

THERMAL AND PHOTO-INDUCED REARRANGEMENTS OF SIGMA-BOUND  
CYCLOPROPYL IRON COMPLEXES:  
SYNTHESIS OF A NOVEL METALLACYCLIC IRON DICARBENE COMPLEX

BY

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To my mother and to my father, who taught me about the things that are of real importance: love, dedication, strength and sacrifice, I dedicate this work.

### ACKNOWLEDGEMENTS

This work would have not been possible without the patience and guidance of Dr. W.M. Jones. It truly has been a pleasure to work for him and learn from him. My stay at Florida was made memorable by the many people who have become my friends. Drs. Daly, Sousa, Lisko, Oon and Dolbier have made utterly unique and quite distinctive contributions to my education. I thank them one and all. Thanks also go to Mr. Charles Lindsey for reasons which I must admit escape me. Finally, I acknowldege Miss Amy Fox Rankin who has sustained me with her warmth, cheered me with her laughter and honored me with her love. From the very first day I spied her on the soccer field she has occupied all of my thoughts and all of my heart.

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THERMAL AND PHOTO-INDUCED REARRANGEMENTS OF SIGMA-BOUND  
CYCLOPROPYL IRON COMPLEXES:  
SYNTHESIS OF A NOVEL METALLACYCLIC IRON DICARBENE COMPLEX

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Major Department: Chemistry

It is herein reported that the alpha-methoxy and ethoxy substituted dicarbonyl( $h^5$ -cyclopentadienyl)(cyclopropyl)iron sigma complexes have been prepared and that upon photolysis they rearrange to form 1-carbonyl-1- $h^5$ -cyclopentadienyl-5-alkoxyferracyclopent-5-en-2-one. The intermediate 1-carbonyl-1- $h^5$ -cyclopentadienyl-2-ethoxy-1-ferracyclobutene has been spectroscopically detected and its chemistry was investigated. Evidence that the alkyl alpha-elimination is reversible has been obtained. Photolysis of the aforementioned sigma complexes also results in the production of two pi-allylic species, carbonyl( $h^5$ -cyclopentadienyl)(exo- $h^3$ -2-ethoxypropenyl)iron and carbonyl( $h^5$ -cyclopentadienyl)(exo- $h^3$ -syn-1-ethoxypropenyl)iron.

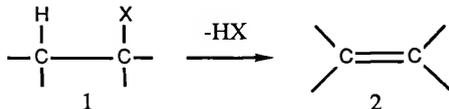
The phosphine substituted carbonyl( $h^5$ -cyclopentadienyl)(1-ethoxycyclopropyl)(triphenylphosphine)iron was used to demonstrate the first reported thermally induced rearrangement of a cyclopropyl complex to form an acyl-carbene. The product, 1- $h^5$ -cyclopentadienyl-1-triphenylphosphine-5-ethoxyferracyclopent-5-en-2-one, was independently prepared by photolysis of the carbonyl substituted ferracyclopentenone in the presence of triphenylphosphine.

Dicarbonyl( $h^5$ -cyclopentadienyl)(1-thiophenylcyclopropyl)iron was prepared and, upon photolysis, lost carbon monoxide forming a sulfur chelate. When heated, the photoproduct rearranged to form the pi-allylic carbonyl( $h^5$ -cyclopentadienyl)(exo- $h^3$ -2-thiophenylpropenyl)iron.

The cis and trans beta fluoro-substituted dicarbonyl( $h^5$ -cyclopentadienyl)cyclopropyliron sigma complexes were prepared. It was found that photolysis of the trans complex produced the carbonyl( $h^5$ -cyclopentadienyl)(exo- $h^3$ -syn-fluoropropenyl)iron pi-allyl complex. Treatment of 1-bromo-1-fluoro-trans-2,3-dimethylcyclopropane with potassium dicarbonyl( $h^5$ -cyclopentadienyl)ferrate produced the fluoride salt of dicarbonyl( $h^5$ -cyclopentadienyl)( $h^2$ -1,3-dimethylallene)iron. Finally, the novel iron dicarbene complex 1-carbonyl-1- $h^5$ -cyclopentadienyl-2-ethoxy-5-methoxyferracyclopenta-1,5-diene tetrafluoroborate was produced from an acyl-carbene complex.

