadiene from the thermal decomposition of (4a) in  $\text{CD}_2\text{Cl}_2$ .

A reasonable mechanism for the decomposition of the  $h^2$ -1,2-cycloheptadiene Fp (4a) is as follows.

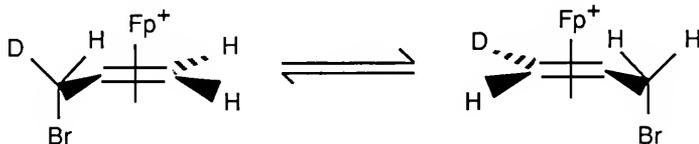


We believe that an initial deprotonation of an appropriately situated hydrogen occurs from either the allene (4) or allyl cation intermediate (5) to form the  $h^1$ -1,3-cycloheptadien-2-yl Fp and trifluoromethanesulfonic acid. In the presence of trifluoromethanesulfonic acid, this  $h^1$ -1,3-cycloheptadien-2-yl Fp is then converted via the conjugated carbene (20) to the  $h^2$ -1,3-cycloheptadiene Fp. Under the experimental conditions it dissociates to the Fp cation and 1,3-cycloheptadiene.

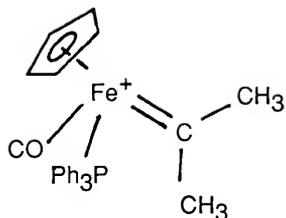
The decomposition reaction would have stopped after the first step, in the absence of trifluoromethanesulfonic acid, giving  $h^1$ -1,3-cycloheptadien-2-yl Fp as the only product. In order to test the validity of this mechanism, the  $h^2$ -1,2-

cycloheptadiene Fp (4a) was subjected to the same decomposition conditions but in a slurry of lithium or sodium carbonate to neutralize the trifluoromethanesulfonic acid. The decomposition mixture did not turn red but remained brown in color. The  $^1\text{H}$  NMR cyclopentadienyl resonance of this brown substance falls within the range typical for most  $\text{h}^1$ -alkyl Fp. Presumably the  $\text{h}^1$ -1,3-cyclopentadien-2-yl Fp was formed, but we were unable to purify it sufficiently for a positive identification. 1,3-Cycloheptadiene and Fp trifluoromethanesulfonate were no longer the decomposition products.

Counter ions have been known to affect the way an organometallic species behaves in solution, a recent example being the intramolecular rearrangement of the  $\text{h}^2$ -3-bromopropene Fp complex.<sup>25</sup>



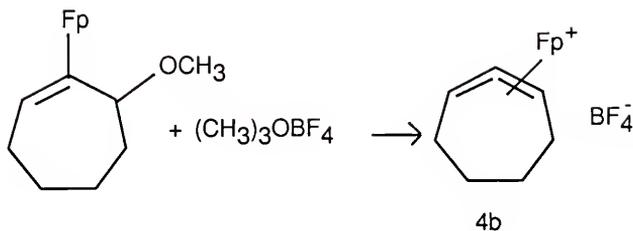
The 1,3 shift of a bromine atom exo to the Fp-olefin bond was greatly accelerated when the counter ion was changed from trifluoromethanesulfonate to hexafluorophosphate. Ion pair association in the salt may have been responsible for such behavior. Casey et al.<sup>26</sup> has also reported that a solution of the tetrafluoroborate salt of the  $(\text{Cp})\text{Fe}(\text{CO})(\text{PPh}_3)$  isopropylidene complex is more stable than its trifluoromethanesulfonate salt.



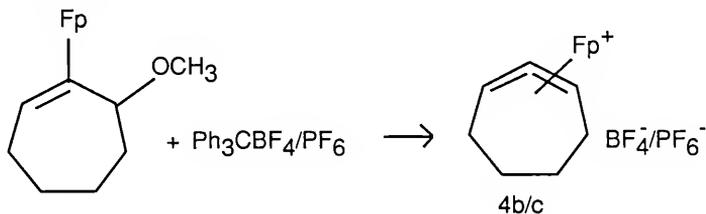
Since we believe that the basicity of the trifluoromethanesulfonate anion is responsible for the decomposition of the  $h^2$ -1,2-cycloheptadiene Fp (4a), we thought it would be desirable to replace it with a non-basic anion. The tetraphenylborate anion was successfully exchanged for the trifluoromethanesulfonate anion in a cold ( $-35^\circ\text{C}$ ) methanol solution. We were disappointed that a methylene chloride solution of the tetraphenylborate salt of  $h^2$ -1,2-cycloheptadiene Fp (4) was also thermally unstable and decomposed within 30 mins at  $+50^\circ\text{C}$  to several unidentifiable products.<sup>27</sup>

The  $h^2$ -1,2-cyclononadiene Fp tetrafluoroborate (8) is the only known stable cyclic allene of iron. If by chance the thermal stability of (8) were due to the tetrafluoroborate anion, this would suggest that the tetrafluoroborate anion may be the counterion of choice for the  $h^2$ -1,2-cycloheptadiene Fp (4).

The  $h^2$ -1,2-cycloheptadiene Fp tetrafluoroborate (4b) was synthesized in good yields by reacting the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp with trimethyloxonium tetrafluoroborate.



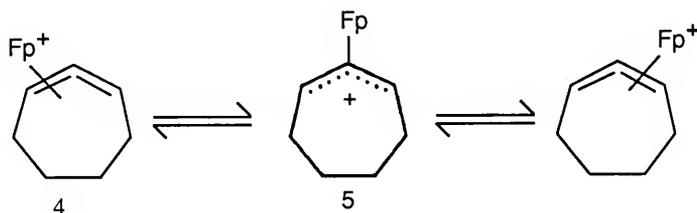
The yellow solid  $h^2$ -1,2-cycloheptadiene Fp (4b) turns red when exposed to air, but a room temperature methylene chloride solution of it is stable for over 3 days. The same solution is also stable for over 2 hrs at +40°C. Thus it would appear that the thermal decomposition of the  $h^2$ -1,2-cycloheptadiene Fp (4a) in methylene chloride is due to the basicity of the trifluoromethanesulfonate anion. The tetrafluoroborate and the hexafluorophosphate salt of  $h^2$ -1,2-cycloheptadiene Fp (4) may also be synthesized by reacting the  $h^1$ -(7-methoxy)cycloheptadien-1-yl Fp with triphenylcarbenium tetrafluoroborate and hexafluorophosphate, respectively. This procedure has a drawback in that the product is sometimes contaminated with the unreacted triphenylcarbenium cation.



We now have on hand the stable  $h^2$ -1,2-cycloheptadiene Fp (4b) and (4c). Both  $h^2$ -1,2-cycloheptadiene Fp (4b) and (4c) react with alcohols to give the same ether adducts as are given by the  $h^2$ -1,2-cycloheptadiene Fp (4a). It was interesting to note that their fluxional barriers were unaffected by the counterions.

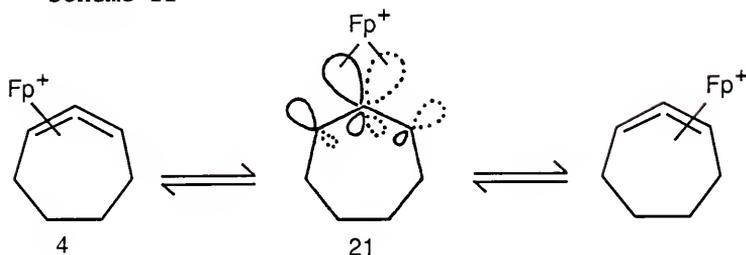
The  $h^2$ -1,2-cycloheptadiene Fp (4) has a fluxional barrier of 13.9 kcal/mole and is the lowest barrier yet measured when compared with other  $h^2$ -Fp complexed acyclic and cyclic allenes. Does this low fluxional barrier signal a new mechanism for the fluxional process, perhaps via the bent planar allene (allyl cation) intermediate (5), Scheme I?

Scheme I

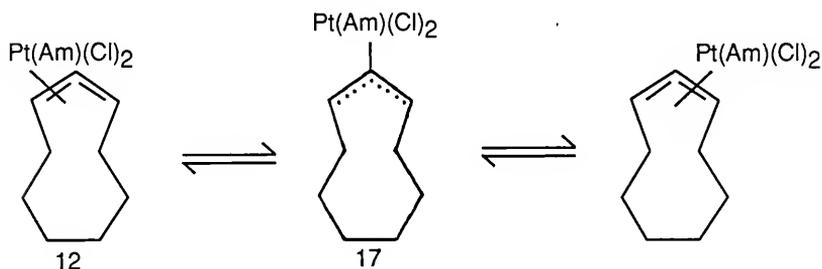


Or perhaps the fluxional process merely involves a simple intramolecular 1,2-Fp shift from one allenic double bond to the other, Scheme II, passing through the allene intermediate (21)? The low fluxional barrier merely reflects in some manner the effect of ring strain in the smaller cyclic allene. Such a simple intramolecular 1,2-Fp shift was demonstrated conclusively for the  $h^2$ -1,2-cyclononadiene Fp (8).

Scheme II

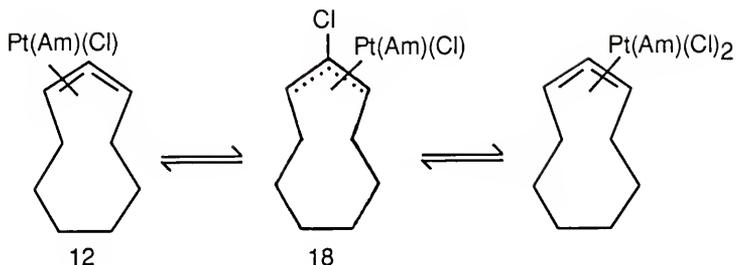


The allene (4) to allyl cation (5) valence isomerization for  $Fp$  complexes is unprecedented. The racemization of optically active 1,2-cyclononadiene complexed onto  $Pt(II)$  (12) was initially proposed to proceed via an allyl species<sup>16</sup> (17).



This allyl species (17), with two electrons in its pi-system, would be formally equivalent to an allyl cation.

It is now accepted that a reversible  $h^2$ -pi-allene (12) to  $h^3$ -pi-allyl (18) isomerization, whereby a chloride is transferred from the  $Pt(II)$  to the pi-allyl, is responsible for the racemization.



Such a  $h^2$ - $\pi$ -allene to  $h^3$ - $\pi$ -allyl isomerization in conjunction with a ligand transfer from the metal to the  $\pi$ -allyl, although rare for  $h^2$ -allene Pt(II) complexes, is quite common among its cogener, the  $h^2$ -allene Pd complexes.<sup>28</sup> In the case of the  $h^2$ -1,2-cycloheptadiene Fp (4), no such ligand is available on the Fp for an analogous transfer to the 1,2-cycloheptadiene ligand. This precludes such a mechanism for an allene to allyl isomerization.

Numerous barriers to the fluxional behavior for  $h^2$ -allene complexes of Pt(II) and Fe(II) have been measured. Fluxional barriers for  $h^2$ -tetramethylallene complexes of Pt(II) are generally low and lie between 7 to 10 kcal/mole.<sup>20,29</sup> The  $h^2$ -1,1-dimethylallene complex of Pt(II) is not fluxional. The Pt(II) remained bonded to the C2-C3 olefinic bond, the less hindered bond. The Fp in the  $h^2$ -1,1-dimethylallene Fp also prefers the distal position.<sup>13</sup> This preference for the distal position is presumed to be steric in origin. Fluxional behavior has not been reported for the  $h^2$ -allene,  $h^2$ -tetramethylallene and  $h^2$ -1,3-diphenylallene Pt(0) complexes.<sup>19,30</sup> They are presumed to be

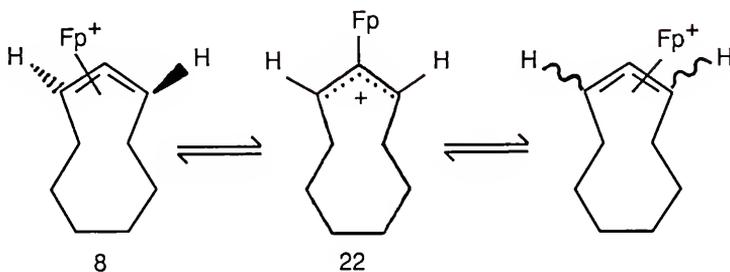
dynamically rigid. The  $h^2$ -1,2-cyclononadiene Pt(0)<sup>16</sup> is also not fluxional at room temperature.

For comparison with the  $h^2$ -1,2-cycloheptadiene Fp (4), the fluxional barriers of  $h^2$ -1-methylallene,  $h^2$ -1,3-dimethylallene,  $h^2$ -tetramethylallene and  $h^2$ -1,2-cyclononadiene (8) Fp complexes<sup>13</sup> are 23.1 kcal/mole, 18.0 kcal/mole, 16.3 kcal/mole and 16.9 kcal/mole, respectively.

It has been well established that the fluxional process for these complexes occurs by a concerted 1,2-Fp shift between the two allenic double bonds and not via an allyl cation. The fluxional barriers decrease gradually with increasing methyl substitution on the allene and are attributed to a steric factor rather than the stabilization of an allyl cationic intermediate by the methyl substituents. The steric bulk of the methyl substituents increases the lability of the Fp-olefin pi-bond making it easier for the Fp to move between the two adjacent double bonds.

The  $h^2$ -1,2-cyclononadiene Fp (8) has a fluxional barrier of 16.9 kcal/mole. In this case it was conclusively demonstrated that the fluxional process did not proceed via an allyl cationic species (22). When a solution of the optically active  $h^2$ -1,2-cyclononadiene Fp (8) was heated to the point of rapid fluxionality, reisolation gave the allene complex without any loss in optical activity.<sup>13</sup> The optically active  $h^2$ -1,2-cyclononadiene Fp (8) would have racemized if the achiral allyl cation (22) were involved in

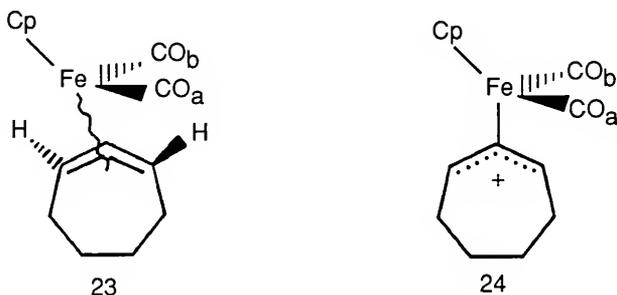
the fluxional process either as an intermediate or as a transition state.



At first thought one would not expect the  $h^2$ -1,2-cycloheptadiene Fp (4) fluxional barrier to be much different from that of the  $h^2$ -1,2-cyclononadiene Fp (8) if both proceeded by the same mechanism. In fact, we would expect the fluxional barrier for the  $h^2$ -1,2-cycloheptadiene Fp (4) to be higher should the Fp-olefin pi-bond strength parallel that of the Pt(0)-olefin pi-bond. The coordinating ability of cyclic allenes onto  $Pt(PPh_3)_2$  was reported to increase with decreasing ring size.<sup>15</sup> This is due to the greater release of ring strain upon coordination. The low fluxional barrier for the  $h^2$ -1,2-cycloheptadiene Fp (4) coupled with the strained ring therefore causes one to wonder if the fluxionality occurs via a mechanism involving an allyl cationic intermediate (5).

To test for this possibility, a temperature dependent  $^{13}C$  NMR study of  $h^2$ -1,2-cycloheptadiene Fp (4b) was undertaken. 1,2-Cycloheptadiene is chiral and when complexed to

Fp causes the carbonyl ligands on the Fp to become diastereotopic and be distinguishable. The two carbonyl [CO] resonances appear at 207.2 ppm and 210.2 ppm. A simple intramolecular 1,2-Fp shift would render the CO<sub>a</sub> and CO<sub>b</sub> unchanged (23). In contrast an allene to allyl cation isomerization would cause the carbonyls to become equivalent and coalesce to a single resonance (24).



As the temperature of a nitromethane-d<sub>3</sub> solution of h<sup>2</sup>-1,2-cycloheptadiene Fp (4b) was raised, the two carbonyl resonances remained unchanged. The allenic carbons C<sub>1</sub> and C<sub>3</sub> however became equivalent at +30°C. The allenic carbon C<sub>2</sub> remained unchanged, Fig. 3. Taken together, it means that the rapid fluxional motion of the h<sup>2</sup>-1,2-cycloheptadiene Fp (4) at +30°C does not involve an allyl cationic intermediate because under this condition, C<sub>1</sub> and C<sub>3</sub> become equivalent whereas the two carbonyls remain distinct. If an allyl cationic intermediate (24) were involved in the fluxional process at +30°C, this would correspond to a free energy of activation of 14.7 kcal/mole. We can safely say

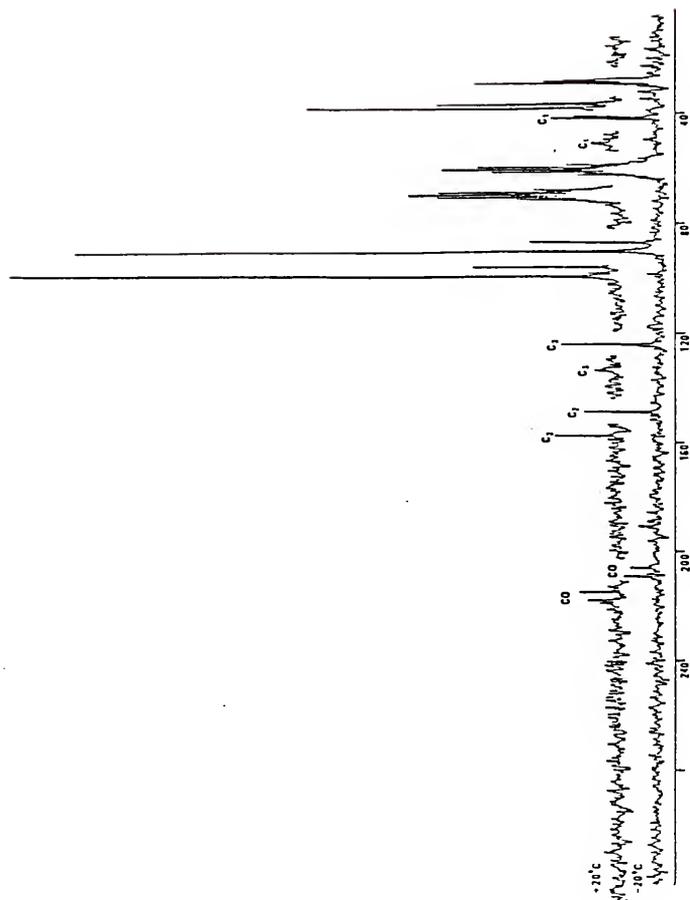


Fig. 3. High temperature  $^{13}\text{C}$  NMR of (4b) in  $\text{CD}_3\text{NO}_2$ .

that the fluxional barrier of 13.9 kcal/mole as determined by  $^1\text{H}$  NMR corresponds to a simple intramolecular 1,2-Fp shift, Scheme II, and that the allene to allyl cation isomerization, Scheme I, requires an energy of greater than 14.7 kcal/mole.

It is reasonable to expect the allene to allyl cation isomerization to be the higher energy process of the two. This isomerization requires bonding and structural changes and a transfer of a positive charge from the iron to the organic ligand, whereas a 1,2-Fp shift merely involves a repositioning of the Fp from one double bond to the other.

It is inconvenient to study any dynamic process of organometallic compounds at high temperatures by  $^1\text{H}$  NMR due to their thermal instability. For example, when seeking NMR evidence for allyl cation formation, a nitromethane- $\text{d}_3$  solution of the  $\text{h}^2$ -1,2-cycloheptadiene Fp (4b) was heated to  $+60^\circ\text{C}$  and was found to decompose rapidly within the time needed to acquire a  $^{13}\text{C}$  spectrum.

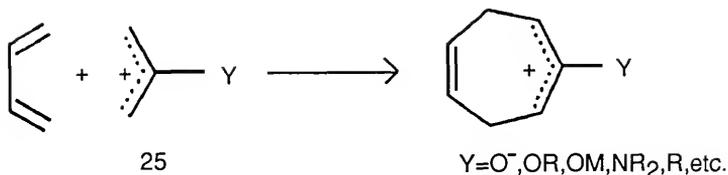
A possible way to study the fluxionality of a thermally sensitive organometallic complex by NMR without raising the probe temperature is to use the spin saturation transfer technique, S.S.T.<sup>31</sup>

The spin saturation technique involves finding a condition whereby saturating one of the spins of an exchanging two-spin system results in a partial saturation of the other spin. From this information and the  $T_1$  of both spins, the energy barrier for the exchange can be calculated. The

advantage of this method was exemplified in the case for  $h^2$ -1,2-cycloheptadiene Fp (4a). The conditions required for obtaining a fluxional barrier from spin saturation transfer described above were met at  $-20^\circ\text{C}$ . It was necessary to heat (4a) to  $+29^\circ\text{C}$  before its fluxional barrier could be obtained by the coalescence method.

For the case of the  $h^2$ -1,2-cycloheptadiene Fp (4), if a simple 1,2-Fp shift were the only process occurring, irradiation of one of the carbonyl resonances would not affect the intensity of the other because they would remain distinct at all times. On the other hand, if an allyl cation were accessible, the carbonyl ligands would become equivalent and if the relaxation of the carbonyl carbon were slower than the fluxional process, irradiation of one of the carbonyl resonances would cause the other carbonyl resonance to diminish in intensity. From this information, it would be possible to calculate the barrier for the fluxional process while maintaining a reasonable probe temperature. Unfortunately, S.S.T. is impractical here for the two carbonyl resonances are too close to each other. We could not selectively irradiate one carbonyl without irradiating the other.

Another possible way to detect the allyl cationic intermediate would be to trap it as it is formed. 2-Substituted allyl cations (25) are known to react with 1,3-dienes.



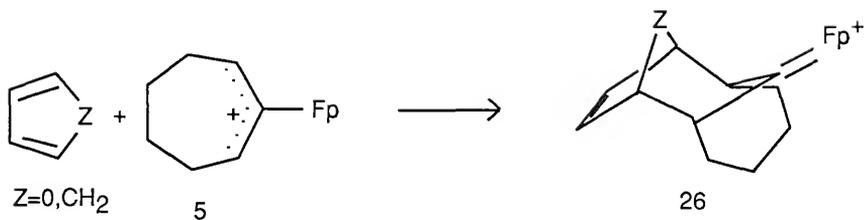
Extensive reviews have been written about the cycloaddition of such allyl cations (25), the most recent one by Hoffmann.<sup>32</sup> These reactions have been exploited in organic synthesis of bi- and tricyclic compounds. Several possible products can result from the cycloaddition of allyl cations (25) to 1,3 dienes depending upon whether the reaction is concerted or stepwise and upon the nature of Y. The reader is best referred to the review article by Hoffmann<sup>32</sup> for all the possible products from concerted and stepwise cycloadditions.

The pi-donating strength of a Fp in the homocyclooctatrienylidene Fp was found to be similar to that of a methoxy group.<sup>33</sup> This would make the 2-Fp substituted allyl cation a good candidate to be trapped by 1,3-dienes. There is however no literature precedent that such a reaction will occur. In fact, allyl cations with Fp substitution at C<sub>2</sub> are not even known to exist at this point.

The cycloaddition products expected from cyclopentadiene and furan with the h<sup>1</sup>-allyl Fp cation (5) by either the concerted or stepwise addition are shown in Scheme III and IV, respectively.