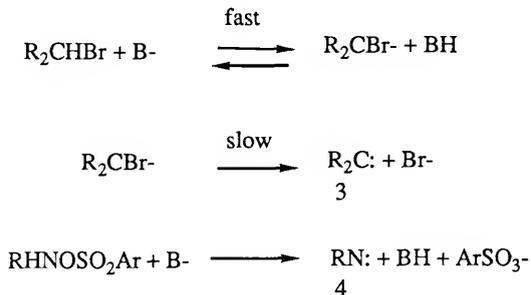
CHAPTER I  
INTRODUCTION

Eliminations are one of the fundamental categories of organic reaction types. Commonly, two atoms or groups of atoms are lost from adjacent atoms to produce a new bond. Such a process is depicted in the conversion of 1 to 2.

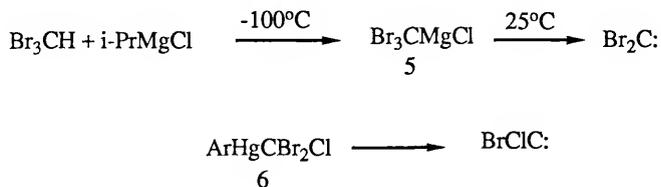


When both groups are lost from the same atom, the term alpha-elimination is used to describe such a reaction.

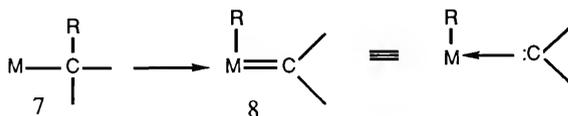
Alpha-eliminations are typically believed to proceed via an  $S_N1cA$  mechanism.<sup>1</sup> The products of such reactions are either carbenes, 3, or nitrenes, 4, depending upon the



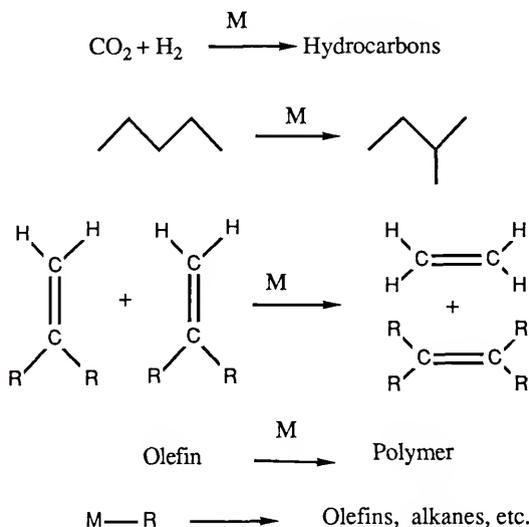
initial reactant. The alpha-elimination of a metal and a halogen atom has also been invoked to explain the formation of carbenes and/or carbenoid species produced when alpha-halo Grignard reagents, 5, are warmed from -100°C to room temperature.<sup>2</sup> It is also implicated in the thermolysis of Seyferth reagents 6.<sup>3</sup>



One also finds the term alpha-elimination used in the realm of the organometallic chemistry of transition metals. Here the reaction involves the migration of an atom or group from an atom adjacent to a metal center to the metal center itself. Using the nomenclature applied to organic systems it may be termed a [1,2] sigmatropic rearrangement; it is more formally referred to as a 1,1-elimination in the organometallic literature.<sup>4</sup> Like its organic counterpart, the product of an organometallic alpha-elimination reaction is a carbene; however, in this case the carbene is complexed to a metal.



The importance of studying the alpha-elimination reaction lies in the fact that it has been postulated as a crucial step in many important catalytic processes and interesting organometallic transformations. These include the Fischer-Tropsch process,<sup>5</sup> hydrocarbon rearrangement catalysts,<sup>6</sup> olefin metathesis catalysts,<sup>7</sup> the Ziegler-Natta polymerization process,<sup>8</sup> and the decomposition of metal alkyl complexes.<sup>9</sup> Study of the alpha-elimination may result



not only in a better understanding of a fundamental organometallic reaction, but may also lead to the improvement of any of the aforementioned industrial or synthetically useful processes.