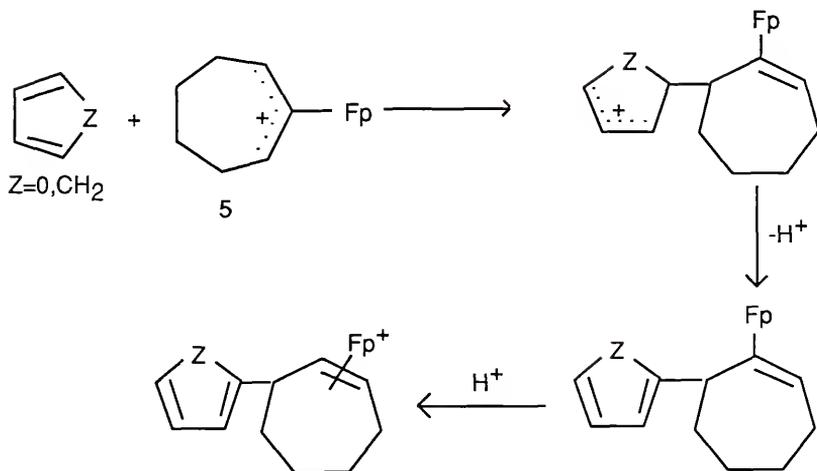
## Scheme III

Concerted addition

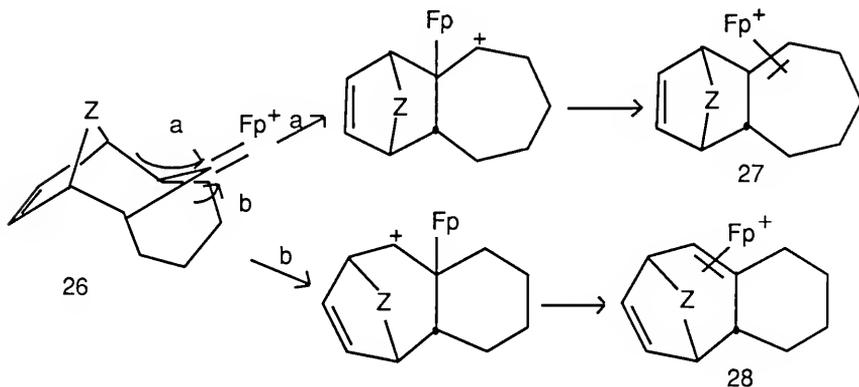


## Scheme IV

Stepwise addition



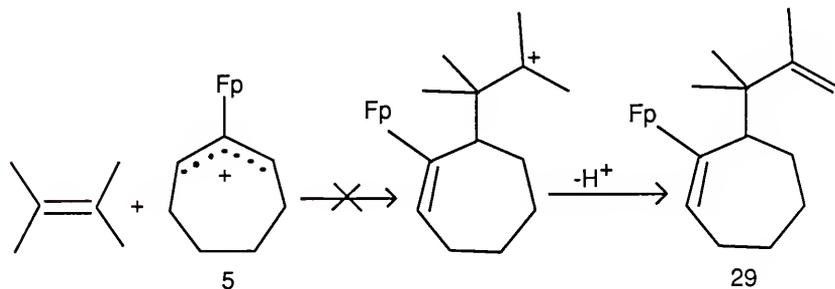
We do not expect to isolate the carbene adduct (26) from the concerted cycloaddition of the  $h^1$ -allyl Fp cation (5) with the 1,3-diene. A rapid 1,2-alkyl shift would probably occur to give the corresponding  $h^2$ -olefin Fp complexes, (27) and (28).



Such a 1,2-alkyl shift to a Fp-carbene carbon is well preceded in the literature.<sup>34</sup>

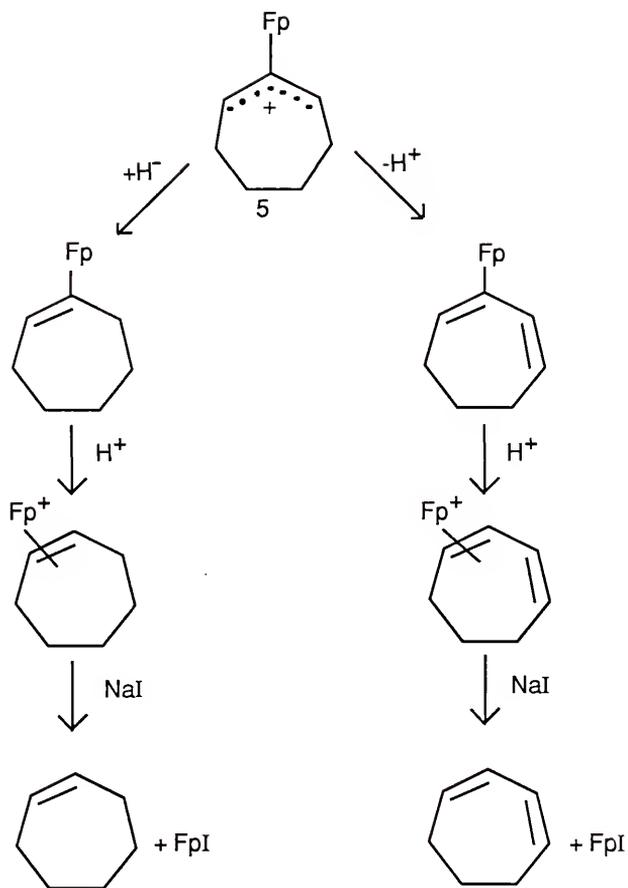
A methylene chloride solution of cyclopentadiene or furan and the  $h^2$ -1,2-cycloheptadiene Fp (4b) was stirred for a day. In no case was there any reaction and (4b) was recovered unchanged. However this does not mean that the allyl cation (5) is not accessible. The allyl cation (5) may have formed but did not react or the concentration of the allyl cation (5) may have been so small that the rate of reaction was negligible. In fact, the allyl cation (5) may possibly be a transition state and not an intermediate in the isomerization pathway.

A methylene chloride solution of tetramethylethylene was also treated with the  $h^2$ -1,2-cycloheptadiene Fp (4b) at room temperature hoping to obtain the  $h^2$ -olefin Fp complexes (29). Again (4) was recovered unchanged.



In a much earlier study, Manganiello<sup>14</sup> discovered that the thermal decomposition of a methylene chloride solution of the trifluoromethanesulfonate salt of  $h^2$ -1,2-cycloheptadiene Fp (4) followed by treatment of the solution with sodium iodide/acetone yielded 1,3-cycloheptadiene (40%) and a trace amount of cycloheptene. The mechanism in Scheme V was proposed to account for the decomposition reaction based on the products observed.

Scheme V



In this scheme, proton loss from the  $h^1$ -allyl Fp cation (5) is responsible for the formation of the 1,3-cycloheptadiene, whereas a hydride abstraction gives the cycloheptene. It was argued that if a hydride source were available to the allyl cation (5) then the amount of the cycloheptene formed relative to 1,3-cycloheptadiene would increase. Indeed, when triphenylmethane (a hydride source) was added to a methylene chloride solution of the  $h^2$ -1,2-cycloheptadiene Fp (4a), cycloheptene was isolated in amounts up to 3/5 of that of 1,3-cycloheptadiene after workup.

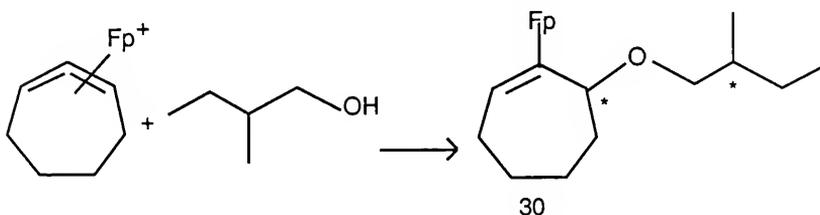
The above experiment was repeated using the tetrafluoroborate salt of the  $h^2$ -1,2-cycloheptadiene Fp (4). Neither cycloheptene nor 1,3-cycloheptadiene were observed but the  $h^2$ -1,2-cycloheptadiene Fp (4b) was reisolated unchanged. There was no reaction between (4b) and triphenylmethane. This cast doubts on the previously proposed mechanism involving the intermediacy of the allyl cation (5).

In principle, clear evidence for the accessibility of the allyl cation (5) may be obtained by using an optically active cyclic allene as the ligand. As can be seen from Scheme I, if the allyl cation (5) is accessible, whether as an intermediate or a transition state, an optically active complex must racemize. One approach to the synthesis of an optically active  $h^2$ -1,2-cycloheptadiene Fp (4) is to displace isobutylene from  $h^2$ -isobutylene Fp with an optically active 1,2-cycloheptadiene in much the same way as was used

in the preparation of optically active  $h^2$ -1,2-cyclononadiene Fp (8). Unfortunately, unlike 1,2-cyclononadiene, 1,2-cycloheptadiene dimerizes too rapidly to displace the isobutylene.

Alternative methods were therefore sought. In the first approach, racemic  $h^2$ -1,2-cycloheptadiene Fp (11) could be treated with less than an equivalent of an optically active alcohol in order to selectively remove one the allene enantiomers. This procedure would only be effective if the racemization of (4) via the allyl cation (5) did not occur or occurred at a very slow rate under the conditions for enantiomeric enrichment.

2-Methylbutanol was tried first. When the racemic alcohol was allowed to react with a suspension of  $h^2$ -1,2-cycloheptadiene Fp (4) in diethyl ether, it gave the ether adduct (30).

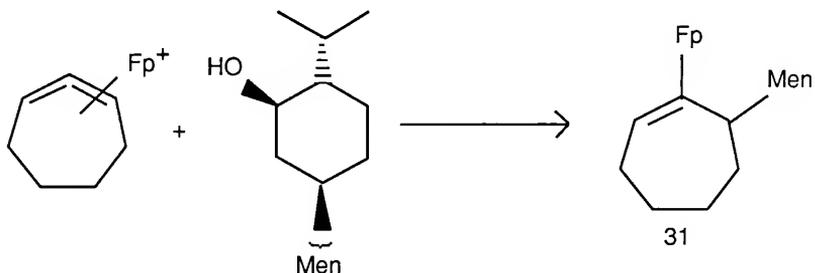


Interestingly, although the ether adduct (30) has two chiral centers as marked, and therefore should exist as a pair of diastereomers, only one set of signals was observed in its  $^1\text{H}$  NMR (we have insufficient material for a  $^{13}\text{C}$  NMR spectrum). It is quite unfortunate that the diastereomers

have coincidental chemical shifts. One would expect that the reaction between an optically active alcohol with a racemic  $h^2$ -1,2-cycloheptadiene Fp (4) should give unequal amounts of the diastereomeric ether adduct (30) provided the reaction is incomplete. If the chemical shifts of the diastereomeric ether adduct (30) were non-coincidental, NMR measurement of the diastereomeric composition of the ether adduct (30) would enable us to draw a conclusion as to the enantiomeric purity of the  $h^2$ -1,2-cycloheptadiene Fp (4) left behind.

Half an equivalent of the (S)-(-)-2-methylbutanol was allowed to react with the racemic  $h^2$ -1,2-cycloheptadiene Fp (4b). The unreacted (4b) recovered, which amounted to a half of the starting material, showed no detectable optical rotation.

The chiral carbon on (S)-(-)-2-Methylbutanol is one carbon away from the alcohol group and may be too far removed for it to effectively induce asymmetry. We decided to try (-)-menthol instead. Under the same conditions, (-)-menthol did not give the ether adduct but a mixture of unidentifiable products and menthol.

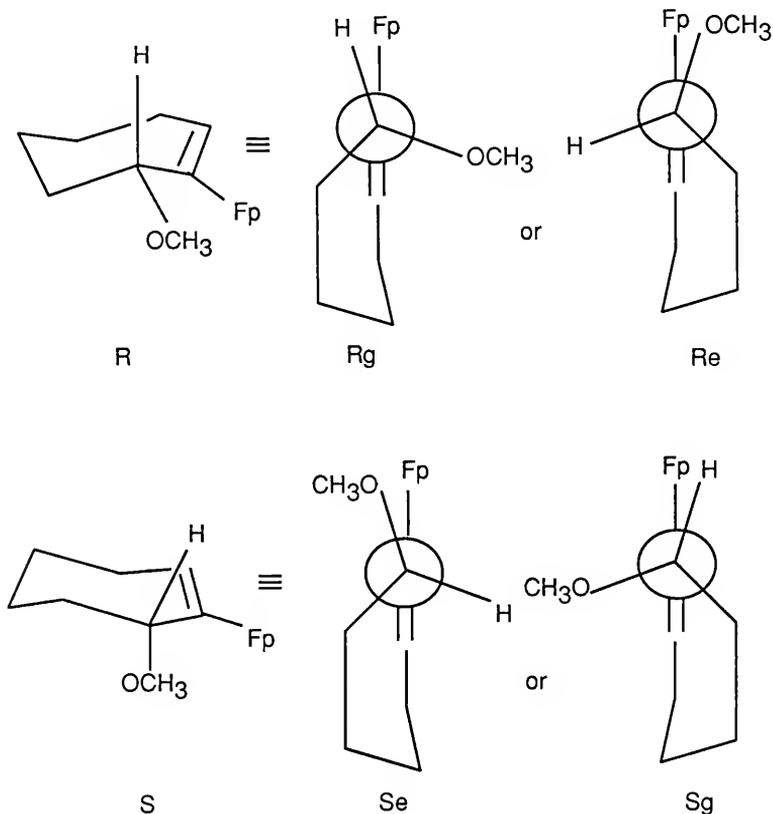


Less than half of the starting  $h^2$ -1,2-cycloheptadiene Fp (4b) was recovered. A solution of the recovered  $h^2$ -1,2-cycloheptadiene Fp (4b) showed no detectable optical rotation. A reaction between  $h^2$ -1,2-cycloheptadiene Fp (4b) and potassium (-)-mentoxide in THF at 0°C resulted in total decomposition of the allene (4b).

Zero optical rotation of the recovered  $h^2$ -1,2-cycloheptadiene Fp (4b) from the above reactions is consistent with an allene to allyl cation isomerization, Scheme I. However, absence of rotation can also be due to other reasons. First, enantiomeric enrichment by (S)-(-)-2-methylbutanol and (-)-menthol might not be successful. Even if the enantiomeric enrichment were successful, the recovered  $h^2$ -1,2-cycloheptadiene Fp (4b) might have such low inherent optical rotation that it could not be measured with certainty. Unfortunately, it is not possible to increase the concentration of the solution of  $h^2$ -1,2-cycloheptadiene Fp (4b) in order to get a measurable optical rotation because the solution which is highly colored absorbs so much light that rotation measurements become quite impossible.

In the second approach, we attempted to synthesize the optically active  $h^2$ -1,2-cycloheptadiene Fp (4) directly via methoxy abstraction with trimethylsilyl trifluoromethanesulfonate starting from an optically active  $h^1$ -(7-methoxy)-cyclohepten-1-yl Fp.

Let us first consider the conformation of the R and S enantiomers of the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp as obtained from CPK space filling models.

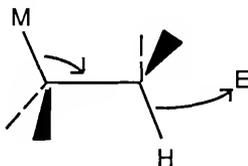


Of the two conformers available to the  $h^1$ -((R)-7-methoxy)-cycloheptadien-1-yl Fp (R) we would expect the gauche conformer (Rg) to be the preferred conformer. Here, the

larger methoxy groups is away from the bulky Fp. Similarly, we expect the (Sg) to be the preferred conformer for the  $h^2$ -((S)-7-methoxy)cyclohepten-1-yl Fp (S).

We shall limit our discussion on methoxy abstraction to one enantiomer,  $h^1$ -((R)-7-methoxy)cyclohepten-1-yl Fp (R).

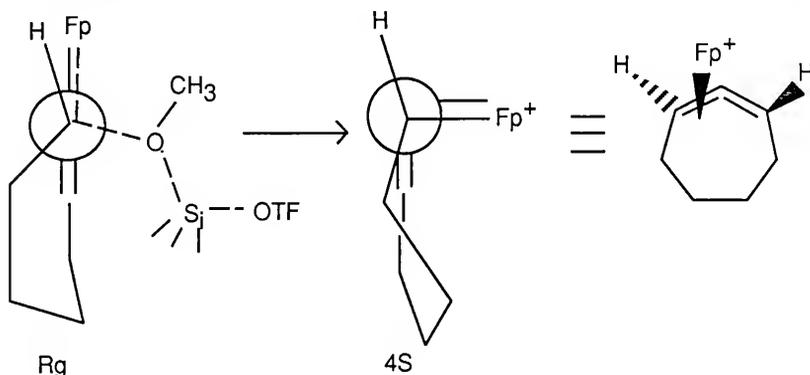
Cationic  $h^2$ -olefin Fp complexes are typically made by a  $\beta$ -hydride abstraction from the  $h^1$ -alkyl Fp.<sup>35</sup> Such  $\beta$ -hydride abstractions are conformationally dependant and widely accepted to proceed via an antiperiplanar transition state with the Fp assisting from the anti face in concert with the hydride loss.



Methoxy abstraction, like hydride abstraction, is also believed to proceed with anti Fp assistance leading to the  $h^2$ -olefin Fp complex. A concerted methoxy abstraction with anti Fp assistance will give an optically active  $h^2$ -olefin Fp complex from an optically active  $h^1$ -alkyl Fp. When the methoxy group is part of a ring as in the case with  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp, it is prevented by the ring from adopting a conformation where it is anti to the Fp. An anti alignment of the Fp with the methoxy group would necessarily force the methoxy group inside the cycloheptene ring, a conformation which is impossibly strained.

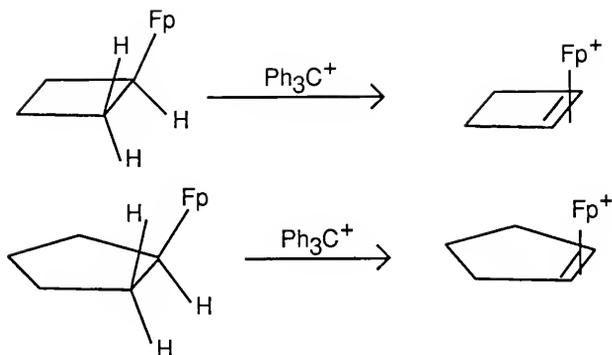
Since a concerted anti methoxy abstraction is unlikely, a concerted syn methoxy abstraction with the Fp moving over to the same face as the leaving methoxy group will also give an optically active  $h^2$ -olefin Fp complex from an optically active  $h^1$ -alkyl Fp. Thus by a concerted mechanism with syn Fp assistance\*, the  $h^1$ -((R)-7-methoxy)cyclohepten-1-yl Fp (R) should give only the  $h^2$ -((S)-1,2-cycloheptadiene Fp (4S), Scheme VI.

Scheme VI



Although syn Fp assisted  $\beta$ -hydride and  $\beta$ -methoxy abstractions have not been substantiated, there are examples where an  $h^2$ -olefin Fp complex is formed by an apparent syn Fp assistance.<sup>36</sup>

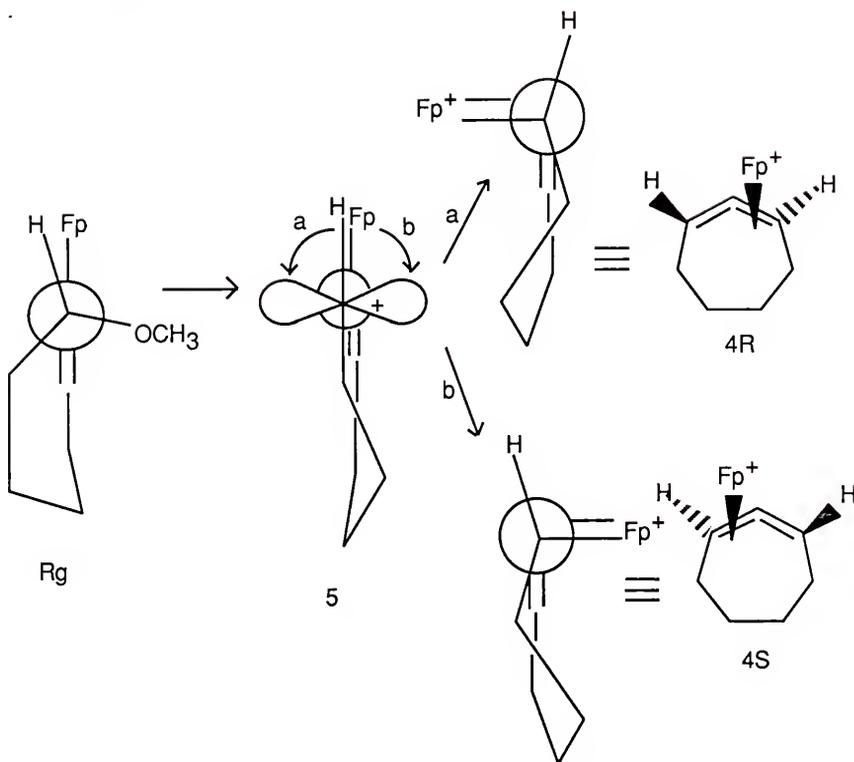
\*The discussion is still valid should for any reason methoxy abstraction involve anti Fp assistance; thus R would give 4R.



There are no hydrogens anti to the Fp in  $h^1$ -cyclobutyl and  $h^1$ -cyclopentyl Fp, and yet they undergo hydride abstraction to give their respective  $h^2$ -cycloalkene Fp complexes. It is not known whether hydride abstraction occurs via a distorted transition state, a  $\beta$ -carbonium cation or by some other mechanism.

If Fp migration is not concerted with methoxy abstraction, an allyl cation intermediate (5) would be formed and should give the racemic  $h^2$ -1,2-cycloheptadiene Fp (4), Scheme VII.

Scheme VII



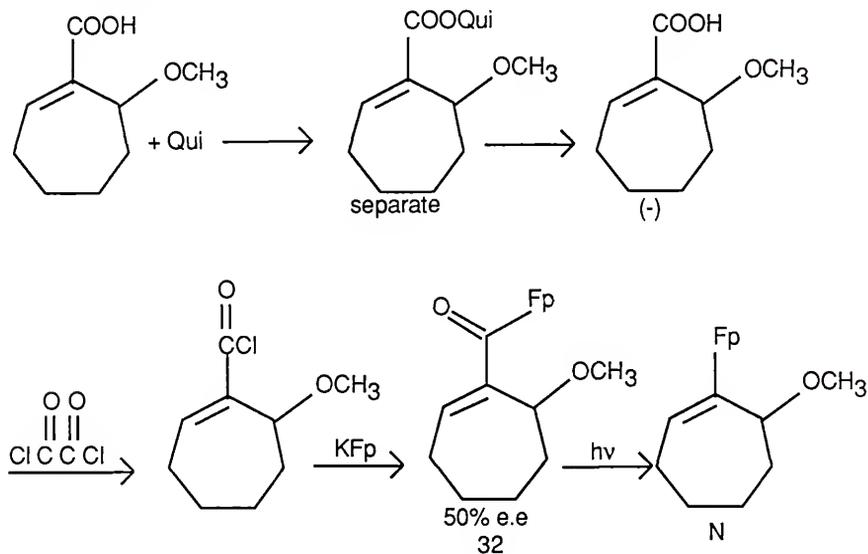
In this case, the  $h^1$ -((R)-7-methoxy)cyclohepten-1-yl Fp (R) would give both the (R)- and the (S)- $h^2$ -1,2-cycloheptadiene Fp, (4R) and (4S).

In short, it is possible to synthesize an optically active  $h^2$ -1,2-cycloheptadiene Fp (4) from syn Fp assisted methoxy abstraction of optically active  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp. An optically inactive  $h^2$ -1,2-cycloheptadiene Fp (4) from this reaction would necessarily mean that

methoxy abstraction proceeded via an allyl cation or that the barrier for isomerization between the allene (4) and the allyl cation (5) is very low.

Optically active  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp was prepared according to Scheme VIII.

Scheme VIII

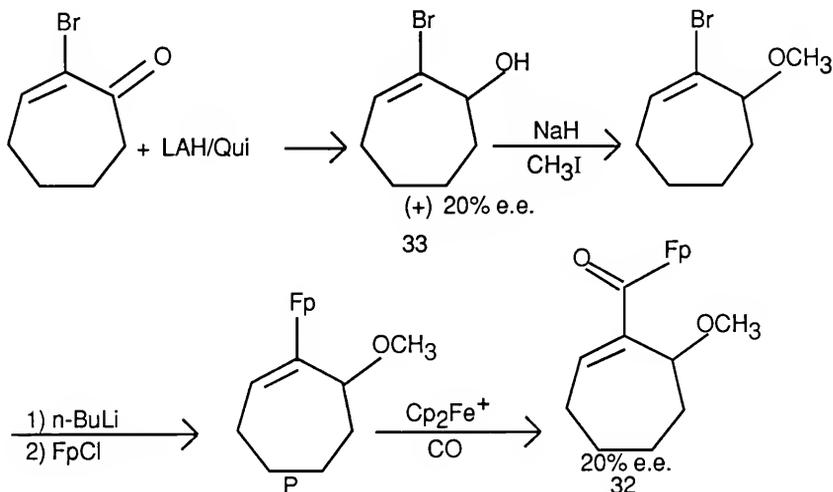


The racemic 7-methoxycycloheptenecarboxylic acid was resolved as its quinine salt via two recrystallizations from absolute ethanol. The acid was released from the quinine salt readily in aqueous acid and was found to have a negative optical rotation. The acid was subsequently converted to the acid chloride which was then reacted with potassium Fp to yield the  $h^1$ -carbonyl-(7-methoxy)cyclohepten-1-yl Fp (32). The  $^1\text{H}$  NMR of the cyclopentadienyl hydrogen

resonances are well separated in a 10 mole % chloroform- $d_1$  solution of  $\text{Eu}(\text{hfc})_3$  and have an integrated ratio of 25 to 75 which indicates a 50% excess of one enantiomer. Decarbonylation under photolytic conditions yielded  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp (N). We presumed that the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp (N) is optically active with the same optical purity as the  $h^1$ -carbonyl-(7-methoxy)cyclohepten-1-yl Fp (32).  $\text{Eu}(\text{hfc})_3$  does not separate the cyclopentadienyl and methoxy resonances of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp (N) and a direct measurement is not possible. It is also very difficult to obtain optical rotations on these Fp complexes because their solutions are highly colored.

A mixture weighted with the other enantiomer was prepared according to Scheme IX.

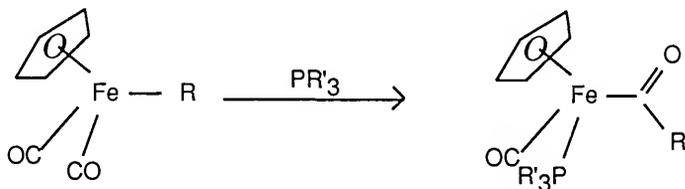
Scheme IX



The 2-bromo-2-cycloheptenone was reduced to its alcohol (33) with a preformed LAH/quinine mixture. The alcohol (33) has a positive optical rotation and was obtained with a 20% enantiomeric excess as determined by  $\text{Eu}(\text{hfc})_3$ . Treating this mixture of alcohols (+33) with sodium hydride followed by methyl iodide gave the 1-bromo-7-methoxycycloheptene. The  $\text{h}^1$ -(7-methoxy)cyclohepten-1-yl Fp was obtained by the well established route. As mentioned above, the  $\text{h}^1$ -(7-methoxy)cycloheptadien-1-yl Fp does not form a complex with  $\text{Eu}(\text{hfc})_3$  and must be converted to its  $\text{h}^1$ -carbonyl-(7-methoxy)cyclohepten-1-yl Fp (32) in order to determine its enantiomeric purity. The  $\text{h}^1$ -carbonyl-(7-methoxy)cyclohepten-1-yl Fp (32) was prepared by stirring a methylene chloride solution of  $\text{h}^1$ -(7-methoxy)cyclohepten-1-yl Fp in 10 mole % of ferrocenium tetrafluoroborate under 55 psi of CO gas. The reaction was complete within an hour giving a quantitative yield of the desired Fp-acyl complex (32). The  $\text{h}^1$ -carbonyl-(7-methoxy)cyclohepten-1-yl Fp (32), in a 10 mole % chloroform- $\text{d}_1$  solution of  $\text{Eu}(\text{hfc})_3$  has a cyclopentadienyl hydrogen integrated ratio of 60 to 40 giving us a 20% excess of the other enantiomer. We shall call this mixture (P). It was comforting to know that this 20% enantiomeric excess was carried forward from the (+)-alcohol (33). We infer from this information that the  $\text{h}^1$ -(7-methoxy)cyclohepten-1-yl Fp (P) made was optically active (20% e.e.) and with an optical rotation opposite to that prepared by Scheme VIII.

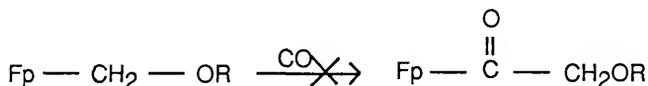
The carbonylation of the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp to  $h^1$ -carbonyl-(7-methoxy)cyclohepten-1-yl Fp (32) is of particular importance here. As far as we know, this is the first case of an unassisted CO insertion into a  $h^1$ -vinyl Fp bond to give a  $h^1$ -acyl Fp complex.

All CO insertions into  $h^1$ -alkyl Fp or  $h^1$ -vinyl Fp complexes are assisted by phosphines under thermal conditions to give the corresponding  $h^1$ -acyl (Cp)Fe(CO)(PPh<sub>3</sub>) complexes.<sup>37</sup>



R  $\equiv$  allyl, vinyl

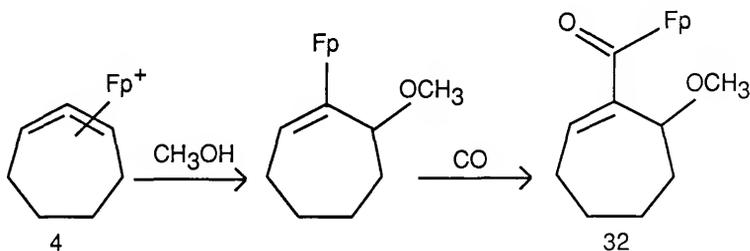
CO insertions catalyzed by oxidants, eg. Ce(IV), Ag(I), Cp<sub>2</sub>Fe<sup>+</sup>, or Lewis acids have only been reported for  $h^1$ -alkyl (Cp)Fe(CO)(L) where L = PPh<sub>3</sub> and P(OPh)<sub>3</sub> and  $h^1$ -vinyl (Cp)Fe(CO)(P(OPh)<sub>3</sub>) complexes;<sup>38</sup> the former complexes carbonylate faster than the latter. To date, CO insertions into  $h^1$ -(alkoxy)methylene Fp to give the corresponding acyls have not been successful.<sup>39</sup>



We have also attempted without success to carbonylate the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp with boron trifluoride etherate under 1 atm. of CO.

The optically active  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp (N) and (P) were treated with trimethylsilyl trifluoromethanesulfonate to yield the  $h^2$ -1,2-cycloheptadiene Fp (4a). A dilute solution of the  $h^2$ -1,2-cycloheptadiene Fp (4a) has a negligible optical rotation. When the concentration of (4a) was increased, the solution became strongly colored and made optical measurement impossible.

Since rotational measurements were experimentally impossible, we decided that an alternative solution would be to convert the  $h^2$ -1,2-cycloheptadiene Fp (4a) to its methyl ether adduct and carbonylate the ether adduct to the  $h^1$ -carbonyl-(7-methoxy)cyclohepten-1-yl Fp (32).

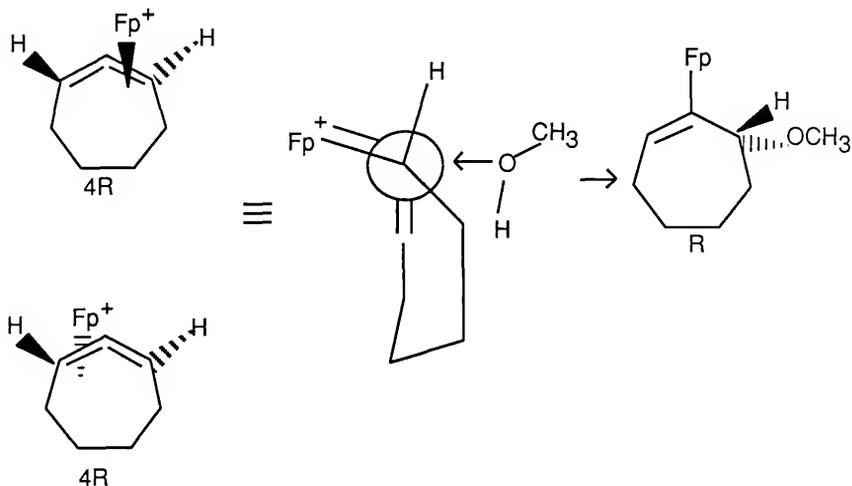


The enantiomeric composition of the  $h^1$ carbonyl-(7-methoxy)cyclohepten-1-yl Fp (32) can then be determined by  $^1\text{H}$  NMR with  $\text{Eu}(\text{hfc})_3$  and this will give us a clue as to the enantiomeric composition of the  $h^2$ -1,2-cycloheptadiene Fp (4).

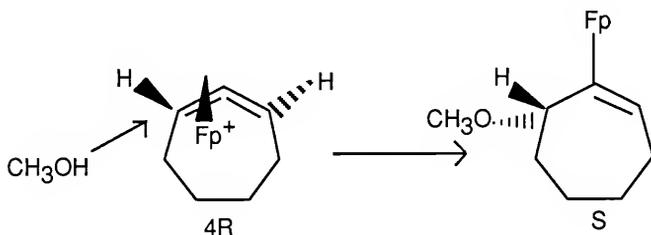
To simplify the discussion, let us assume that the fluxional process proceeds only via the 1,2-Fp shift, Scheme II, and that the addition of methanol is stereospecific.

Anti attack of a nucleophile at a  $h^2$ -olefin Fp bond is well documented in the literature.<sup>40</sup> Anti attack of a methanol onto the  $h^2$ -(R)-1,2-cycloheptadiene Fp (4R) regardless of which double bond the Fp is bonded to should give the same  $h^1$ -(R)-7-methoxycyclohepten-1-yl Fp (R), Scheme X.

Scheme X



The above statement is true because only two of the four sides of the allene double bonds are available for complexation with the Fp. If the Fp were bonded to the other two sides of the allene double bond, an impossible geometry which puts the Fp inside the ring (see 4R below), the allene (4R) would add methanol in an anti fashion to give the (S) methyl ether adduct.



It should be noted that the anti face of the  $h^2$ -(R)-1,2-cycloheptadiene Fp (4R), where the methanol comes in, is only partially shrouded by the allene ring. A syn attack, however, would be hindered by the bulky Fp group.

At first glance, eliminating the possibility of a syn attack by methanol would seem to violate the principle of microscopic reversibility;<sup>41</sup> especially when we suggest syn assistance as one of the ways methoxy abstraction can occur. Furthermore, by the principle, anti attack of methanol would necessarily require the 7-membered ring to adopt an impossible conformation of putting the methanol inside the ring. We must keep in mind that neither the methoxy abstraction nor the methanol addition reactions are reversible and that the methoxy group is leaving the

$h^1$ -(7-methoxy)cyclohepten-1-yl Fp as a methyltrimethylsilyl ether and not as a methanol. Thus, methoxy abstraction and addition is not bound by microscopic reversibility. Regardless of the pathway methoxy abstraction follows (syn or anti), we should be able to arrive at the enantiomeric composition of the  $h^2$ -1,2-cycloheptadiene Fp (4) from the enantiomeric composition of the  $h^1$ -carbonyl-(7-methoxy)-cyclohepten-1-yl Fp (32) provided methanol addition is stereospecific.

The  $h^2$ -1,2-cycloheptadiene Fp (4a), from the reaction of the optically active  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp (N) with trimethylsilyl trifluoromethanesulfonate, was reacted with methanol and then carbonylated to give the  $h^1$ -carbonyl-(7-methoxy)cyclohepten-1-yl Fp (32). The integrated cyclopentadienyl hydrogen intensities of  $h^1$ -carbonyl-(7-methoxy)cyclohepten-1-yl Fp (32) in a chloroform- $d_1$  solution containing  $Eu(hfc)_3$  were equal, Fig. 4 and 5. At some point complete racemization had occurred. The optically active  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp (P) was put through the same series of reactions with the same results, Fig. 6 and 7. Again complete racemization had occurred.

Based upon the experimental results it appeared that an allyl cation (5) had been formed at some point in the sequence of reactions. One possibility is the concerted formation of the optically active  $h^2$ -1,2-cycloheptadiene Fp (4) which then racemizes via the allyl cation (5). An

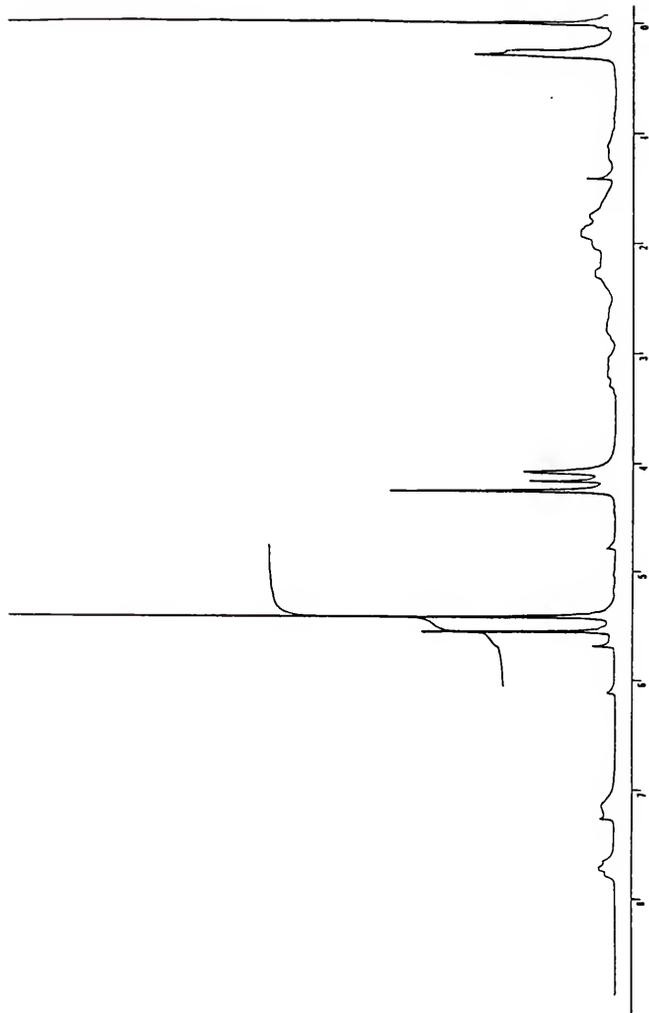


Fig. 4. A  $\text{CDCl}_3$  solution of 10 mole %  $\text{Eu}(\text{hfc})_3$  and (32) from (N) showing a 25:75 diastereomeric composition.

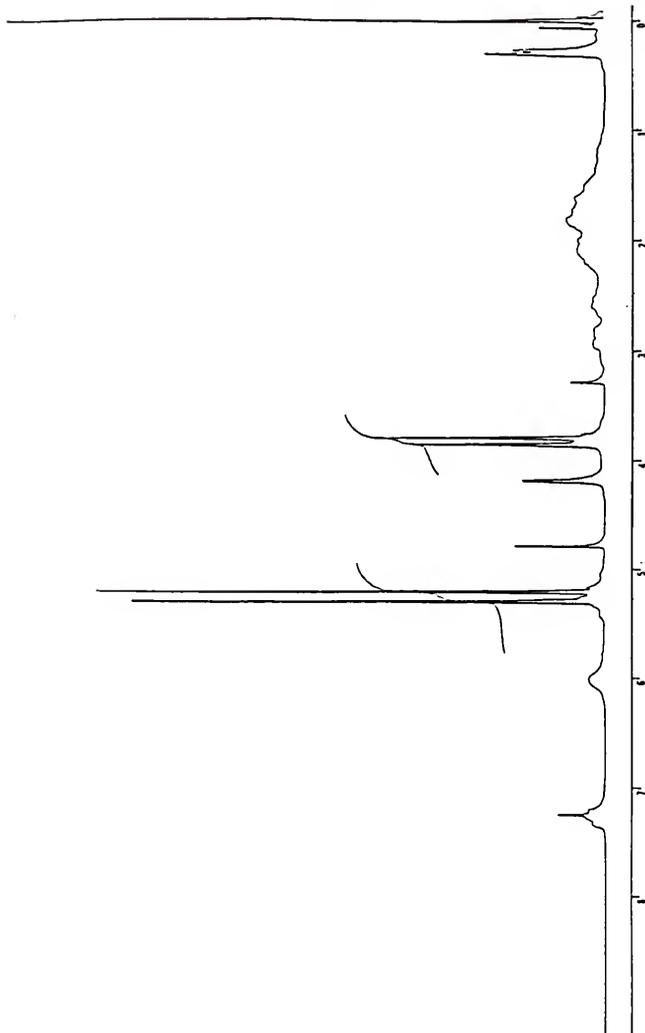


Fig. 5. A  $\text{CDCl}_3$  solution of 10 mole %  $\text{Eu}(\text{hfc})_3$  and (32) from methoxy abstraction and addition of (N) showing a 50:50 diastereomeric composition.

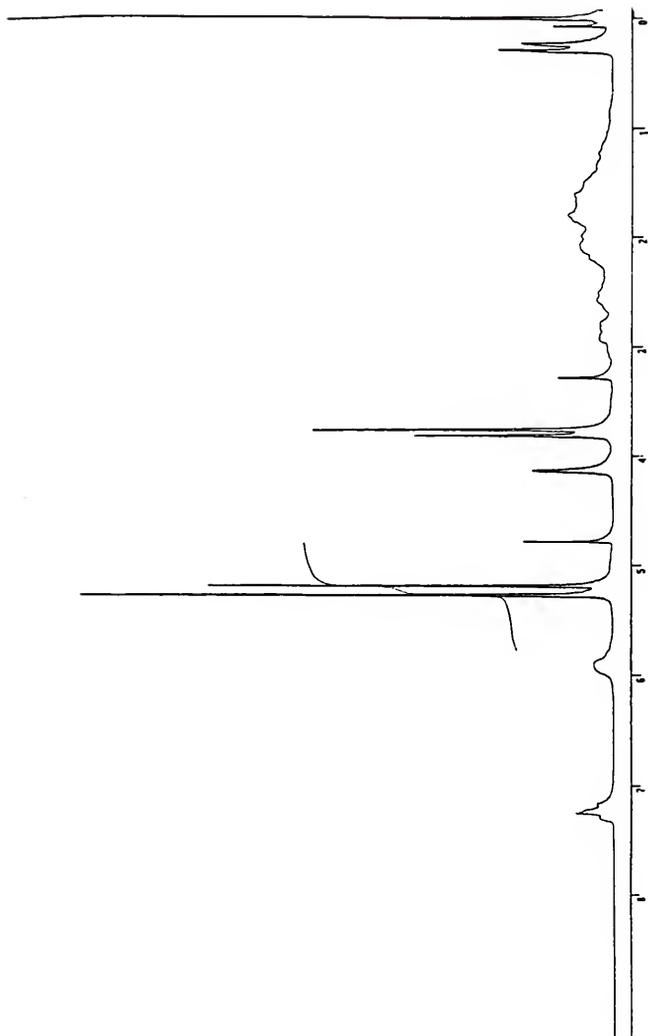


Fig. 6. A  $\text{CDCl}_3$  solution of 10 mole %  $\text{Eu}(\text{hfc})_3$  and (32) from (P) showing a 60:40 diastereomeric composition.



Fig. 7. A  $\text{CDCl}_3$  solution of 10 mole %  $\text{Eu}(\text{hfc})_3$  and (32) from methoxy abstraction and addition of (P) showing a 50:50 diastereomeric composition.

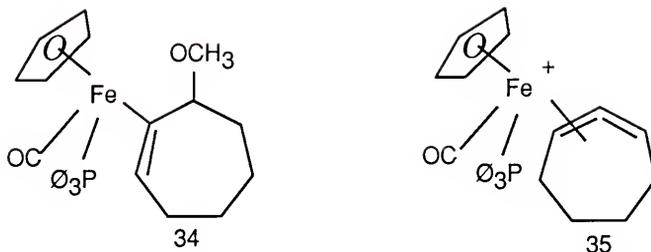
alternative is allyl cation formation as methoxy is abstracted followed by collapse to the  $h^2$ -1,2-cycloheptadiene Fp (4). In either case we would have to invoke an allyl cation intermediate (5).

### CHAPTER III

#### CARBONYL ( $h^5$ -CYCLOPENTADIENYL) TRIPHENYLPHOSPHINEIRON (II) COMPLEXED 1,2-CYCLOHEPTADIENE

Methoxy abstraction from optically active  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp led to the racemic  $h^2$ -1,2-cycloheptadiene Fp (4). Two mechanistic pathways were considered; one involving a concerted stereospecific methoxy abstraction to the optically active  $h^2$ -1,2-cycloheptadiene Fp (4) followed by racemization via the achiral allyl cation intermediate (5) and the other involving the achiral allyl cation intermediate (5) from methoxy abstraction and prior to complexation by the Fp.

In order to complete the stereochemical picture and to shed light on the methoxy abstraction and the racemization process, we shall turn our attention to the  $h^1$ - and  $h^2$ - carbonyl( $h^5$ -cyclopentadienyl)triphenylphosphineiron(II) [Fpp] complexes of 7-methoxycycloheptadien-1-yl (34) and 1,2-cycloheptadiene (35), respectively.



There are quite a few advantages to moving from the Fp system to the Fpp system. The most obvious is that the triphenylphosphine ligand generally imparts additional stability to these type of complexes against exposure to air and therefore makes them easier to manipulate.

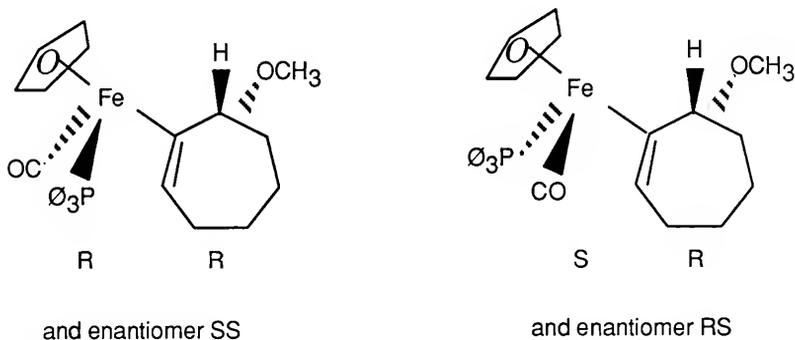
More important to us is that the triphenylphosphine ligand introduces another chiral center, at the iron, in both the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) and the  $h^2$ -1,2-cycloheptadiene Fpp (35) complexes. The consequence of this is that both complexes exist as enantiomeric pairs of diastereomers. Diastereomers, unlike enantiomers, can often be separated by physical methods and their diastereomeric compositions determined directly by NMR spectroscopic measurements.