The alpha-elimination reaction resembles in some ways two familiar rearrangements from organic chemistry: the Wagner-Meerwein rearrangement and the 1,2-carbene rearrangement. In these processes a vacant orbital exists on a carbon atom adjacent to the migrating group. After the group migrates to the vacant orbital with its electron pair, the result of this electronic reorganization is the formation of a new carbocation, 9, in the former and a carbon-carbon double bond in 10 in the latter. The



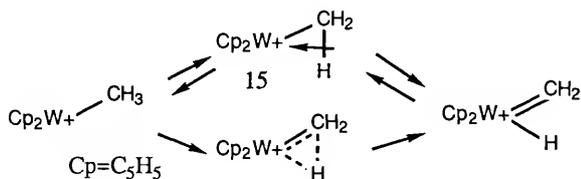
alpha-elimination reaction occurs when the metal center possesses a vacant orbital as in 11 and an atom or group on



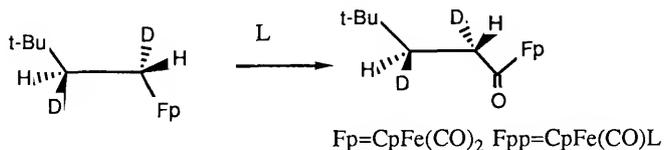
an adjacent carbon atom which can migrate with its electron pair. The resulting species contains a carbon atom sigma bound to the metal and possessing an empty p-orbital as in 12. If the metal has a filled d-orbital properly disposed and favorably matched energetically such as in 13, (d-p) pi backbonding can occur resulting in the formation of a carbene complex 14.



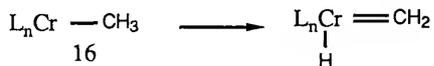
The mechanism of the alpha-elimination process has not been established. There is evidence indicating that electron transfer<sup>10</sup> and intermolecular radical abstraction<sup>11</sup> operate in some metal systems. Migrations both concerted and proceeding through discrete intermediates involving agostic interactions as in 15 have also been invoked to explain experimental results.<sup>12</sup> In studying decarbonylation



reactions of iron systems, a process which is formally the reverse of a 1,1-or alpha-elimination, Whitesides found that the reaction proceeds with retention of configuration at the migrating carbon.<sup>13</sup> The principle of microscopic reversibility suggests therefore that the reverse reaction, which is an alpha-elimination from a carbonyl center, may be concerted.

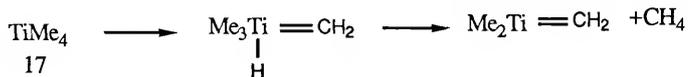


The observation of alpha-eliminations of hydride from a metal alkyl has been reported by several research groups and for many different metal systems. One of the earliest reports of an alpha-elimination of hydride appeared in 1968 for the chromium methyl complex 16.<sup>14</sup> Zeiss performed



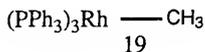
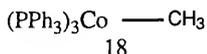
labelling studies on these compounds which supported the alpha-elimination mechanism proposed by Michmann.<sup>15</sup>

As was previously stated, the decomposition of metal alkyl complexes is thought to involve alpha-eliminations. Khrushch studied the decomposition of the homoleptic alkyl complex 17.<sup>16</sup> His findings were consistent with a mechanism

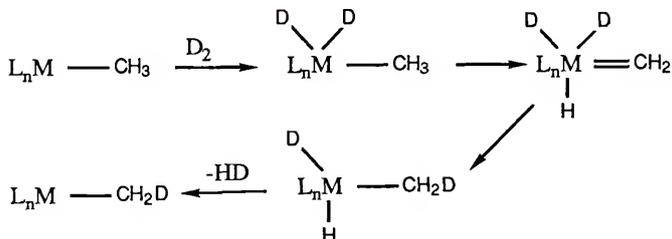


involving alpha-elimination followed by reductive elimination.