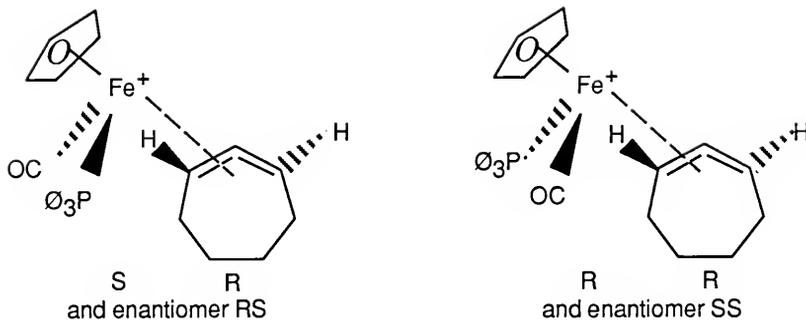
Phosphinylation therefore provides us a means to separate  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) into its diastereomers. We felt that examination of the diastereomeric composition of  $h^2$ -1,2-cycloheptadiene Fpp (35) formed from different diastereomers of  $h^1$ -(7-methoxy)cycloheptene-1-yl Fpp (34) should enable us to elucidate the pathway by

which methoxy abstraction occurs. Also, if  $h^2$ -1,2-cycloheptadiene Fpp (35) can be separated into its diastereomers, we can follow directly by NMR the allene to allyl cation isomerization because such isomerization necessarily converts one diastereomer to a mixture of both diastereomers.

Lastly, since we were unable to grow crystals of the  $h^2$ -1,2-cycloheptadiene Fp (4) suitable for X-ray studies, we would like to try to grow crystals of its Fpp analogue.

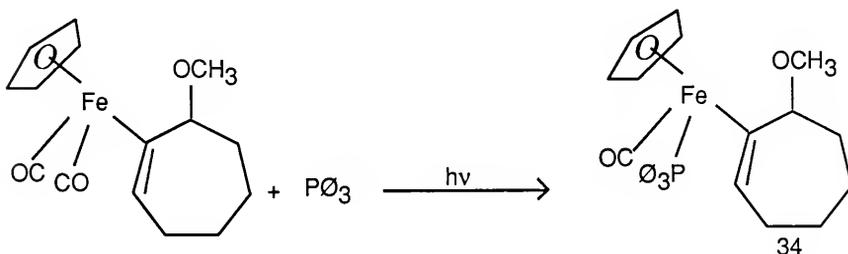
Before we proceed any further, the iron center of the Fpp can be designated as either R or S according to the Cahn-Ingold-Prelog (CIP) system adapted to organotransition metal complexes.<sup>42</sup> The configurations of the isomers of  $h^1$ -(7-methoxy)cycloheptadien-1-yl Fpp (34) and  $h^2$ -1,2-cycloheptadiene Fpp (35) according to the modified CIP system are shown below.





\* note that the iron center with the R configuration in  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) and  $h^2$ -1,2-cycloheptadiene Fpp (35) have opposite absolute configuration.

$h^2$ -(7-Methoxy)cyclohepten-1-yl Fpp (34) was synthesized by photolyzing a mixture of the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp with excess triphenylphosphine in an equal mixture of n-pentane and benzene.



Photolysis was conducted in a quartz photochemical reactor at room temperature under a stream of  $N_2$  to remove the CO gas evolved. The reaction proceeded rapidly and was complete within 20 mins without forming the bistrisphenylphosphine adduct.  $h^1$ -(7-Methoxy)cycloheptadien-1-yl Fpp (34) was purified via column chromatography and was obtained as an air stable red paste. Residual triphenylphosphine may

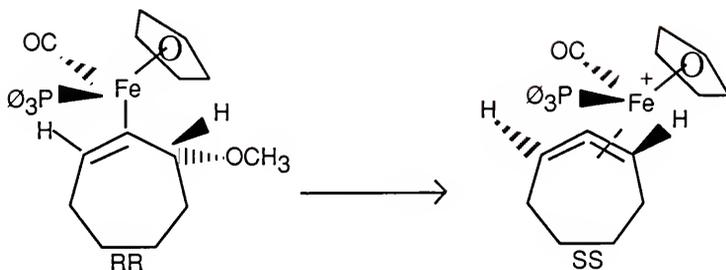
be removed by filtration as its insoluble methyltriphenylphosphonium iodide salt after warming a n-pentane solution of the crude  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) with methyl iodide.

The  $^1H$  NMR for  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) showed two sets of resonances, one for each diastereomer. The hydrogen resonances for the methoxy hydrogens and the ring hydrogens on carbons 2 and 7 are well separated. The cyclopentadienyl hydrogen resonances are barely separated from each other at 100 MHz and each is coupled to the phosphorus.

Let us now consider first the methoxy abstraction of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) within the context of a concerted stereospecific Fpp assisted pathway.

Following the same lines of analysis as the Fp analogue, let us assume that the ring conformation necessary to place the methoxy group anti to the Fpp cannot be achieved and that any concerted stereospecific pathway for methoxy abstraction must necessarily proceed with syn Fpp assistance. Therefore, concerted stereospecific methoxy abstraction of a single diastereomer of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) should lead to a single diastereomer of  $h^2$ -1,2-cycloheptadiene Fpp (35), Scheme XI.

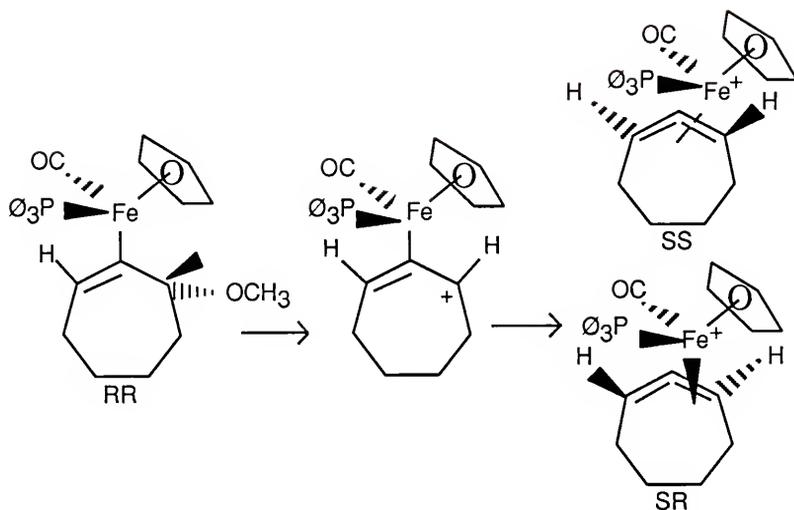
Scheme XI.



This argument still holds should for any reason methoxy abstraction proceed via anti Fpp assistance.

The other alternative is for methoxy abstraction to proceed via a free allyl cation. The Fpp then collapses onto the free allyl cation to give the  $h^2$ -1,2-cycloheptadiene Fpp (35). In this case, methoxy abstraction from one diastereomer of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) should lead to a mixture of diastereomers of  $h^2$ -1,2-cycloheptadiene Fpp (35), Scheme XII.

Scheme XII.



It is clear that in order to establish unequivocally the mechanism of methoxy abstraction, we need to separate  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) into its two diastereomers.

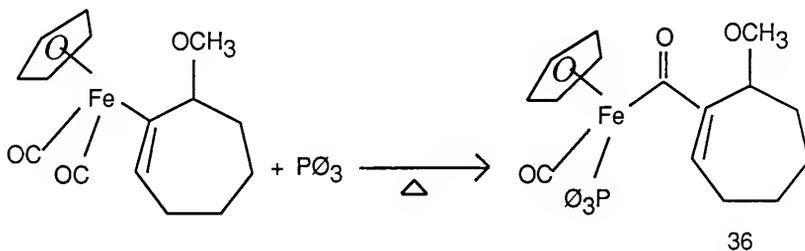
$h^1$ -(7-Methoxy)cyclohepten-1-yl Fpp is isolated as a red oil and its diastereomeric composition typically falls around 60:40.\* The diastereomeric composition was determined by  $^1H$  NMR integration of the methoxy hydrogen resonances because the cyclopentadienyl hydrogen resonances were not well resolved. We first attempted the separation by recrystallization at  $-35^\circ C$  from a variety of solvents; the

\* Diastereomeric composition will always be presented as such a : b where (a) corresponds to the composition of the low field cyclopentadienyl hydrogen resonance and (b) corresponds to the high field resonance.

solvents tried include pentane, hexane, hexane/benzene mixture and acetone/water mixture. In each case the diastereomeric composition of the crystals of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) remained unchanged. The diastereomers were also not separated by TLC.

An alternative approach to this problem was to synthesize the  $h^1$ -carbonyl-(7-methoxy)cyclohepten-1-yl Fpp (36), which also exists as enantiomeric pairs of diastereomers, separate this complex into its diastereomers and then convert them back to the corresponding  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34).

The  $h^1$ -(carbonyl-(7-methoxy)cyclohepten-1-yl Fpp (36) was readily synthesized by warming  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp (34) with triphenylphosphine in acetonitrile.



The acyl complex (36) is an air stable orange solid and is formed as a mixture of equal amounts of the two diastereomers. After numerous recrystallization attempts, we discovered that a 20:80 ratio of diastereomers of (36) could be obtained in one recrystallization from a 1:2 v/v mixture of ethyl acetate and n-pentane at +10°C with excellent recovery, Fig. 8. The mother liquor was concentrated to give the

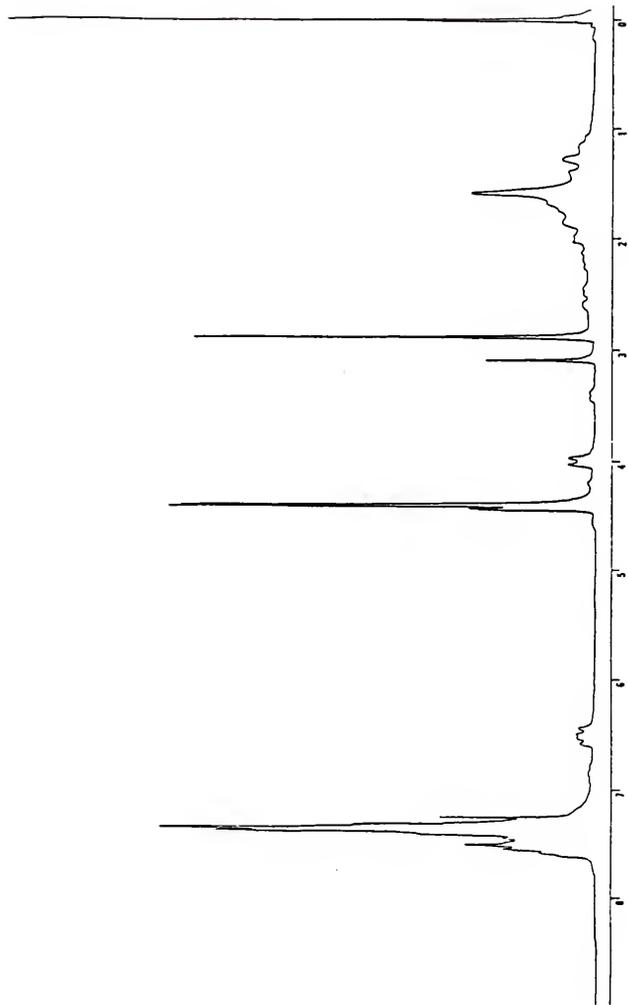


Fig. 8.  $^1\text{H}$  NMR of (36) in  $\text{CDCl}_3$  showing a 20:80 diastereomeric composition.

other diastereomer in a 65:35 ratio. A second recrystallization led to further enrichment giving a 10:90 ratio of diastereomers of (36).

Attempts to decarbonylate the  $h^1$ -carbonyl-(7-methoxycyclohepten-1-yl) Fpp by either of the standard photolytic or chemical methods were unsuccessful. Surprisingly, CO was not evolved when a benzene solution of the acyl complex (36) was photolyzed with a low pressure Hg lamp even though other phosphinylated iron acyl alkyl complexes have been reported not only to decarbonylate under photolytic conditions but also to retain high stereospecificity at the iron.<sup>43</sup> The acyl complex (36) was isolated with its diastereomeric composition unchanged. No reaction was observed when the acyl complex (36) was allowed to react with trimethylamine-N-oxide, chlorobis(triphenylphosphine)rhodium dimer or iodosobenzene. In all cases the acyl complex (36) was reisolated with its diastereomeric composition unchanged. One should note the tenacity of this acyl complex (36) against epimerization at the iron center. The acyl complex (36) gave predominantly decomposition products when refluxed in dioxane although a small amount of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp was formed presumably via phosphine dissociation followed by migration of the organic ligand onto the iron.

We finally succeeded in inducing decarbonylation in the acyl complex (36) by a combined photolysis and ultrasonication process. Unfortunately, the  $h^1$ -(7-methoxy)cyclo-

hepten-1-yl Fpp (34) isolated had epimerized to a 55:45 diastereomeric mixture.

It was later discovered that eluting  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) from a 8" x 1" alumina column (neutral, grade II) with a 1:1 v/v n-pentane/benzene as the eluant afforded an enriched diastereomeric mixture of the complex (34). The diastereomeric mixture of complexes (34) appeared on the column as a broad red band and was collected in two halves. Surprisingly, the first half and the second half of this red band both gave mixtures of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) enriched in the same diastereomer (75:25 and 85:15, respectively), Fig. 9. The alumina apparently did not separate the mixture of diastereomers but selectively decomposed one of them. Selective decomposition of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) with trimethylsilyl trifluoromethanesulfonate also afforded an enriched diastereomeric mixture of the complex but this time in a 10:90 ratio, Fig. 10. We shall postpone the discussion of the latter selective decomposition to an appropriate time.

We have also attempted to synthesize other phosphinylated  $h^1$ -(7-methoxy)cyclohepten-1-yl iron complexes but without much success. The respective phosphinylated complexes were not isolated when  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp was photolyzed in the presence of either trimethylphosphine or triphenylphosphite. When a cold (-78°C) solution of 1-lithio-7-methoxycycloheptene was treated with carbonyl( $h^5$ -cyclopentadienyl)tri-n-butylphosphineiron(II)

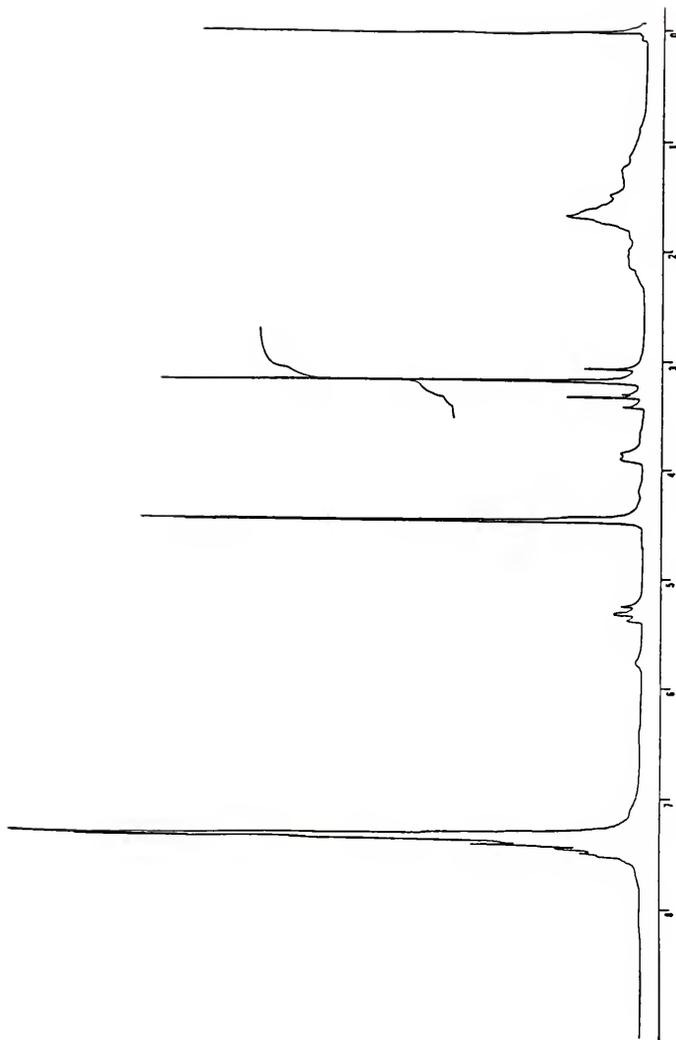


Fig. 9.  $^1\text{H}$  NMR of (34) in  $\text{CDCl}_3$  showing a 85:15 diastereomeric composition.

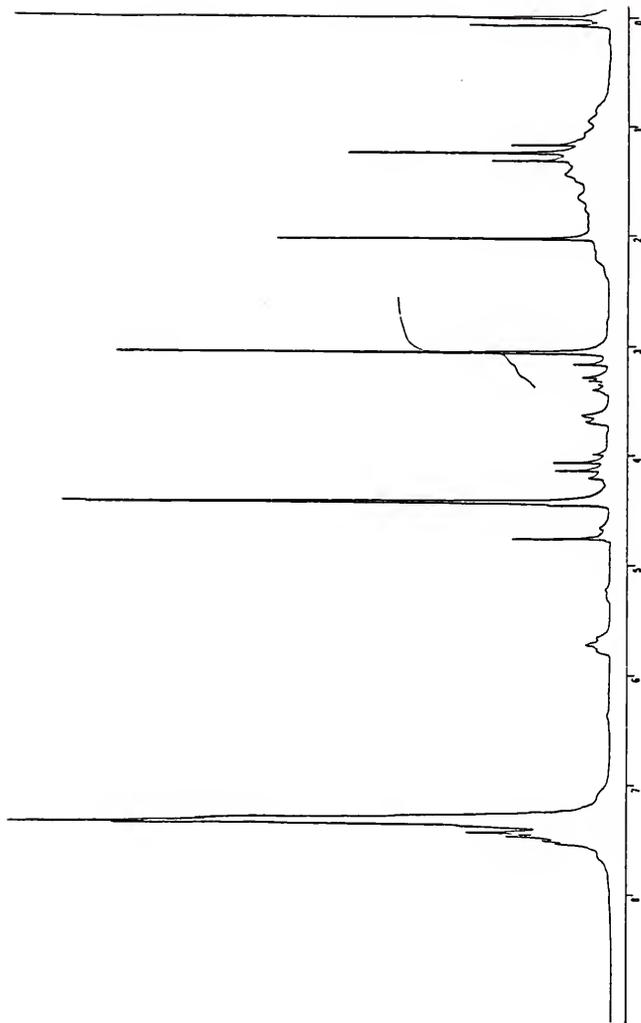
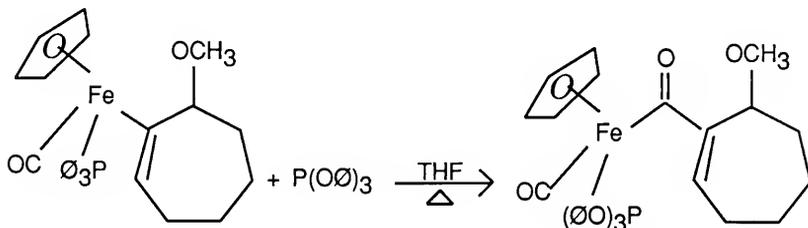


Fig. 10.  $^1\text{H}$  NMR of (34) in  $\text{CDCl}_3$  showing a 10:90 diastereomeric composition.

[Fpp<sub>bu</sub>] iodide, the major product isolated was unreacted Fpp<sub>bu</sub> iodide and a minor product perhaps resulting from the attack of the vinyl lithium reagent on the cyclopentadienyl ring.

Triphenylphosphite substituted h<sup>1</sup>-(7-methoxy)cyclohepten-1-yl iron complex was synthesized via a thermal exchange for triphenylphosphine in h<sup>1</sup>-(7-methoxy)cyclohepten-1-yl Fpp with an excess triphenylphosphite in refluxing THF.<sup>37a</sup>



The equilibrium of this reaction lies strongly to the right despite the stronger nucleophilicity of the triphenylphosphine and is attributed to a steric effect. The triphenylphosphine ligand being very bulky is unable to displace the triphenylphosphite ligand once the latter is coordinated at the iron. We could only isolate this triphenylphosphite iron complex as a crude mixture containing free triphenylphosphine and triphenylphosphite.

At this point, we have not succeeded in isolating h<sup>1</sup>-(7-methoxy)cyclohepten-1-yl Fpp (34) as a single

diastereomer but we have developed the methodology which enables us to separate  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) from a 60:40 diastereomeric mixture to a mixture with a diastereomeric ratio of 85:15 and 10:90.

Before we look at the methoxy abstraction process, it is imperative to examine the stereochemical integrity of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34). We discovered that  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) with diastereomeric compositions of 85:15 or 60:40 maintained their respective compositions indefinitely when frozen in the refrigerator. A chloroform- $d_1$  solution of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) with a 85:15 diastereomeric composition however epimerizes very slowly as measured by  $^1H$  NMR but only at elevated temperatures. The diastereomeric composition of a 60:40 mixture of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) remained unchanged by  $^1H$  NMR under the same conditions. Therefore, we feel it is safe to assume that  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) does not epimerize under the conditions for methoxy abstraction, i.e., short duration and low temperature.

We tried a number of methods to effect methoxy abstraction. Trimethyloxonium tetrafluoroborate was used first instead of the trimethylsilyl trifluoromethanesulfonate because we anticipated that the trifluoromethanesulfonate anion might affect the  $h^2$ -1,2-cycloheptadiene Fpp (35) in an adverse manner similar to what was observed with the

$h^2$ -1,2-cycloheptadiene Fp (4). Treating  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) with trimethyloxonium tetrafluoroborate in methylene chloride at  $-10^\circ\text{C}$  for 7 hrs gave an impure green substance after the reaction mixture was quenched with diethyl ether.

Discouraged by the ineffectiveness of trimethyloxonium tetrafluoroborate as a methoxy abstracting reagent, we went back to trimethylsilyl trifluoromethanesulfonate. The reaction did not fair any better and a black intractable paste was obtained. The same reaction in pentane at  $0^\circ\text{C}$  gave a greenish yellow precipitate which dissolved when washed with diethyl ether. If the reaction in pentane was quenched with diethyl ether, again a black pasty residue was formed. We discovered, quite by accident, that if this black paste is dissolved in ethyl acetate, the trifluoromethanesulfonate salt of  $h^2$ -1,2-cycloheptadiene Fpp (35a) precipitates from the solution as a bright orange air stable solid. In fact, prior quenching with diethyl ether is unnecessary. Pentane was removed from the reaction mixture in vacuo to leave a dark greenish brown paste from which  $h^2$ -1,2-cycloheptadiene Fpp (35a) was precipitated with ethyl acetate in the open air. The reaction was also run in an equal mixture of n-pentane and benzene at  $0^\circ\text{C}$  with similar results; the solvent mixture was removed in vacuo to leave a residue from which  $h^2$ -1,2-cycloheptadiene Fpp (35) was precipitated with ethyl acetate.