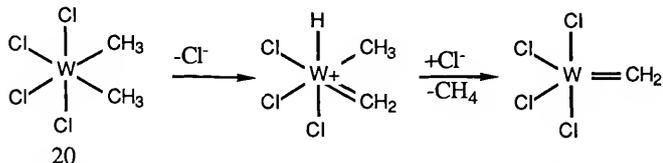
Yamamoto performed studies involving cobalt and rhodium methyl complexes.<sup>17</sup> When exposed to D<sub>2</sub> the compounds 18 and 19 were found to incorporate deuterium into their methyl



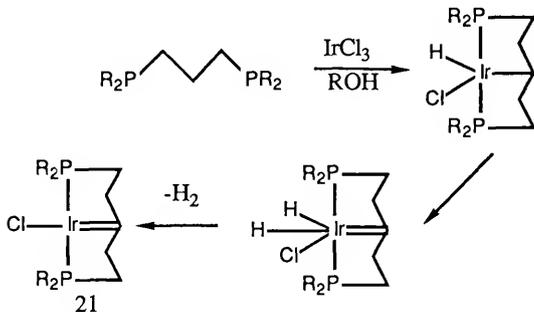
groups. His mechanistic studies support the involvement of the alpha-elimination in the reaction pathway.



Muetterties proposed an alpha-elimination of hydride from a dimethyl tungsten complex 20.<sup>18</sup> As with the examples above, the final product, a carbene, was thought to form via a reductive elimination of methane.

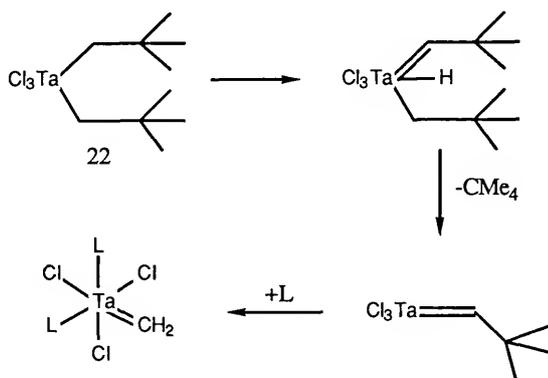


The oxidative addition of a C-H bond as well as an alpha-elimination of hydride was proposed by McDonald in order to explain the isolation of carbene complex 21 upon

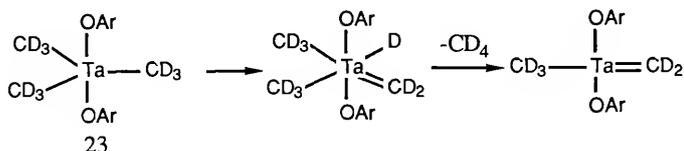


combining iridium(III)chloride with an alpha, omega-diphosphine.<sup>19</sup> It is of interest to note that both the oxidative addition and the alpha-elimination involve the same carbon atom. This is equivalent to the conversion of  $R_2CH_2$  into  $R_2C$ : by the iridium center with the concomitant loss of dihydrogen, a formidable task if restricted to classical organic techniques of carbene preparation.

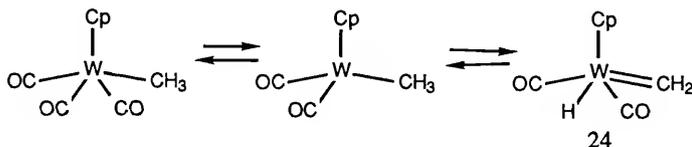
There has been much work done involving tantalum systems which alpha-eliminate hydride. Both Skapski<sup>20</sup> and Schrock<sup>21</sup> have studied electron deficient tantalum species such as 22 and their reactions with nucleophiles or



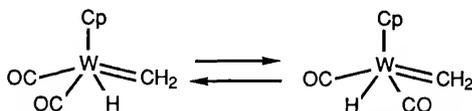
nucleophilic donor ligands. Chamberlain has reported photolytically induced alpha-elimination of hydride from 23.<sup>22</sup>



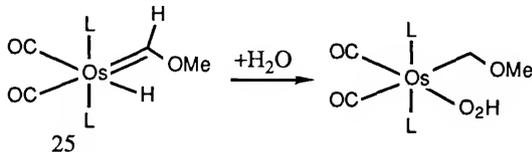
Another system in which photo-induced alpha-elimination of hydride was found is the chromium methyl complex  $\text{CpW}(\text{CO})_3\text{Me}$ . Matrix IR studies reveal that upon loss of carbon monoxide to create a vacant site on the metal, the methylidene complex 24 is formed. Upon exposure to CO, the



sigma complex is again formed indicating that the hydride elimination is reversible.<sup>23</sup> Peters reproduced this work and found that the trans hydrido-methylidene complex 24 is the thermodynamic product of the reaction. He observed that the first formed carbene has a cis configuration and quickly