The  $^1\text{H}$  NMR of the  $\text{h}^2\text{-1,2-cycloheptadiene Fpp}$  (35a) is consistent with a pair of diastereomers, Fig. 11. The two cyclopentadienyl hydrogen resonances, each coupled to the phosphorus, and three of the four allenic hydrogen resonances are well separated. One allenic hydrogen resonance is obscured by the ring methylene resonances and is confirmed by  $^2\text{H}$  NMR of the appropriately deuterated complex. The assigned structure was confirmed by X-ray (vide infra).

The trifluoromethanesulfonate anion was readily exchanged for the hexafluorophosphate anion by adding water to a methanol solution of the trifluoromethanesulfonate salt of the  $\text{h}^2\text{-1,2-cycloheptadiene Fpp}$  (35) containing an excess of ammonium hexafluorophosphate. This gave a yellow precipitate which was filtered to give the pure hexafluorophosphate salt (35b) in quantitative yield. The procedure was performed in open air which demonstrated the stability of  $\text{h}^2\text{-1,2-cycloheptadiene Fpp}$  (35). The  $\text{h}^2\text{-cycloheptadiene Fp}$  (4a,b) would have decomposed in the presence of air, methanol or moisture.

Unfortunately, treating carbonyl( $\text{h}^5\text{-cyclopentadienyl}$ ) ( $\text{h}^1\text{-}(7\text{-methoxy)cyclohepten-1-yl}$ ) triphenylphosphiteiron(II) with trimethylsilyl trifluoromethanesulfonate failed to give the  $\text{h}^2\text{-1,2-cycloheptadiene}$  complex. We believe that trimethylsilyl trifluoromethanesulfonate is incompatible with the triphenylphosphite ligand and results in complete decomposition of the iron complex.

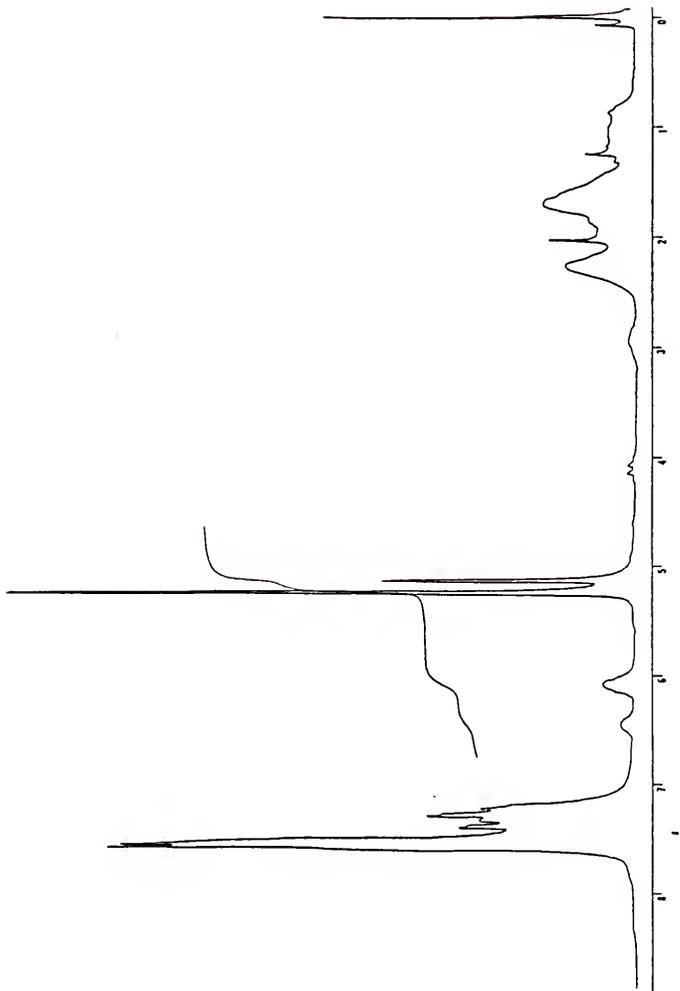


Fig. 11.  $^1\text{H}$  NMR of (35a) in  $\text{CDCl}_3$ .

We have thus developed the methodology to synthesize and purify both the trifluoromethanesulfonate and hexafluorophosphate salt of the  $h^2$ -1,2-cycloheptadiene Fpp (35). Both (35a) and (35b) are air stable and moderately stable in solution.

We are finally ready to look into the process of methoxy abstraction, paying particular attention to the  $h^2$ -1,2-cycloheptadiene Fpp (35) diastereomeric composition obtained starting with a majority of one of the diastereomers of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34).

Methoxy abstraction from a 60:40 mixture of  $h^1$ -(7-methoxy)cycloheptadien-1-yl Fpp (34) in a 1:1 v/v n-pentane/benzene solvent mixture at 0°C typically gives a 65:35 to 60:40 diastereomeric mixtures of  $h^2$ -1,2-cycloheptadiene Fpp (35) after precipitation from ethyl acetate. The diastereomeric composition was determined by  $^1H$  NMR based on the integrated cyclopentadienyl hydrogen resonances. Repeated precipitation from ethyl acetate does not change this diastereomeric composition.

The diastereomeric composition of  $h^2$ -1,2-cycloheptadiene Fpp (35) was found to be dependent upon the solvent in which methoxy abstraction was performed. When the reaction was repeated under identical conditions but in n-pentane, the crude product (35a) was found to have a diastereomeric composition of around 65:35. The  $^1H$  NMR of the crude product (35a) is broad and poorly resolved and one should consider the diastereomeric ratio of 65:35 a very

rough value. A single precipitation from ethyl acetate gave (35b) in a 80:20 diastereomeric composition. Just in case the discrepancy in the crude and pure diastereomeric compositions of  $h^2$ -1,2-cycloheptadiene Fpp (35a) was in some way caused by the precipitation process, the filtrate was collected and was examined for  $h^2$ -1,2-cycloheptadiene Fpp (35a). We were unable to detect by  $^1H$  NMR any trace of  $h^2$ -1,2-cycloheptadiene Fpp (35a). This 80:20 composition also remained invariant after repeated precipitations. Regardless of the solvent used, the  $h^2$ -1,2-cycloheptadiene Fpp was obtained at 45% to 55% yields.

Methoxy abstraction of a 80:20\* mixture of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) in the n-pentane/benzene solvent mixture at 0°C gives a 60:40 diastereomeric mixture of the  $h^2$ -1,2-cycloheptadiene Fpp (35a) after precipitation. The yields are slightly higher; over 55%.

The most interesting observation regarding methoxy abstraction is from a 60:40 mixture of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) with half an equivalent of trimethylsilyl trifluoromethanesulfonate at 0°C in n-pentane/benzene solvent mixture. We were able to isolate a 60:40 diastereomeric mixture of  $h^2$ -1,2-cycloheptadiene Fpp (35a) in over 90% yield (based on trimethylsilyl trifluoromethanesulfonate used). Recovered from the reaction mixture in

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\* The 85:15 mixture of (34) has epimerized to a 80:20 mixture.

almost a quantitative amount was  $h^1$ -(7-methoxy)cycloheptene-1-yl Fpp (34) with a 10:90 diastereomeric ratio! Note that the major diastereomer now is the one with a cyclopentadienyl hydrogen resonance at a higher field.

Methoxy abstraction of the 10:90 mixture of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp with trimethylsilyl trifluoromethanesulfonate at 0°C in the n-pentane/benzene solvent gave  $h^2$ -1,2-cycloheptadiene Fpp (35a) in less than a 10% yield but with a 80:20 diastereomeric ratio!

The results of the methoxy abstractions were summarized in Table 2.

Ethoxy abstraction from  $h^1$ -(7-ethoxy)cyclohepten-1-yl Fpp by trimethylsilyl trifluoromethanesulfonate under the conditions developed for methoxy abstraction also gave  $h^2$ -1,2-cycloheptadiene Fpp (35a). The results of ethoxy abstraction from enriched diastereomeric mixtures of  $h^1$ -(7-ethoxy)cycloheptene-1-yl Fpp parallel that of its methoxy analogue in terms of diastereomeric compositions and percent yields of  $h^2$ -1,2-cycloheptadiene Fpp (35a).

We have a few reasons to believe that the diastereomeric composition of  $h^2$ -1,2-cycloheptadiene Fpp (35a) from methoxy abstraction of various diastereomeric mixtures of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) represents the initial diastereomeric ratio immediately upon methoxy abstraction and does not reflect the different solubilities of the  $h^2$ -1,2-cycloheptadiene Fpp (35a) diastereomers in ethyl acetate.

Table 2. Methoxy abstraction from h<sup>1</sup>--(7-methoxy)cyclohepten-1-yl Fpp (34) to give h<sup>2</sup>-1,2-cycloheptadiene Fpp (35a).

Diast. comp. of (34)	solvent	TMSOTf <sup>a</sup>	Diast. comp. <sup>b</sup> of (35a) recryst.	% yield <sup>c</sup>
60:40	pentane	1 eq.	80:20	50
60:40	pentane/benzene	1 eq.	60:40	50
60:40	pentane/benzene	1/2 eq.	60:40	>90 <sup>d</sup>
80:20	pentane/benzene	1 eq.	60:40	55
10:90	pentane/benzene	1 eq.	80:20	5

<sup>a</sup>Trimethylsilyl trifluoromethanesulfonate.

<sup>b</sup>The ratios are good to within ±5 and are an average of two trials.

<sup>c</sup>Average yields based on two trials.

<sup>d</sup>Based on recovered (34).

First of all, the ethyl acetate filtrate from the initial precipitation of  $h^2$ -1,2-cycloheptadiene Fpp (35a) was collected and examined for any residual  $h^2$ -1,2-cycloheptadiene Fpp (35a). We did not detect any trace of  $h^2$ -1,2-cycloheptadiene Fpp (35a) by  $^1H$  NMR from this filtrate. Also, repeated precipitations of  $h^2$ -1,2-cycloheptadiene Fpp (35a) from ethyl acetate did not affect its diastereomeric compositions.

Lastly, we also tried a different procedure to precipitate  $h^2$ -1,2-cycloheptadiene Fpp (35) from the reaction mixture. Instead of precipitating  $h^2$ -1,2-cycloheptadiene Fpp (35a) from the crude reaction mixture with ethyl acetate, we dissolved the crude reaction mixture in methanol saturated with ammonium hexafluorophosphate and precipitated the  $h^2$ -1,2-cycloheptadiene Fpp as its hexafluorophosphate salt (35b) with water. We found by  $^1H$  NMR measurements that the diastereomeric compositions of  $h^2$ -1,2-cycloheptadiene Fpp (35b) obtained by this method are similar to those obtained by the previous method.

We conclude that methoxy abstraction of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) by trimethylsilyl trifluoromethanesulfonate occurs from only one diastereomer. The other diastereomer merely decomposes in the presence of trimethylsilyl trifluoromethanesulfonate. Therefore, when a 60:40 diastereomeric ratio of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) was treated with half an equivalent of trimethylsilyl trifluoromethanesulfonate, only one diastereomer

reacted to give  $h^2$ -1,2-cycloheptadiene Fpp (35a) in a 60:40 diastereomeric ratio in almost quantitative yields while the other diastereomer was recovered from the reaction mixture. This other diastereomer gave negligible amounts of  $h^2$ -1,2-cycloheptadiene Fpp (35a) when treated with trimethylsilyl trifluoromethanesulfonate.

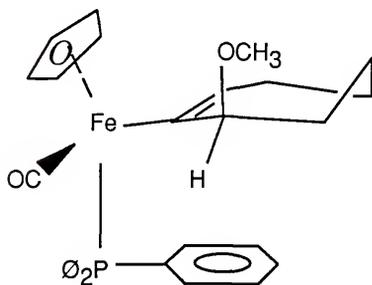
From the above observation, it becomes clear why methoxy abstraction in a pentane/benzene solvent from either a 80:20 or a 60:40 mixture of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) results in the same 60:40 mixture of  $h^2$ -1,2-cycloheptadiene Fpp (35a). In each case only one diastereomer, the major diastereomer, reacted with the trimethylsilyl trifluoromethanesulfonate.

The choice of solvent for methoxy abstraction affects the diastereomeric ratio of  $h^2$ -1,2-cycloheptadiene Fpp (35a). In a non-polar pentane solvent, we are probably seeing methoxy loss through Fpp assistance (probably syn Fpp assistance) leading to an enriched diastereomeric mixture of  $h^2$ -1,2-cycloheptadiene Fpp (35a). Methoxy loss in a more polar pentane/benzene solvent probably proceeds via the allyl cation to give an almost equal diastereomeric mixture of the  $h^2$ -1,2-cycloheptadiene Fpp (35a).

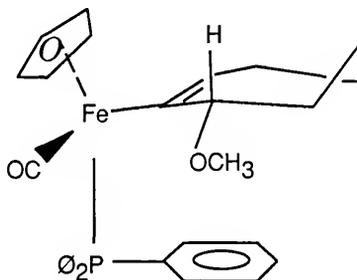
At the present moment we are unable to guess as to the significance of the 80:20 diastereomeric ratio of  $h^2$ -1,2-cycloheptadiene Fpp (35a) obtained from the methoxy abstraction of a 10:90 diastereomeric mixture of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34).

Our conjecture as to why only one  $h^1$ -(7-methoxy)-cyclohepten-1-yl Fpp (34) diastereomer undergoes methoxy abstraction to give the desired complex (35a) is that only this diastereomer has its methoxy group accessible to trimethylsilyl trifluoromethanesulfonate. The methoxy group of the other diastereomer is occluded from trimethylsilyl trifluoromethanesulfonate.

Based upon extended Huckel calculations of Seeman and Davies<sup>44</sup> and X-ray crystal structures<sup>45</sup> of similar types of complexes, we arrived at what we believe to be the most stable conformers of each of the two  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) diastereomers shown below.



SR



SS

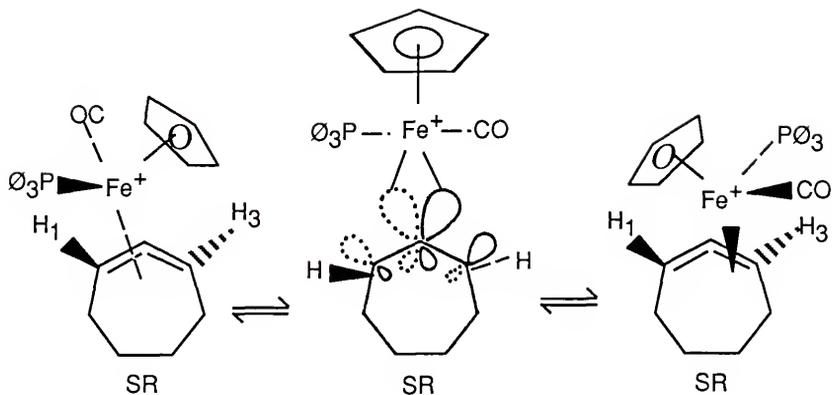
The phosphorus to phenyl bond here is eclipsed with the iron to (7-methoxy)cyclohepten-1-yl bond forcing the planes of both rings to lie parallel to each other. This conformation places the methoxy group of one diastereomer (SR) above the

plane of the cycloheptene ring and places the methoxy group of the other diastereomer (SS) below the plane of the cycloheptene ring. The methoxy group of the diastereomer (SR) is therefore exposed to trimethylsilyl trifluoromethanesulfonate whereas the methoxy group of the other diastereomer (SS) is shielded from abstraction by the phenyl ring below. MMX calculations<sup>46</sup> for the two diastereomers of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp (34) confirmed the conformation of the structures drawn above.

Let us now consider the consequences of an Fpp cation alternating between the adjacent double bonds of the 1,2-cycloheptadiene in terms of its  $^1H$  NMR spectrum and diastereomeric ratio based upon the two schemes described below.

In one case, the Fpp fragment moves between the two allenic double bonds as shown in Scheme XIII. The allyl cation intermediate is not involved in the 1,2-Fpp shift and the stereochemical integrity of each diastereomer is retained; ie. the SR diastereomer (and its RS enantiomer) does not interconvert with its RR (or SS) diastereomer.

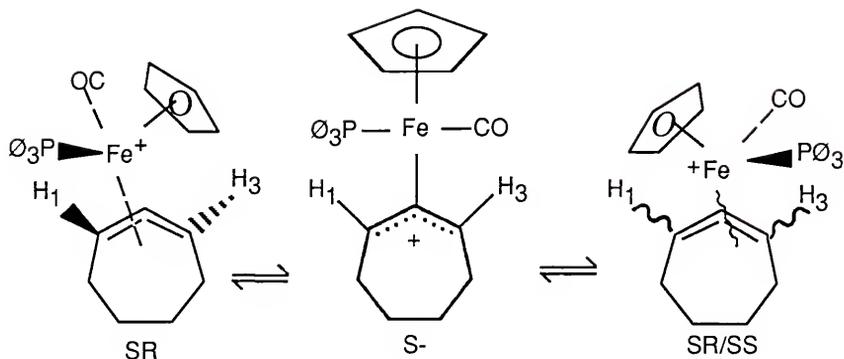
Scheme XIII.



A rapid 1,2-Fpp shift in the NMR time scale will render the two allenic hydrogens of each diastereomer equal. This effect should be similar to that observed in the case of  $h^2$ -1,2-cycloheptadiene Fp (4) when the allenic hydrogen resonances coalesce. In this case both diastereomers would still be observed and their diastereomeric composition after coalescence would remain unchanged. In other words, the two sets of allenic hydrogen resonances will coalesce and at the same time the two cyclopentadienyl hydrogen resonances will remain distinct and separated.

In the other case involving an allyl cation intermediate as shown in Scheme XIV, both cyclopentadienyl hydrogen resonances and the two pairs of the allenic hydrogen resonances would coalesce.

Scheme XIV.



The allyl cation intermediate (S-) no longer exists as enantiomeric pairs of diastereomers but just as a pair of enantiomers. The consequence of this is that starting out with the SR diastereomer we end up with both SR and SS diastereomers.

The  $^1\text{H}$  NMR of a chloroform- $d_1$  solution of the trifluoromethanesulfonate salt of the  $h^2$ -1,2-cycloheptene Fpp (35) with a diastereomeric composition of 60:40 remained unchanged up to  $+60^\circ\text{C}$ . We saw neither coalescence of the allenic hydrogen resonances or the cyclopentadienyl hydrogen resonances. We also did not see any change in the diastereomeric composition of the complex up to 3 hrs at that temperature. Any attempt to raise the temperature beyond this point resulted in decomposition of the complex. This negative result does not necessarily mean that the

1,2-cycloheptadiene Fpp (35a) is not fluxional because the fluxional process may not be within the appropriate time scale to be observed. This process may be observed at a higher temperature which is unattainable due to thermal instability of the complex. The fact that the diastereomeric composition remains unchanged does not necessarily mean that the allyl cation is not accessible because we may have started with a thermodynamic mixture of  $h^2$ -1,2-cycloheptadiene Fpp (35a). If coalescence of the allenic hydrogens were to occur at  $+60^\circ\text{C}$ , this would put the free energy of activation for a 1,2-Fpp shift at about 15 kcal/mole. The free energy of activation for an allene to allyl cation isomerization is therefore higher than 15 kcal/mole.

Since we were unable to raise the solution temperature over  $+60^\circ\text{C}$ , a way that might overcome this limitation is to use spin saturation transfer. The spin saturation transfer technique<sup>31</sup> allows one to observe by NMR a dynamic process at a lower probe temperature than is required for coalescence.

Take the SR diastereomer of the  $h^2$ -1,2-cycloheptadiene Fpp (35) as an example and consider the case where the Fpp cation moves rapidly between the two allenic double bonds via a 1,2-Fpp shift, Scheme XIII. We see that this process causes the allenic  $H_3$  to exchange with the allenic  $H_1$ . Therefore, if  $H_3$  were saturated by an irradiation frequency, this saturation could be transferred to  $H_1$ . The net effect

is a diminished  $H_1$  signal. Of course, in order to observe saturation transfer, the relaxation time,  $T_1$ , of the allenic hydrogens must be long compared to the fluxional process. If this condition is not met, then the saturation on  $H_3$  would have decayed before the 1,2-Fpp shift could occur and saturation would not be transferred to  $H_1$ .

Experimentally, it was found that irradiation of the allenic hydrogen  $H_3$  (6.40 ppm) of the minor diastereomer at +60°C led to complete saturation transfer to the allenic hydrogen  $H_1$  (2.92 ppm). Similarly, irradiating the allenic hydrogen  $H_1$  resulted in complete saturation transfer to allenic hydrogen  $H_3$ . Blind irradiation<sup>47</sup> of the allenic hydrogen  $H_1$  (1.96 ppm) of the major diastereomer resulted in a diminished signal for the allenic hydrogen  $H_3$  (6.15 ppm) of this diastereomer. It is clear that the Fpp is indeed fluxional about the adjacent double bonds of the 1,2-cycloheptadiene at +60°C even though this fluxional process is not observed by the coalescence method at the same temperature. Approximately half saturation transfer is observed at +40°C, Fig. 12.

It was not possible to derive an accurate free energy of activation for the fluxional motion from the S.S.T. experiments because only the allenic hydrogens belonging to the minor diastereomer could be used. The major diastereomer has one of its allenic hydrogen buried beneath the ring methylene hydrogen resonances.

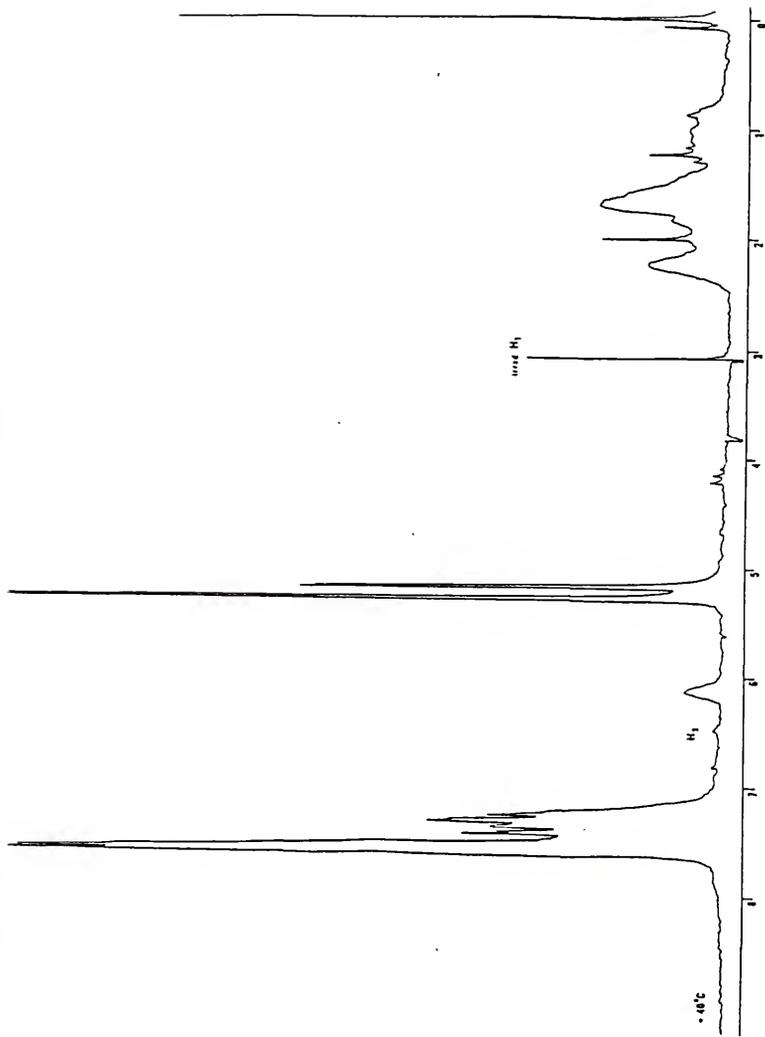


Fig. 12.  $^1\text{H}$  S.S.T. of (35a) in  $\text{CDCl}_3$ . (See Fig. 8, pg. 78, for  $^1\text{H}$  NMR of (35a) in  $\text{CDCl}_3$ .)

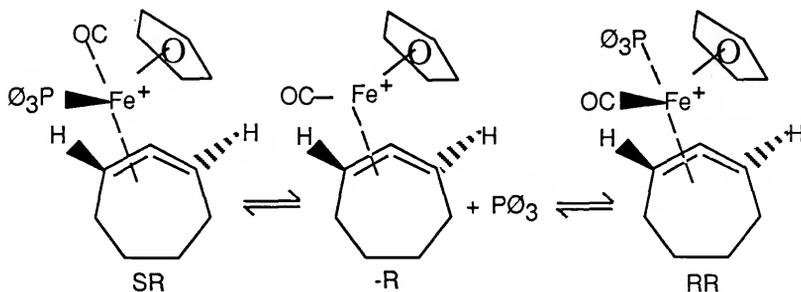
Furthermore, the allenic hydrogen resonances are quite broad which make accurate  $T_1$  and area measurements very inaccurate. However, if we take  $+40^\circ\text{C}$  as the condition for a half saturation transfer and assume conservatively a  $T_1$  between 0.1 s and 0.5 s, we can arrive at a very rough value of no more than 17-18 kcal/mole for the fluxional barrier.

It is important to note that irradiating the allenic hydrogen of the minor diastereomer did not affect the allenic hydrogen's intensities of the major diastereomer and vice versa. A pathway by which saturation transfer can occur between the allenic hydrogens of the two diastereomers is through the allyl cation. We can see from Scheme XIV that the allyl cationic species is the common link between the two diastereomers. If the allenic hydrogen  $H_3$  of the SR diastereomer is irradiated, saturation transfer would not be confined only to the SR diastereomer but should also leak into the SS diastereomer. Thus this result shows that within the time scale for the S.S.T. experiment, the allene to allyl cation isomerization is slower than the 1,2-Fpp shift.

Although the 60:40 mixture of the  $h^2$ -1,2-cycloheptadiene Fpp (35b) diastereomers did not isomerize in 3 hrs at  $+60^\circ\text{C}$  during coalescence studies, a chloroform- $d_1$  solution of  $h^2$ -1,2-cycloheptadiene Fpp (35b) with a diastereomeric composition of 80:20 did change slowly at room temperature. The equilibration was followed by  $^1\text{H}$  NMR and ultimately stopped at a 65:35 diastereomeric mixture

within one day. A second solution containing a 65:35 mixture of  $h^2$ -1,2-cycloheptadiene Fpp (35b) remained unchanged during this time period. This observation is consistent with an allene to allyl cation isomerization which interconverts diastereomers and the diastereomeric ratio of 65:35 represents a thermodynamical mixture of  $h^2$ -1,2-cycloheptadiene Fpp (35).

It should be noted that the above arguments assume that the triphenylphosphine ligand is not labile under the equilibration conditions. When a phosphine ligand leaves the Fpp fragment, it can re-coordinate with the iron resulting in a Fpp fragment with the same or opposite stereochemistry.



Such epimerization of the iron center is indistinguishable from the allene to allyl cation isomerization in that if we start with one diastereomer of the  $h^2$ -1,2-cycloheptadiene Fpp (SR) we end up with a mixture of the two diastereomers (SR and RR). We do not think that this process is occurring because  $h^2$ -olefin Fpp cationic complexes generally lose the

olefin ligand (and decompose) before the phosphine ligand. Nevertheless, we did not see any exchange of triphenylphosphite for triphenylphosphine when a chloroform solution of the  $h^2$ -1,2-cycloheptene Fpp (35) and triphenylphosphite was allowed to stand at room temperature for 95 hrs.\* Moreover, the rate of equilibration of a 80:20 diastereomeric composition of 1,2-cycloheptadiene Fpp (35a) is unaffected in the presence of 0.15 M triphenylphosphine. One would expect the rate of equilibration to be suppressed should epimerization occur about the iron center by dissociation and reassociation of triphenylphosphine.

Both  $h^2$ -1,2-cycloheptadiene Fp (4) and  $h^2$ -1,2-cycloheptadiene Fpp (35) exhibit fluxional behavior via a 1,2-iron shift. Whereas the fluxional barrier of  $h^2$ -1,2-cycloheptadiene Fp (4) is 13.9 kcal/mole, the fluxional barrier for  $h^2$ -1,2-cycloheptadiene Fpp (35) falls between 15 kcal/mole to no more than 18 kcal/mole. The higher fluxional barrier for  $h^2$ -1,2-cycloheptadiene Fpp (35) is probably the result of a stronger Fpp to olefin back bonding. This stronger back bonding is reflected in a longer C(2)-C(1) bond (1.385 $\overset{\circ}{\text{A}}$ ) and a larger difference in the complexed and uncomplexed allene double bond (0.047 $\overset{\circ}{\text{A}}$ ) (vide infra) when compared with the Fp complexed tetramethylpropadiene<sup>23</sup> (1.267 $\overset{\circ}{\text{A}}$  and 0.032 $\overset{\circ}{\text{A}}$ , respectively).

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\* The steric bulk of the more nucleophilic triphenylphosphine prevents it from displacing the coordinated triphenylphosphite.

The allene to allyl cation isomerization for  $h^2$ -1,2-cycloheptadiene Fpp (35) is very slow and should have a barrier of over 18 kcal/mole, the upper limit for a 1,2-Fpp shift. Allene to allyl cation isomerization involves the transfer of a positive charge from the iron to the allyl moiety. This isomerization is necessarily slower for the relatively electron rich Fpp because the Fpp is better able to stabilize the positive charge in its allene form compared to the relatively electron poor Fp. For this reason, we infer that the barrier for allene to allyl cation isomerization of  $h^2$ -1,2-cycloheptadiene Fp (4) is lower than  $h^2$ -1,2-cycloheptadiene Fpp (35).

Another area of interest to us besides isomerization of allene to allyl cation is the effect of ring strain on the structure and bonding of cyclic allenes. Theoretical calculations of Johnson<sup>5</sup> in particular predicted substantial deformation of both  $C_1$ - $C_2$ - $C_3$  bond angles and dihedral angles of strained cyclic allenes, see Table 1. There are no theoretical studies yet on transition metal complexed cyclic allenes.

Although transition metal complexed cyclic allenes are well known<sup>15,16</sup>, no X-ray studies have been reported. X-ray<sup>48</sup> studies of acyclic allenes however revealed a bent structure with the  $C_1$ - $C_2$ - $C_3$  bond angles between 134° and 159° but with little distortion of the dihedral angles.

We have succeeded in growing crystals of  $h^2$ -1,2-cycloheptadiene Fpp hexafluorophosphate (35b) suitable for X-ray

studies. The air stable orange colored crystals were grown from a methylene chloride/n-heptane solvent mixture at  $-35^{\circ}\text{C}$  in a nitrogen atmosphere. This is the first cyclic allene transition metal complex characterized by X-ray and its structure is shown in Fig. 13.

Interactions between iron and the C(2)-C(1) double bond lengthens it ( $1.385(6)\text{\AA}$ ) whereas the uncomplexed C(1)-C(7) bond length is typical of a double bond ( $1.303(7)\text{\AA}$ ). The hybridization at C(2) and C(1) is closer to  $sp^3$  and  $sp^2$ , respectively. The consequence of rehybridization is that the C(2)-C(1)-C(7) angle contracts to  $138.1(3)^{\circ}$  from a calculated value of  $153.4^{\circ}$  for the free 1,2-cycloheptadiene. Considerable ring strain is perhaps relieved. This angle is one of the smallest for a monomeric transition metal allene complex. Only the  $h^2$ -phenylallene complex of  $(\text{diphos})_2\text{ReCl}$  has a smaller angle of  $138.1(3)^{\circ}$ .<sup>48a</sup> The iron is also displaced toward the C(1) carbon; the Fe-C(1) and Fe-C(2) bond lengths are  $2.007(4)\text{\AA}$  and  $2.168(3)\text{\AA}$ , respectively.

The dihedral angle defined by the planes C(3)-C(2)-C(1)-H(21) and C(6)-C(7)-C(1)-H(71) is  $70.7^{\circ}$  versus  $90^{\circ}$  for an unstrained acyclic allene and  $55.2^{\circ}$  calculated for 1,2-cycloheptadiene. The dihedral angle is increased upon complexation but the ring still prevents it from returning to its normal value of  $90^{\circ}$ .

The bonding between 1,2-cycloheptadiene and Fpp is typical of all metal to olefin bonds.

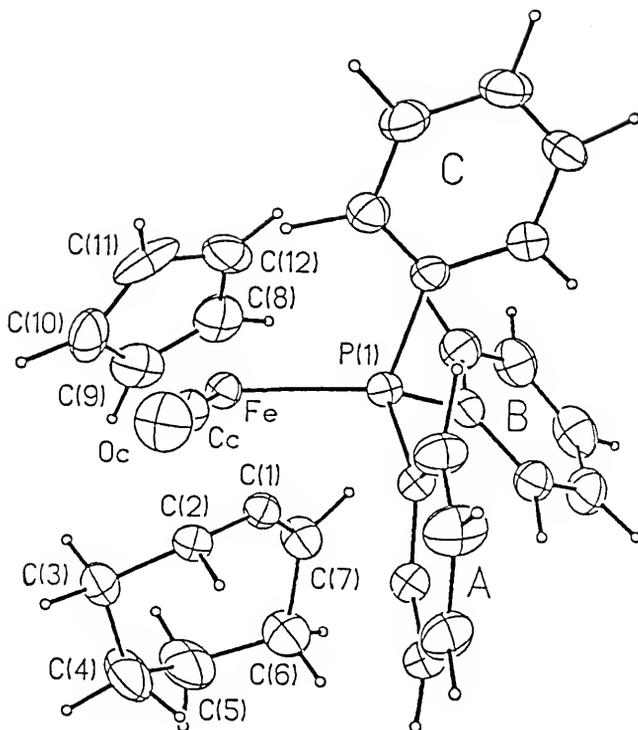


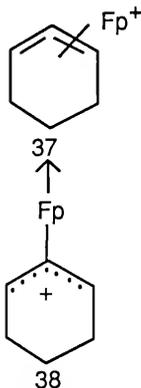
Fig. 13. X-ray structure of  $h^2$ -1,2-cycloheptadiene Fpp cation.

An illustration of the  $[\text{FeCp}(\text{CO})(\text{PPh}_3)(\text{C}_7\text{H}_{10})]^+$  ion. Selected bond lengths: Fe-C(1), 2.007(4); Fe-C(2), 2.168(3); C(1)-C(2), 1.385(6); C(1)-C(7), 1.303(7); Fe-Cc, 1.777(5); Cc-Oc, 1.137(6); Fe-P(1), 2.250(1), P(1)-C(1A), 1.828(4); P(1)-C(1B), 1.825(4); P(1)-C(1C), 1.831(3); Fe-C(Cp) Avg 2.097(5)Å. Selected bond angles: P(1)-Fe-Cc, 89.5(1); P(1)-Fe-C(1), 82.9(1); Cc-Fe-C(1), 111.3(2); Fe-C(1)-C(2), 77.0(2); Fe-C(1)-C(7), 141.9(3); C(2)-C(1)-C(7), 138.1(3); Fe-Cc-Oc, 177.8(3); Fe-P(1)-C(1A), 110.8(1); Fe-P(1)-C(1B), 117.3(1); Fe-P(1)-C(1C), 115.1(1).

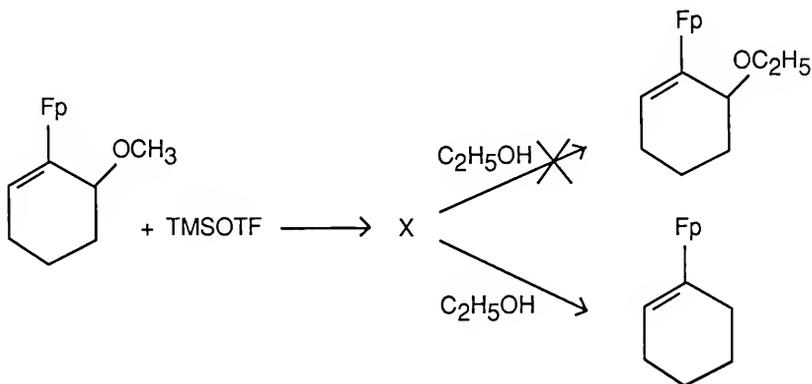
CHAPTER IV

$h^2$ -IRON COMPLEX OF 1,2-CYCLOHEXADIENE

One can further strain the linear and perpendicular allene by incorporating it into a smaller six-membered ring. MNDO calculated geometries of 1,2-cyclohexadiene show that it is even more distorted compared with the larger cyclic allenes. The allene  $C_1-C_2-C_3$  bond angle is  $138.5^\circ$  versus  $153.4^\circ$  calculated for 1,2-cycloheptadiene and the dihedral angle of  $22.9^\circ$  is very close to planarity.<sup>5</sup> Despite the large bending and torsional strain, the allene form is still the ground state but the allyl cationic form lies only 15 kcal/mole higher. On the contrary, EHMO<sup>11</sup> predicts that the  $h^1$ -allyl Fp cationic form (38) is actually 14 kcal/mole lower in energy than the  $h^2$ -allene Fp form (37).

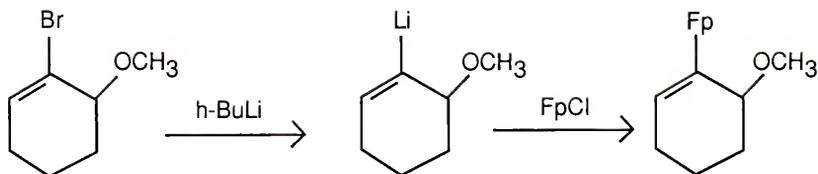


Earlier attempts<sup>14</sup> to generate  $h^2$ -1,2-cyclohexadiene Fp (37) and observe this allene to allyl cation isomerization were not successful. Treating a solution of the  $h^1$ -(6-methoxy)cyclohexen-1-yl Fp with trimethylsilyl trifluoromethanesulfonate followed by ethanol gave  $h^1$ -cyclohexen-1-yl Fp instead of the expected ethyl ether adduct.



Adding an acetone solution of sodium iodide to the crude reaction mixture gave a 3:1 mixture of cyclohexene and cyclohexadiene, respectively. A mechanism similar to that for the decomposition of the  $h^2$ -1,2-cycloheptadiene Fp (4a), Scheme V, was proposed to account for the decomposition products observed.

The  $h^1$ -(6-methoxy)cyclohexen-1-yl Fp was synthesized in good yields according to the method developed for its 7-membered ring analogue.

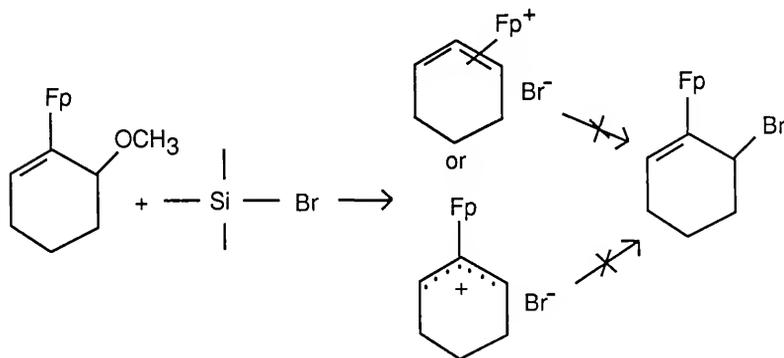


The reaction between a methylene chloride solution of  $h^1$ -(6-methoxy)cyclohexen-1-yl Fp and trimethylsilyl trifluoromethanesulfonate at  $-78^\circ\text{C}$  gave a flocculant yellow precipitate upon quenching with diethyl ether ( $-78^\circ\text{C}$ ). The precipitate was extremely sensitive to temperature and turned to a dark red paste when we attempted to isolate it via filtration at room temperature. The red paste could not be characterized but was presumed to contain Fp trifluoromethanesulfonate along with other decomposition products. An acetone solution of sodium iodide added to this red paste gave Fp iodide as the only identifiable product.

This suggested that  $h^2$ -1,2-cyclohexadiene Fp (37) may be extremely prone to decomposition. We therefore attempted to trap it at low temperatures. The yellow flocculant precipitate from the reaction of  $h^1$ -(6-methoxy)cyclohexen-1-yl Fp with trimethylsilyl trifluoromethanesulfonate can be isolated and kept from turning red momentarily via a cold filtration ( $-78^\circ\text{C}$ ) under  $\text{N}_2$  in a jacketed filter funnel. However, when ethanol with a slurry of sodium carbonate was

added to this precipitate again the ethyl ether adduct could not be detected from the reaction mixture. The same reaction in pentane also afforded a yellow precipitate as soon as trimethylsilyl trifluoromethylsulfonate was added. Again the ethyl ether adduct could not be detected from the reaction mixture when ethanol/sodium carbonate was added to this precipitate.

Trimethylsilyl bromide is known to be a methoxy abstracting reagent.<sup>49</sup> The advantage of this reagent is that the bromide anion resulting from the reaction between trimethylsilyl bromide and  $h^1$ -(6-methoxy)cyclohexen-1-yl Fp may act as an internal trap to give the  $h^1$ -(6-bromo)cyclohexen-1-yl Fp. However, the reaction gave Fp bromide as the only isolatable product. 1,3-Cyclohexadiene was not detected in the reaction mixture by  $^1H$  NMR.



Previous experimental evidence showed that trifluoromethanesulfonate anion was responsible for the thermal

decomposition of  $h^2$ -1,2-cycloheptadiene Fp (4a). It would be reasonable to assume that the trifluoromethanesulfonate anion may also decompose the  $h^2$ -1,2-cyclohexadiene Fp (37); perhaps even more rapidly if indeed it is formed. The procedure for room temperature methoxy abstraction with trimethyloxonium tetrafluoroborate developed for the seven-membered ring analogue was therefore tried here. Unfortunately, unlike the seven-membered ring, the reaction at room temperature yielded only a black intractable solid. There was no reaction between the  $h^1$ -(6-methoxy)cyclohexen-1-yl Fp and trimethyloxonium tetrafluoroborate at low temperatures ( $-78^\circ\text{C}$ ) and the starting material was isolated unchanged.

Trimethyloxonium tetrafluoroborate is not very soluble in methylene chloride used in the above experiment and it was suspected that the long reaction times necessary for methoxy abstraction may be detrimental to either the  $h^1$ -allyl Fp cation (38) or the  $h^2$ -1,2-cyclohexadiene Fp (37). Triethyloxonium tetrafluoroborate was substituted as the methoxy abstracting reagent. The advantage of this reagent is that it is soluble in methylene chloride, the reaction solvent. We therefore expect reaction times to be shortened considerably. Methoxy abstraction with triethyloxonium tetrafluoroborate at  $-78^\circ\text{C}$  in methylene chloride did not give a yellow solid upon quenching with diethyl ether but turned red when warmed to room temperature. The same reaction in either n-pentane or diethyl ether gave an intractable red substance which coats the reaction vessel.

Triphenylmethanecarbenium tetrafluoroborate was also reacted with  $h^1$ -(6-methoxy)cyclohexen-1-yl Fp according to the procedure developed for its seven-membered ring analogue but this reaction mixture also decomposed to a red substance.

Having failed to synthesize or trap the  $h^2$ -1,2-cyclohexadiene Fp (37), or its  $h^1$ -allyl Fp cation (38), we decided, as a last recourse, to attempt to generate and observe  $h^2$ -1,2-cyclohexadiene Fp (37) by low temperature  $^1H$  NMR. Trimethylsilyl trifluoromethanesulfonate and  $h^1$ -(6-methoxy)cyclohexen-1-yl Fp were introduced into a low temperature NMR tube reactor as separate plugs frozen in methylene chloride. The plugs were thawed in cold pentane ( $-80^\circ C$ ), mixed and then refroze in liq.  $N_2$  and the NMR tube was then sealed under vacuum. The contents of the tube were thawed inside a precooled NMR probe and the reaction was followed by  $^1H$  NMR. There was no evidence for either the  $h^2$ -1,2-cyclohexadiene Fp (37) or  $h^1$ -allylic Fp cation (38) at  $-85^\circ C$ . Instead, only a signal of 5.21 ppm taken to be the Fp trifluoromethanesulfonate grew steadily while the cyclopentadienyl hydrogen resonances for  $h^1$ -(6-methoxy)cyclohexen-1-yl Fp decrease with time, Fig. 14. The contents of the NMR tube also turned red again indicating the presence of Fp trifluoromethanesulfonate. There was no sign of cyclohexene and cyclohexadiene or the Fp cation complexes of either. Methyltrimethylsilyl ether was the only other product identified by  $^1H$  NMR.

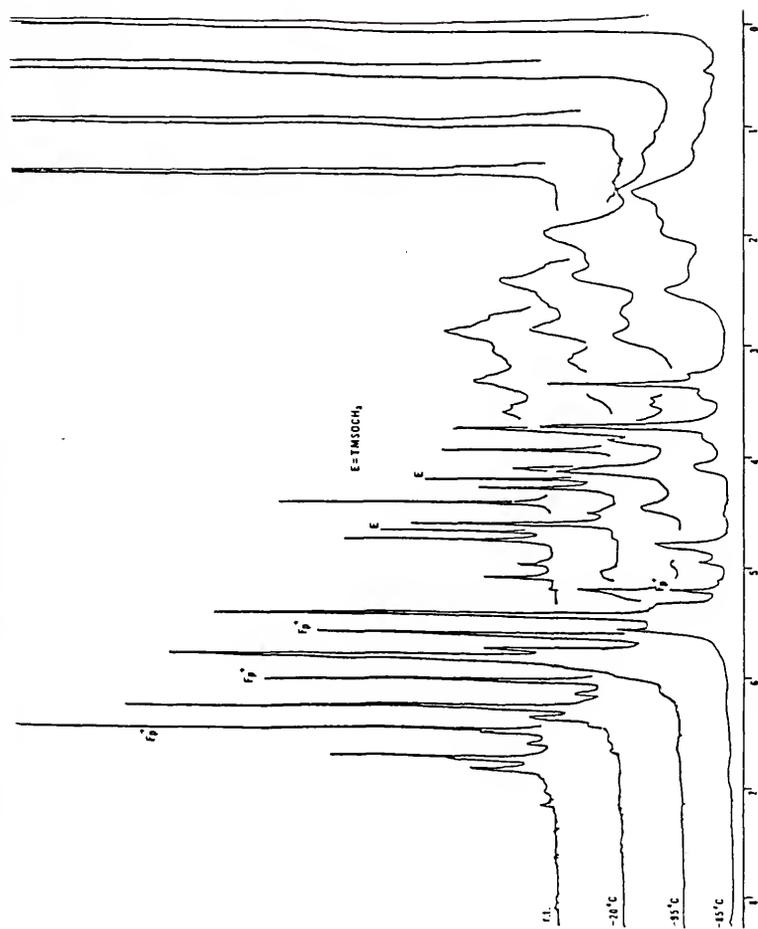
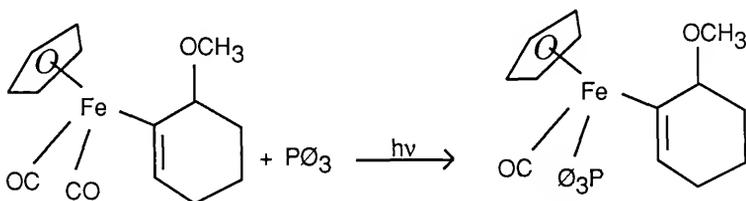


Fig. 14. Reaction between  $\text{h}^1$ -(6-methoxy)cyclohexen-1-yl Fp and trimethylsilyl trifluoromethanesulfonate followed by low temperature  $^1\text{H}$  NMR.

We have seen the dramatic effect of a triphenylphosphine ligand on the physical and chemical properties of the  $h^2$ -1,2-cycloheptadiene Fpp (35). We therefore hoped that the triphenylphosphine ligand would impart additional stability to the  $h^2$ -1,2-cyclohexadiene Fp such that it could be synthesized and isolated or observed by low temperature NMR.

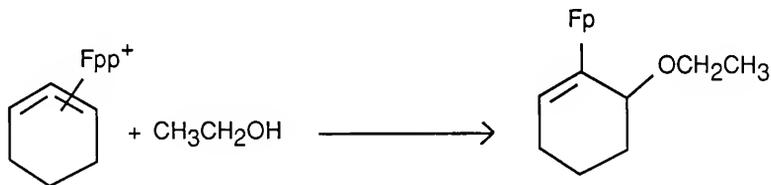
$h^1$ -(6-Methoxy)cyclohexen-1-yl Fpp was synthesized in reasonable yields according to the procedure developed for its seven-membered ring analogue.



When  $h^1$ -(6-methoxy)cyclohexen-1-yl Fpp was treated with trimethylsilyl trifluoromethanesulfonate in a *n*-pentane/benzene solvent mixture at 0°C, a brownish yellow precipitate fell out of solution. This pasty precipitate could not be isolated via filtration and turned dark rust colored after the reaction solvent was removed in vacuo. The paste dissolved in ethyl acetate but unlike its seven-membered ring analogue, did not give an orange colored precipitate.

Treating  $h^1$ -(6-methoxy)cyclohexen-1-yl Fpp with triphenylmethanecarbenium fluoroborate led to a black decomposed mixture.

The same reaction in pentane, however, gave a greenish yellow precipitate which can be isolated by filtration under  $N_2$  at room temperature. The solid decomposes instantly in solution but can be kept in solid form for several days at  $-35^\circ C$ . We were unable to characterize this solid fully due to its instability but we believed it to be the  $h^2$ -1,2-cyclohexadiene Fpp. If this solid were the  $h^2$ -cyclohexadiene Fpp, we hope to trap it as its ethyl ether adduct.



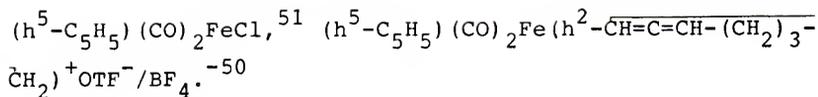
When the solid was reacted with ethanol at  $-78^\circ C$ ,  $h^1$ -(6-ethoxy)cyclohexen-1-yl Fpp was indeed isolated as the only product. One should note that  $h^2$ -1,2-cycloheptadiene Fpp (35) does not react with either methanol or ethanol. This difference in reactivity perhaps attests to the strained nature of the six-membered cyclic allene.

To date, we failed to synthesize  $h^2$ -1,2-cyclohexadiene Fp (37) but we have evidence for  $h^2$ -1,2-cyclohexadiene Fpp.

Replacing a carbonyl ligand on the iron with triphenylphosphine stabilizes the  $\eta^2$ -1,2-cyclohexadiene Fpp to a point where we can isolate it as a solid.

CHAPTER V  
EXPERIMENTAL

Hexane, diethyl ether and tetrahydrofuran were distilled from benzophenone ketyl. Methylene chloride was distilled from  $P_4O_{10}$  under  $N_2$  and degassed. Benzene was distilled from SilicaPent under  $N_2$ . Acetonitrile, p-dioxane, furan and cyclopentadiene were distilled under  $N_2$ . The initial fractions were discarded. n-Pentane and n-heptane were degassed by bubbling a stream of  $N_2$  into them. Alumina was Brockman 80-200 mesh (neutral, activity I) and was reduced to activity II by adding 3% by weight of water and degassed before use.  $^1H$  NMR and  $^{13}C$  NMR were taken on a JEOL FX-100 (100 MHz). IR were taken on a Perkin Elmer 283B. X-ray crystal structure was obtained from a Nicolet R3m diffractometer. Elemental analyses were performed by Atlantic Microlabs, Atlanta. Melting points were uncorrected and obtained using a Thomas Hoover apparatus. The following compounds were prepared as described in the literature: 7,7-dibromobicyclo[4.1.0<sup>1,6</sup>]heptane,<sup>14</sup> 6,6-dibromobicyclo[3.1.0<sup>1,5</sup>]hexane,<sup>14</sup> 1-bromo-7-methoxycycloheptene,<sup>50</sup> 1-bromo-6-methoxycyclohexene,<sup>14</sup> 1-bromo-7-ethoxycycloheptene,<sup>14</sup> 7-methoxycycloheptene-1-carboxylic acid,<sup>50</sup> 7-methoxycycloheptene-1-carboxylic acid chloride,<sup>50</sup>



All organometallic reactions, unless otherwise specified, were conducted under  $\text{N}_2$  using Schlenk techniques or in a dry box by Vacuum Atmospheres Corporation.

Improved synthesis of dicarbonyl( $\eta^5$ -cyclopentadienyl)( $\eta^1$ -(7-methoxy)cyclohepten-1-yl) iron(II)

n-Butyllithium (1.6 M in hexane) (6 ml; 9.6 mmole) was added dropwise to a cold ( $-78^\circ\text{C}$ ) solution of 7-methoxy-1-bromocycloheptene (2.24 g; 11 mmole) in 20 ml of THF. The reaction mixture was stirred for 2 hrs at  $-78^\circ\text{C}$  after which a solution of Fp chloride (2.1 g; 10 mmole) in 5 ml of THF was added. The reaction mixture was allowed to stir for 1 hr at  $-78^\circ\text{C}$  and then warmed to room temperature. The reaction mixture was then adsorbed onto alumina and eluted down a 3" x 1" alumina column (neutral; grade II) with hexane. The only yellow band was collected and yielded 2.08 g (63%) of the product as a brown oil. The NMR and IR are consistent with those of the known compound.<sup>50</sup> IR (neat) 2010s, 1920s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ ) 0.80-2.50 (m, 8H), 3.30 (s, 3H), 3.8 (m, 1H), 4.75 (s, 5H), 5.80 (t, 1H).

Thermal decomposition of dicarbonyl( $\eta^2$ -1,2-cycloheptadiene)( $\eta^5$ -cyclopentadienyl) iron(II) trifluoromethanesulfonate

A methylene chloride- $\text{d}_2$  solution of the title compound (10 mg) was vacuum sealed in an NMR tube and heated to  $+40^\circ\text{C}$

in the NMR. The progress of the thermal decomposition was monitored at regular intervals. Refer to Fig. 1a and 1b and discussion in Chapter II.

NMR scale synthesis of dicarbonyl( $h^5$ -cyclopentadienyl) iron(II) trifluoromethanesulfonate

To a dilute solution of Fp chloride in methylene chloride- $d_2$  (cyclopentadienyl hydrogen resonance at 5.06 ppm) was added a small amount of silver trifluoromethanesulfonate. The orange colored solution turned red with the appearance of a new cyclopentadienyl hydrogen resonance at 5.20 ppm in the  $^1H$  NMR. The result is in agreement with that reported by Mattson and Graham<sup>52</sup> (5.25 ppm,  $CDCl_3$ ).

Attempted Thermal decomposition of dicarbonyl( $h^2$ -1,2-cycloheptadiene) ( $h^5$ -cyclopentadienyl) iron(II) tetrafluoroborate

A methylene chloride solution of the title compound was heated to +40°C in a vacuum sealed NMR tube for 16 hrs. The  $^1H$  NMR remained unchanged.

Variable temperature  $^{13}C$  NMR studies of the dicarbonyl( $h^2$ -1,2-cycloheptadiene) ( $h^5$ -cyclopentadienyl) iron(II) tetrafluoroborate

A nitromethane- $d_3$  solution of the title compound was sealed under vacuum in an NMR tube. The  $^{13}C$  NMR was obtained at 15°C intervals. The carbonyl signals remained distinct up to +45°C whereas the  $C_1$  and  $C_3$  signals vanished.

The compound decomposed at +60°C. Refer to Fig. 2 and discussion in Chapter II.

The reaction between dicarbonyl( $h^2$ -1,2-cycloheptadiene) ( $h^5$ -cyclopentadienyl) iron(II) tetrafluoroborate and triphenylmethane

A methylene chloride- $d_2$  solution of the title compound (6.8 mg; 0.019 mmole) and triphenylmethane (5.4 mg; 0.022 mmole) was vacuum sealed in an NMR tube. The solution was heated to +40°C for 3 hrs with no detectable change in its  $^1H$  NMR. The solution remained yellow in color and clear. There was no reaction between the two compounds.

Attempted enantiomeric enrichment of racemic dicarbonyl ( $h^2$ -1,2-cycloheptadiene) ( $h^5$ -cyclopentadienyl) iron(II) tetrafluoroborate with (S)-(-)-2-methylbutanol

To a suspension of the title compound (0.10 g; 0.36 mmole) in diethyl ether was added (S)-(-)-2-methylbutanol (0.02 ml; 0.18 mmole). The reaction was allowed to stir overnight at room temperature. The remaining solid (0.07 g) was isolated via filtration and washed with diethyl ether. The solid,  $h^2$ -1,2-cycloheptadiene Fp, has a negligible optical rotation,  $[\alpha]_{r.t.}^{546} = -0.7^\circ$  (c 0.001 g/ml  $CH_2Cl_2$ ). The solution was too dark for rotation measurements at higher concentrations. The ether adduct was isolated from the filtrate and eluted down a short alumina column (neutral, grade II) with hexane. IR ( $CDCl_3$ ) 2015s, 1955s  $cm^{-1}$ ;  $^1H$  NMR (100 MHz,  $CDCl_3$ ) 0.80-1.00 (m, 6H), 1.08-2.32

(m,11H), 3.16 (dd,2H), 3.94 (d,1H), 4.80 (s,5H), 5.80 (t,1H).

Resolution of 7-methoxy-1-cycloheptenecarboxylic acid

The title compound was dissolved in abs. ethanol at the concentration of 1 g of the acid to 3 ml of the ethanol. One equivalent of the (-)-quinine was added and the mixture was heated to dissolution. The solution was filtered and allowed to stand at room temperature. Translucent crystals were formed. The solution was allowed to stand until the first sign of a white crystal appeared. The translucent crystals were collected via filtration, washed with abs. ethanol and air dried to give a white solid, m.p. 160°C-162°C.

The acid was regenerated by adding a few milliliters of dilute HCl(aq) to a diethyl ether solution the crystals. The solution was heated briefly over a steam cone. The diethyl ether layer was collected, dried and the diethyl ether removed in vacuo to give the acid as a yellowish clear oil,  $[\alpha]_{r.t.}^{546} = -8.41^\circ$ .

Synthesis of optically active dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(h<sup>1</sup>- (7-methoxy)cyclohepten-1-yl) iron(II) (N)

The title compound was made in two steps in a 35% yield from the optically active 7-methoxycycloheptene-1-carboxylic acid chloride and potassium Fp followed by photolytic decarbonylation according to a previously established route

for the racemic complex.<sup>50</sup> The NMR and IR are in agreement with the known racemic compound synthesized here by treating 1-lithio-7-methoxycycloheptene with Fp chloride. Optical rotation measurements were not obtained. The enantiomeric excess of 50% was determined by NMR measurements of the cyclopentadienyl hydrogen resonances of a 10 mole % Eu(hfc)<sub>3</sub> chloroform-d<sub>1</sub> solution of the acyl complex (before photolytic decarbonylation).

#### Synthesis of optically active 1-bromo-7-methoxycycloheptene

The title compound was synthesized in two steps. Stereospecific reduction of 2-bromo-2-cycloheptenone with LAH/quinine according to the method of Jones and Balci<sup>10</sup> gave the optically active alcohol (20% e.e.) in a 82% yield. The enantiomeric purity was determined by NMR measurements of the C7 hydrogen in a chloroform-d<sub>1</sub> solution of Eu(hfc) and not by optical rotation. The optically active alcohol was treated with sodium hydride followed by methyl iodide according to the method of Manganiello<sup>14</sup> to give the optically active 1-bromo-7-methoxycycloheptene in 77% yield. Optical rotation was not determined. <sup>1</sup>H NMR is consistent with the known racemic compound<sup>50</sup>. <sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>) 1.20, 1.75 (m, 8H), 3.40 (s, 3H), 4.05 (m, 1H), 6.30 (t, 1H).

Synthesis of the optically active dicarbonyl( $h^5$ -cyclopentadienyl)( $h^1$ -(7-methoxy)cyclohepten-1-yl)iron(II) (P)

The title compound was made from the optically active 1-bromo-7-methoxycycloheptene according to the method developed here. The NMR and IR are in agreement with the known racemic compound synthesized here by treating 1-lithio-7-methoxycycloheptene with Fp chloride. The enantiomeric excess of 20% was determined by NMR measurement of the cyclopentadienyl hydrogen resonances of a 10 mole % Eu(hfc) chloroform- $d_1$  solution of the acylated compound.

Synthesis of dicarbonyl( $h^5$ -cyclopentadienyl) $h^1$ -(7-methoxy)cyclopentadien-1-yl)iron(II) from dicarbonyl( $h^2$ -1,2-cycloheptadiene)( $h^5$ -cyclopentadienyl)iron(II) trifluoromethanesulfonate

The title compound was made according to the method by Manganiello<sup>14</sup> in 30% yields substituting methanol for ethanol. The NMR and IR are in agreement with the known compound synthesized here by treating 1-lithio-7-methoxycycloheptene with Fp chloride.

Synthesis of dicarbonyl( $h^1$ -carbonyl-(7-methoxy)cycloheptene-1-yl)( $h^5$ -cyclopentadienyl)iron(II) via carbonylation of dicarbonyl( $h^5$ -cyclopentadienyl)( $h^1$ -(7-methoxy)cycloheptene-1-yl)iron(II)

A methylene chloride solution of the  $h^1$ -(7-methoxy)cyclohepten-1-yl Fp (0.08 g; 0.26 mmole) and ferrocenium tetrafluoroborate (0.01 g; 0.037 mmole) in a thick wall glass reactor was cooled to  $-78^\circ\text{C}$  and charged with 55 psi of

CO gas. The reaction mixture was stirred for 1 hr after which the pressure was released.

The reaction mixture was adsorbed onto alumina and eluted down a 1" x 1" alumina column (neutral, grade II) first with hexane then with methylene chloride. A quantitative yield of the product was obtained. The NMR and IR are consistent with the known compound.<sup>50</sup> IR (neat) 2010s, 1960s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ ) 1.00-2.90 (m, 8H), 3.20 (s, 3H), 4.20 (m, 1H), 4.90 (s, 5H), 6.45 (m, 1H).

Synthesis of carbonyl( $\text{h}^5$ -cyclopentadienyl)( $\text{h}^1$ -(7-methoxy)cyclohepten-1-yl)triphenylphosphineiron(II)

The  $\text{h}^1$ -(7-methoxy)cycloheptene Fp (1.10 g; 3.6 mmole) dissolved in a 1:1 v/v mixture of n-pentane and benzene was introduced into a quartz photolysis well equipped with a low pressure Hg lamp (Hanovia, 450 W). The solution was photolyzed while being flushed with a stream of  $\text{N}_2$  and triphenylphosphine dissolved in 15 ml of the same solvent mixture was added at a rate of 1 ml/min. The photolysis was terminated 5 mins after all of the triphenylphosphine was added.

The solvent was removed and the red viscous residue was chromatographed down a 3" x 1" alumina column (neutral, grade II) first with hexane then with benzene giving 0.94 g (48%) yield of a red oil. The compound was obtained in a 60:40 diastereomeric composition determined by NMR measurements of the methoxy hydrogen resonances. An analytical sample was recrystallized from a 4:1 v/v of acetone/water to

give a dark red solid. Mp. 138°-140°d; IR (CDCl<sub>3</sub>) 1920s cm<sup>-1</sup>; <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) a) diastereomer A 0.80-2.30 (bm, 8H), 3.19 (s, 3H), 3.90 (dd, 1H), 4.46 (d, <sup>3</sup>J<sub>PH</sub>=0.98Hz, 5H), 5.32 (dt, 1H), 7.33 (s, 15H); b) diastereomer B 0.80-2.30 (bm, 8H), 3.08 (s, 3H), 4.43 (d, <sup>3</sup>J<sub>PH</sub>=0.98Hz, 5H), 5.76 (dt, 1H), 7.33 (s, 15H); <sup>13</sup>C NMR (25 MHz, CDCl<sub>3</sub>) 25.8, 26.7, 27.9, 31.7 (C3-C6), 55.8 (C8), 84.4 (Cp), 92.0 (C7), 127.8 (o-C, <sup>2</sup>J<sub>PC</sub>=8.54Hz), 133.5 (m-C, <sup>3</sup>J<sub>PC</sub>=9.76Hz), 136.8 (i-C, <sup>1</sup>J<sub>PC</sub>=39.06Hz), 141.7 (C2, <sup>3</sup>J<sub>PC</sub>=6.1Hz), 151.1 (C1, <sup>1</sup>J<sub>PC</sub>=23.19Hz), 211.6 (CO); Anal. calcd. for C<sub>32</sub>H<sub>33</sub>O<sub>2</sub>P<sub>1</sub>Fe<sub>1</sub>: C, 71.65; H, 6.20; Found: C, 71.62; H, 6.22. TLC (benzene) rf: 0.35.

Synthesis of carbonyl(h<sup>2</sup>-1,2-cycloheptadiene)(h<sup>5</sup>-cyclopentadienyl)triphenylphosphineiron(II) trifluoromethanesulfonate

To the h<sup>1</sup>-(7-methoxy)cyclohepten-1-yl Fpp (0.15 g; 0.28 mmole) dissolved in 15 ml of an equal volume mixture of n-pentane and benzene at 0°C was added an excess of TMSOTf (0.10 ml; 0.4 mmole). The reaction mixture was stirred for 10 mins at 0°C and the solvent removed to yield a dark greenish paste. Ethyl acetate was added to the paste and the desired product precipitated as an orange solid (0.1 g; 56%) with a diastereomic composition of 60:40. The same reaction in n-pentane gave the product in a 80:20 ratio after precipitation from ethyl acetate. The diastereomeric compositions were determined by NMR measurements of the cyclopentadienyl hydrogen resonances. This orange solid is

air stable. An analytical sample was recrystallized from ethyl acetate. Mp. 170°-173°d; IR (KBr) 1996s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) a) diastereomer A 1.73, 2.23(b,8H), 2.92(b,1H), 5.12(d,  $^3J_{\text{PH}}=1.22\text{Hz}$ ,5H), 6.40(b,1H), 7.00-7.60(b,15H); b) diastereomer B 1.73, 2.23(b,8H), 1.96(b,1H), 5.23(d,  $^3J_{\text{PH}}=1.22\text{Hz}$ ,5H), 6.15(b,1H), 7.00-7.60(b,15H);  $^{13}\text{C}$  NMR (25 MHz,  $\text{CDCl}_3$ ) 17.5(C1,  $^2J_{\text{PC}}=170.5\text{Hz}$ ), 27.63, 28.75, 31.29, 32.11(C3-C6), 90.4(Cp), 126.71(C3,  $^3J_{\text{PC}}=17.25\text{Hz}$ ), 129.0-132.8( $\text{PPh}_3$ ), 154.27(C2,  $^2J_{\text{PC}}=20.75\text{Hz}$ ), 217.94(CO); Anal. calcd. for  $\text{C}_{32}\text{H}_{30}\text{O}_4\text{F}_3\text{P}_1\text{S}_1\text{Fe}_1$ : C,58.72; H,4.62; Found: C,58.74; H,4.72.

#### Synthesis of 1-bromo-7-methoxycycloheptene-7d<sub>1</sub>

The title compound was made in four steps by the method adapted from Jones and Balci<sup>10</sup> with two changes. The 2-bromo-1-cycloheptenone was reduced with LAD instead of LAH/quinine mixture and the resulting alcohol was reacted with methyl iodide instead of methanesulfonyl chloride to give the compound at a 25% overall yield. With the exception of the deuterium, the NMR is consistent with the known protiated compound.  $^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ ) 1.20, 1.75 (m,8H), 3.40 (s,3H), 6.30 (t,1H).

#### Synthesis of carbonyl( $h^2$ -1,2-cycloheptadiene-1d<sub>1</sub>)( $h^5$ -cyclopentadienyl)triphenylphosphineiron(II) trifluoromethanesulfonate

The title compound was made in three steps starting from 1-bromo-7-methoxycycloheptene-7d, and  $\text{Fp}$  chloride

according to the method developed here. The NMR and IR are in agreement with the known protiated compound synthesized here.

The exchange of hexafluorophosphate anion for trifluoromethanesulfonate anion in carbonyl( $h^2$ -1,2-cycloheptadiene)( $h^5$ -cyclopentadienyl)triphenylphosphineiron(II)

A methanol solution containing the  $h^2$ -1,2-cycloheptadiene Fpp trifluoromethanesulfonate and an excess ammonium hexafluorophosphate was filtered into water. A yellow precipitate fell out of solution. The compound was isolated via filtration, washed with water and air dried. The exchange was quantitative and the NMR is identical to the trifluoromethanesulfonate salt of the compound synthesized here. The IR shows hexafluorophosphate absorption ( $850\text{ cm}^{-1}$ ) in place of the trifluoromethanesulfonate absorption ( $1270, 1150\text{ cm}^{-1}$ ).

Synthesis of carbonyl( $h^1$ -carbonyl-(7-methoxy)cyclohepten-1-yl)( $h^5$ -cyclopentadienyl)triphenylphosphineiron(II)

A mixture of  $h^1$ -(7-methoxy)cyclohepten-1-yl) Fp (1.11 g; 3.6 mmole) and triphenylphosphine (1.29 g; 4.8 mmole) in 30 ml of acetonitrile was heated to  $+50^\circ\text{C}$  for 20 hrs. Acetonitrile was removed and the red oil was eluted down a 3" x 1" alumina column (neutral, grade II) first with a 1:1 v/v mixture of n-pentane/benzene followed by a 1:1 v/v mixture of benzene/ethyl acetate. A red band was collected

giving 1.0 g (37%) of the desired product as an orange solid. The compound was obtained in a 50:50 diastereomeric composition determined by NMR measurements of the methoxy hydrogen resonances. Mp. 120°-122°d; IR (KBr) 1914s, 1558s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) a) diastereomer A 1.00-2.70 (b,8H), 3.11 (s,3H), 3.44 (d,1H), 4.45 (d,  $^3J_{\text{PH}}=1.16\text{Hz}$ ,5H), 6.87 (dt,1H), 7.24-7.64 (b,15H); b) diastereomer B 1.00-2.70 (b,8H), 2.89 (s,3H), 4.02 (d,1H), 4.41 (d,  $^3J_{\text{PH}}=1.22\text{Hz}$ ,5H), 6.54 (dt,1H), 7.24-7.64 (b,15H);  $^{13}\text{C}$  NMR (25 MHz,  $\text{CDCl}_3$ ) 24.95, 27.05, 27.53, 29.97 (C3-C6), 55.55 (C8), 75.49 (C7), 85.09 (Cp), 127.78-137.57 (PPh<sub>3</sub>), 146.88 (C2), 158.67, 158.48 (C1), 210.97, 211.11 (CO), 272.71 (>CO); Anal. calcd. for  $\text{C}_{33}\text{H}_{33}\text{O}_3\text{P}_1\text{Fe}_1$ : C,70.22; H,5.89; Found: C,70.21; H,5.94.

Separation of diastereomers of carbonyl(h<sup>1</sup>-carbonyl-(7-methoxy)cyclohepten-1-yl)(h<sup>5</sup>-cyclopentadienyl)triphenylphosphineiron (II)

The title compound dissolved in a 1:2 v/v mixture of ethyl acetate/n-pentane was cooled to +10°C. The solid residue was enriched up to 80% of the diastereomer B. The process may be repeated once more with up to 90% enrichment of that diastereomer. The filtrate was only moderately enriched (40%) with the diastereomer A. The diastereomeric compositions were determined by NMR measurements of the methoxy hydrogen resonances.

Attempted decarbonylation of carbonyl(h<sup>1</sup>-carbonyl-(7-methoxy)cyclohepten-1-yl)(h<sup>5</sup>-cyclopentadienyl)triphenylphosphineiron (II)

1) Photolysis

A solution of the title compound was photolyzed at room temperature in benzene with a low pressure Hg lamp (Hanovia; 450 W). The progress of the reaction was followed by IR. There was no reaction after 2 1/2 hrs.

2) Photolysis in an ultrasonic bath

The above experiment was repeated in an ultrasonic bath. A rapid evolution a gas (CO) was observed. The decarbonylated compound was isolated but as a racemate. The unreacted compound recovered has its diastereomeric composition intact.

3) Reaction with trimethylamine-N-oxide

A 5 ml benzene solution of the title compound (0.05 g; 0.08 mmole) and trimethylamine-N-oxide (0.04 g; 0.53 mmole) was stirred at room temperature for 24 hrs. There was no reaction and the compound was recovered with its diastereomeric composition intact.

4) Reaction with chlorobis(triphenylphosphine)rhodium dimer

A 4 ml acetonitrile solution of the title compound (0.02 g; 0.035 mmole) and the rhodium dimer (0.02 g; 0.018 mmole) was stirred at room temperature for 36 hrs.

There was no reaction and the compound was recovered with its diastereomeric composition intact.

#### 5) Reaction with iodosobenzene

A 10 ml methylene chloride solution of the title compound (0.12 g; 0.21 mmole) and iodosobenzene (0.07 g; 0.32 mmole) was stirred at room temperature for 24 hrs. There was no reaction and the compound was recovered unchanged.

#### 6) Thermal decarbonylation

The title compound was heated to +100°C in a p-dioxane for 4 hrs. Both the starting compound and the dephosphinylated compound was recovered from the reaction.

#### Separation of diastereomer of carbonyl(h<sup>5</sup>-cyclopentadienyl)h<sup>1</sup>-(7-methoxy)cyclohepten-1-yl)triphenylphosphineiron(II)

The title compound was eluted down a 8" x 1" alumina column (neutral; grade II) with a 1:1 v/v n-pentane/benzene solvent mixture. The broad red band was collected in two halves. Both fractions were enriched in the same diastereomer, diastereomer A, the second fraction (70% enrichment) greater than the first (50% enrichment). Diastereomeric compositions were determined by <sup>1</sup>H NMR measurements of the methoxy hydrogen resonances.

Synthesis of carbonyl( $h^2$ -1,2-cycloheptadiene) ( $h^5$ -cyclopentadienyl) triphenylphosphineiron(II) trifluoromethanesulfonate from the enriched carbonyl( $h^5$ -cyclopentadienyl) ( $h^1$ -(7-methoxy)cyclohepten-1-yl) triphenylphosphineiron(II) (80:20)

The title compound was synthesized from a 80:20 diastereomeric mixture of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp in a 1:1 v/v pentane/benzene solvent mixture according to procedures developed here. The compound with a diastereomeric ratio of 60:40 was isolated in 40% yields. The diastereomeric composition was determined by NMR measurements of the cyclopentadienyl hydrogen resonances. The  $^1H$  NMR and IR are in agreement with the known compound synthesized here.

Reaction between carbonyl( $h^5$ -cyclopentadienyl) ( $h^1$ -(7-methoxy) cyclohepten-1-yl) triphenylphosphineiron(II) with a half equivalent of trimethylsilyl trifluoromethanesulfonate

To the title compound (0.63 g; 1.17 mmole) with a 55:45 diastereomeric ratio in a 1:1 v/v n-pentane/benzene solvent mixture was added TMSOTf (0.11 ml; 0.6 mmole). The solvent was removed leaving behind a residue from which  $h^2$ -1,2-cycloheptadiene Fpp was precipitated from ethyl acetate and isolated via filtration (0.33 g; 85% yield based on TMSOTf) in a 64:36 diastereomeric ratio. The starting material was reisolated quantitatively (based on TMSOTf) from the filtrate in a 10:90 diastereomeric ratio.

Synthesis of carbonyl( $h^2$ -1,2-cycloheptadiene) ( $h^5$ -cyclopentadienyl) triphenylphosphineiron(II) trifluoromethanesulfonate from the enriched carbonyl( $h^5$ -cyclopentadienyl) ( $h^1$ -(7-methoxy)cyclohepten-1-yl) triphenylphosphineiron(II) (15:85)

The title compound was synthesized from a 15:85 diastereomeric mixture of  $h^1$ -(7-methoxy)cyclohepten-1-yl Fpp in a 1:1 v/v pentane/benzene solvent mixture according to procedures developed here. The compound with a diastereomeric ratio of 80:20 was isolated in negligible yields. The  $^1H$  NMR and IR are in agreement with the known compound synthesized here.

Synthesis of dicarbonyl( $h^5$ -cyclopentadienyl) ( $h^1$ -(7-ethoxy)cycloheptadien-1-yl) iron(II)

The title compound was made according to the procedure developed here substituting 1-bromo-7-ethoxycycloheptene for 1-bromo-7-methoxycycloheptene with a 48% yield. The NMR and IR are consistent with the known compound.<sup>14</sup> IR (neat) 2005s, 1950s  $cm^{-1}$ ,  $^1H$  NMR (100 MHz,  $CDCl_3$ ) 1.20 (t,3H), 1.08-2.40 (m,8H), 3.43 (m,2H), 3.97 (d,1H), 4.80 (s,5H), 5.81 (t,1H).

Synthesis of carbonyl( $h^5$ -cyclopentadienyl) ( $h^1$ -(7-ethoxy)cycloheptadien-1-yl) triphenylphosphineiron(II)

The title compound with a diastereomeric of 50:50 was synthesized according to the same procedure developed here for its 7-methoxy analogue in a 76% yield. Diastereomeric composition was determined by NMR measurements of the

cyclopentadienyl hydrogen resonances. IR ( $\text{CHCl}_3$ ) 1910s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) a) diastereomer A 1.11(t,3H), 0.92-2.32(b,8H), 3.10(m,2H), 3.79(d,1H), 4.35(d,  $^3J_{\text{PH}}=0.95\text{Hz}$ ,5H), 5.63(t,1H), 7.12-7.43(m,15H); b) diastereomer B 1.11(6,3H), 0.92-2.32(b,8H), 3.50(m,2H), 3.91(d,1H), 4.40(d,  $^3J_{\text{PH}}=0.97\text{Hz}$ ), 5.25(t,1H), 7.12-7.43(m,15H);  $^{13}\text{C}$  NMR (25 MHz,  $\text{CDCl}_3$ ) 15.89(- $\text{CH}_3$ ), 25.93, 17.63, 20.17, 31.58(C3-C6), 63.21(- $\text{OCH}_2$ -), 84.36(Cp), 91.28(C7), 127.54-137.82( $\text{PPh}_3$ ), 141.76(C2), 151,15(C1), 223.49, 222.08(CO); Anal. Calcd. for  $\text{C}_{33}\text{H}_{35}\text{O}_2\text{P}_1\text{Pe}_1$ : C,72.00; H,6.41; Found: C,71.90; H,6.48.

Separation of the diastereomer of carbonyl( $\text{h}^5$ -cyclopentadienyl)( $\text{h}^1$ -(7-ethoxy)cycloheptadien-1-yl)triphenylphosphineiron (II)

The title compound was eluted down a 8" x 1" alumina column (neutral, grade II) with a 1:1 v/v n-pentane/benzene mixture. The broad red band was collected in two parts, the first 1/3 and the second 2/3. Both fractions were enriched in the same diastereomer, diastereomer B, the second fraction (60% enrichment) greater than the first fraction (20% enrichment). Diastereomeric compositions were determined by  $^1\text{H}$  NMR measurements of cyclopentadienyl hydrogen resonances.

Synthesis of carbonyl( $h^2$ -1,2-cycloheptadiene) ( $h^5$ -cyclopentadienyl) triphenylphosphineiron(II) trifluoromethanesulfonate from carbonyl( $h^5$ -cyclopentadienyl) ( $h^1$ -(7-ethoxy)cyclohepten-1-yl) triphenylphosphineiron(II)

1) Equal mixture of each diastereomer

The title compound was synthesized according to the procedures developed for its 7-methoxy analogue with a 31% yield using a 1:1 v/v pentane/benzene solvent mixture. The product was isolated as an equal mixture of two diastereomers. The NMR, IR and m.p. are in agreement with the product synthesized here from its 7-methoxy analogue.

2) A 4:1 mixture of diastereomer

The title compound was synthesized according to the above procedures. The product was isolated as an equal mixture of two diastereomers.

Epimerization of carbonyl( $h^2$ -1,2-cycloheptadiene) ( $h^5$ -cyclopentadienyl) triphenylphosphineiron(II) hexafluorophosphate in the presence of triphenylphosphite

A chloroform- $d_1$  solution of the title compound (0.01 g; 0.018 mmole) and triphenylphosphite (0.03 g; 0.097 mmole) were followed by  $^1H$  NMR for 45 hrs. The NMR remained unchanged and there was no indication (e.g. new cyclopentadienyl hydrogen resonance) that the free triphenylphosphite had replaced the bound triphenylphosphine.

Epimerization of carbonyl(h<sup>2</sup>-1,2-cycloheptadiene)(h<sup>5</sup>-cyclopentadienyl)triphenylphosphineiron(II) trifluoromethanesulfonate in the presence of triphenylphosphine

Two chloroform-d<sub>1</sub> solutions of the title compound with a 80:20 diastereomeric composition were made up; the first (a) containing 10 mg of the compound in 1/2 ml of chloroform-d<sub>1</sub> and the second (b) containing 10 mg of the compound and 20 mg of triphenylphosphine (0.15 M) in 1/2 ml of chloroform-d<sub>1</sub>. The solutions were heated at +30°C and the change in diastereomeric compositions with time were determined by NMR measurements of the cyclopentadienyl hydrogen resonances (accurate to ±2).

	<u>a</u>	<u>b</u>
t= 0 min.	83:17	81:19
10 min.	73:27	72:28
20 min.	70:30	70:30
30 min.	67:33	65:35
∞	63:37	65:35

There was no difference in the rate of equilibration between (a) and (b). The equilibration process is consistent with allene to allyl cation racemization and not epimerization about the iron center via dissociation and reassociation of triphenylphosphine.

Synthesis of dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(h<sup>1</sup>-(6-methoxy)cyclohexen-1-yl)iron(II)

The title compound was synthesized according to the method developed here for its cycloheptene analogue with a

60% yield. The NMR and IR are consistent with the known compound.<sup>14</sup> IR (neat) 2005s, 1950s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ ) 1.15-2.35 (b,6H), 3.40 (s,3H), 3.50 (bs,1H), 4.87 (s,5H), 5.75 (t,1H).

Attempted synthesis of dicarbonyl( $\text{h}^2$ -1,2-cyclohexadiene)( $\text{h}^5$ -cyclopentadienyl)iron(II) trifluoromethanesulfonate

To a cold ( $-78^\circ\text{C}$ ) solution of title compound (0.034 g; 0.12 mmole) in 10 ml of methylene chloride was added TMSOTf. The reaction was allowed to stir for 30 mins at  $-78^\circ\text{C}$  and was quenched with cold ( $-78^\circ\text{C}$ ) diethyl ether. A reddish yellow flocculent precipitate appeared. The precipitate promptly decomposed to a black paste while being filtered at room temperature in an inert atmosphere box.

Attempted synthesis of dicarbonyl( $\text{h}^1$ -1,2-cyclohexadiene)( $\text{h}^5$ -cyclopentadienyl)iron(II) tetrafluoroborate

1) With trimethyloxonium tetrafluoroborate

To a suspension of trimethyloxonium tetrafluoroborate (0.34 g; 2.3 mmole) in 7 ml of cold ( $-78^\circ$ ) methylene chloride was added a 2 ml methylene chloride solution of the  $\text{h}^1$ -(6-methoxy)cyclohexen-1-yl Fp (0.45 g; 1.6 mmole). There was no reaction after 4 hrs and the starting compound was recovered unchanged.

2) With triethyloxonium tetrafluoroborate

To a 5 ml methylene chloride solution of  $\text{h}^1$ -(6-methoxy)cyclohexen-1-yl Fp (0.26 g; 0.9 mmole) at  $-78^\circ\text{C}$  was added

triethyloxonium tetrafluoroborate (1 M solution in  $\text{CH}_2\text{Cl}_2$ ; 0.9 ml; 0.9 mmole). Cold ( $-78^\circ\text{C}$ ) diethyl ether was added 1 hr later to quench the reaction. The reaction mixture remained unchanged but decomposed to a red oil after the solvent was removed and warmed to room temperature.

Low temperature NMR scale synthesis of dicarbonyl( $\text{h}^2$ -1,2-cyclohexadiene) ( $\text{h}^5$ -cyclopentadienyl)iron(II) trifluoromethanesulfonate

The open end of an NMR tube was attached to a 19/22 male joint with a side mounted 3-way stopcock. A narrow stir rod was inserted into the NMR tube and the whole assembly was capped with a closed end 19/22 female joint.

This NMR tube reactor was charged with a plug of a TMSOTf/methylene chloride- $\text{d}_2$  mixture followed by methylene chloride- $\text{d}_2$  and a  $\text{h}^1$ -(6-methoxy)cyclohexen-1-yl Fp/methylene chloride- $\text{d}_2$  mixture. Each of the solvent mixture or solvent was frozen in liq.  $\text{N}_2$  before the next one was added. The frozen plugs were then thawed in cold ( $-78^\circ\text{C}$ ) n-pentane. The female joint was removed under a rapid flushing stream of  $\text{N}_2$  and the reaction mixture were stirred. The stir rod was withdrawn, the female joint replaced and the reaction mixture was frozen again in liq.  $\text{N}_2$ . The NMR tube was sealed under vacuum. The reaction mixture was thawed in the NMR probe with the probe temperature preset at  $-95^\circ\text{C}$ . The progress of the reaction was followed at low temperatures. Refer to Fig. 11 and discussion in Chapter IV.

Synthesis of carbonyl(h<sup>5</sup>-cyclopentadienyl)(h<sup>1</sup>-(6-methoxy)cyclohexen-1-yl)triphenylphosphineiron(II)

The title compound was synthesized in a 35:65 diastereomeric ratio according to the method developed here for its cycloheptene analogue with a 15% yield. Diastereomeric composition was determined by NMR measurements of the methoxy hydrogen resonances. IR (CHCl<sub>3</sub>) 1915s cm<sup>-1</sup>; <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) 1.0-2.2(b,6H), 3.18, 3.35(s,3H), 3.23(m,1H), 4.42, 4.30(d, <sup>3</sup>J<sub>PH</sub>=1.22,5H), 5.16, 5.40(m,1H), 7.32(s,15H); <sup>13</sup>C NMR (25 MHz, CDCl<sub>3</sub>) 17.93, 22,97, 31,26(C3-C5), 55.61(C7), 84.11(Cp), 86.65, 86.75(C6), 140.06, 140.21(C2), 144,50, 145.47(C1), 127.58-136.06(PPh<sub>3</sub>), 222.13, 223.42(CO); Anal. calcd. for C<sub>31</sub>H<sub>31</sub>O<sub>2</sub>P<sub>1</sub>Fe<sub>1</sub>: C,71.27; H,5.98; Found: C, 72.69; H, 6.30.

Attempted synthesis of carbonyl(h<sup>2</sup>-1,2-cyclohexadiene)(h<sup>5</sup>-cyclopentadienyl)triphenylphosphineiron(II) trifluoromethanesulfonate

To h<sup>1</sup>-(6-methoxy)cyclohexen-1-yl Fpp (0.55 g; 1.0 mmole) dissolved in an 1:1 v/v mixture of n-pentane and benzene at -10°C was added TMSOTf (0.2 ml; 1.0 mmole). The reaction mixture was allowed to stir for 1 hr after which the solvent mixture was removed in vacuo. Ethyl acetate was added to the dark residue but the desired product failed to precipitate from the solution.

The same reaction in pentane yielded a greenish yellow solid isolated via filtration under N<sub>2</sub>. The solid is stable and can be kept at -35°C for several days. A solution of

the solid decomposes instantly to a dark green solution.  
M.p. >200°C (the solid does not melt); IR (KBr) 1962s  $\text{cm}^{-1}$ .

Reaction of carbonyl( $\text{h}^1$ -(6-methoxy)cyclohexen-1-yl)( $\text{h}^5$ -cyclopentadienyl) triphenylphosphineiron(II) with trimethylsilyl trifluoromethanesulfonate followed by addition of ethanol

To the title compound (0.33 g/ 0.63 mmole) dissolved in 10 ml of pentane at 0°C was added TMSOTF (0.2 ml; 0.63 mmole). An orange precipitate fell out of solution immediately. The precipitate was allowed to settle and the pentane above was removed via a cannula. The precipitate was washed twice (15 ml each) with cold (-78°C) pentane and the wash removed via a cannula. The precipitate was then cooled to -78°C and a slurry of sodium carbonate in cold ethanol (-78°C) was added. The reaction mixture was allowed to warm to room temperature over a 2 hr period.

The reaction mixture was adsorbed onto alumina and eluted down a 1 1/2" x 1" alumina column (neutral, grade II) first with hexane followed by benzene. A red band eluted by benzene was collected and gave 0.17g (50% yield) of the  $\text{h}^1$ -(6-ethoxy)cyclohexen-1-yl Fpp as a red oil. IR (KBr) 1905s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ) 1.17 (t, 3H), 1.24-2.00 (b, 6H), 3.27 (s, 1H), 3.50 (m, 2H), 4.35 (d, 5H,  $^3\text{J}_{\text{PH}}=0.97\text{Hz}$ ), 5.04 (t, 1H), 7.21 (s, 15H);  $^{13}\text{C}$  NMR (25 MHz,  $\text{CDCl}_3$ ) 16.14(- $\text{CH}_3$ ), 18.96, 30, 12, 30.95 (C3-C5), 63.99(- $\text{OCH}_2$ -), 84.12(C6), 84.65(Cp), 139.38(C2,  $^3\text{J}_{\text{PC}}=7.33\text{Hz}$ ), 145.08(C1,  $^2\text{J}_{\text{PC}}=26.86\text{Hz}$ ), 127.54-137.77( $\text{PPh}_3$ ),

222.44 (CO,  $^2J_{PC}=32.95\text{Hz}$ ); Anal. calcd. for  $\text{C}_{32}\text{H}_{33}\text{O}_2\text{P}_1\text{Fe}_1$ :  
C, 71.64; H, 6.20; Found: C, 71.78; H, 6.26.

APPENDIX

X-RAY CRYSTAL STRUCTURE OF  
 CARBONYL ( $h^2-1,2$ -CYCLOHEPTADIENE) ( $h^5$ -CYCLOPENTADIENYL)  
 TRIPHENYLPHOSPHINEIRON(II) HEXAFLUOROPHOSPHATE

Crystal data:  $[C_{31}H_{30}OPFe]^+PF_6^-$ ,  $M=650.4$ , triclinic, space group  $P\bar{1}$ ,  $a=9.998(3)\text{\AA}$ ,  $b=10.801(3)\text{\AA}$ ,  $c=14.675(4)\text{\AA}$ ,  $\alpha=91.40(2)^\circ$ ,  $\beta=107.32(2)^\circ$ ,  $\gamma=101.24(2)^\circ$ ,  $V=1478.1(6)\text{\AA}^3$ ,  $D_c=1.46\text{ g cm}^{-3}$ ,  $F(000)=668$ ,  $\mu(\text{Mo K}\alpha)+7.0\text{ cm}^{-1}$ . Nicolet R3m diffractometer, 4406 reflections [ $1.5 < 2\theta < 47.0^\circ$ ]. 3743 observed with  $F_o > 3\sigma(F_o)$ . The structure was solved by direct methods (SOLV included in SHELXTL system) and refined using the 'blocked cascade' least-square method. 380 parameters refined: coordinates and anisotropic thermal parameters of non-H atoms, and isotropic thermal factors of H-atoms in 7-membered ring, and a scale factor. The final R and  $R_w$  ( $w=1/\sigma^2$ ) values are 0.052 and 0.042, respectively. The atomic coordinates for this work are available on request from the Director of Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW.

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49. D.L. Thorn; Organometallics, 4, 192 (1985).
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## BIOGRAPHICAL SKETCH

The author was born on September 6, 1956, in Singapore. His family later moved to Malaysia where he grew up and became a citizen. He received his early education at Sam Tet School in Ipoh. He left Malaysia before completing his Sixth Form studies and came to Furman University in South Carolina. He graduated from Furman in June 1979 with a B.S. in chemistry. The author also received a M.S. in polymer science and engineering from the University of Massachusetts in September 1980. He came to the University of Florida in September 1980 and studied under Dr. W.M. Jones.

The author enjoys cooking and is often told that he is an excellent cook and baker. He also considers organic chemistry a great culinary experience. His hobbies include scuba diving, sailing, downhill skiing and bicycling. He also holds a private pilot license and prefers flying to jumping out of perfectly good airplanes. He loves classical music, theater, ballet and opera and is a piano student.

The author is a big brother with the Big Brothers and Big Sisters of Gainesville and supports the manatees in Florida.

The author has accepted a postdoctoral position with Dr. Michael Doyle of Trinity University in San Antonio, Texas.

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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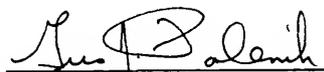
William M. Jones, Chairman  
Professor of Chemistry

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.

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John F. Helling  
Professor of Chemistry

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Gus J. Palenik  
Professor of Chemistry

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John G. Dorsey  
Associate Professor of  
Chemistry

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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 School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May 1987

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