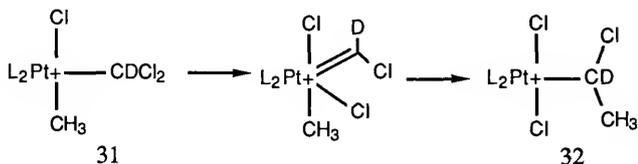
isomerizes to the trans.<sup>24</sup> Indeed the reverse of hydride alpha-elimination was demonstrated by Roper for the osmium complex 25.<sup>25</sup>



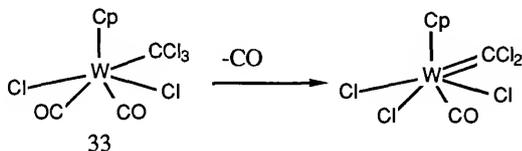
The most thoroughly studied system in which an alpha-elimination of hydride occurs is Green's dicyclopentadienyl



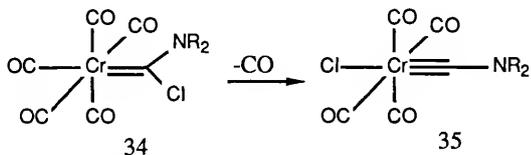
the elimination of halogen atom from 31 followed by the migration of a methyl group to the carbenic center (the



reverse of the alpha-elimination) to produce the metal alkyl 32.<sup>11, 32</sup> Goldman and Tyler have postulated the alpha-elimination of chloride in the tungsten complex 33.<sup>33</sup>

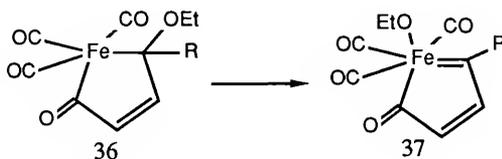


Finally, Fischer reported a rearrangement which produces the carbyne complex 35.<sup>34</sup> He postulates that an alpha-elimination of chloride concomitant with CO loss from 34 is responsible for producing the carbyne complex.

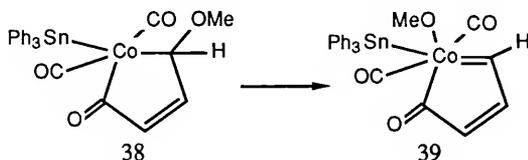


The alpha-elimination of an alkoxy group has been postulated by two groups to rationalize products isolated in their works. Semmelhack proposes the elimination of ethoxide from 36 to produce the ephemeral carbene complex 37

which reacts further to produce various organic products which can be rationalized from the structure of 37.<sup>35</sup> Wulff

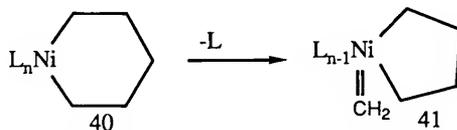


proposes a similar rearrangement involving methoxide from the cobalt complex 38 to give the carbene complex 39.<sup>36</sup>



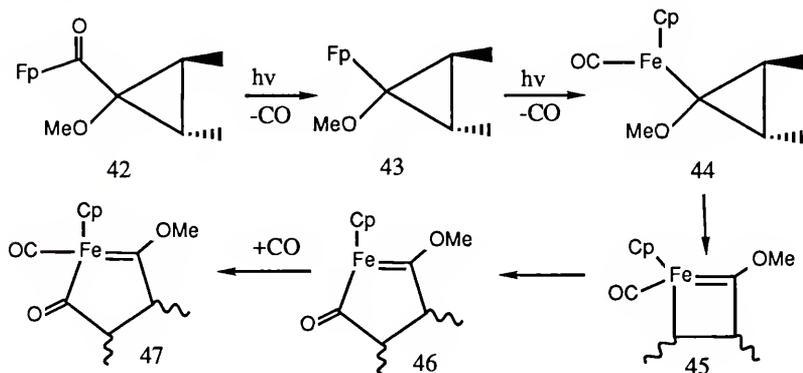
Little if any experimental evidence was given for the existence of the carbene complexes 37 or 39.

Prior to investigations carried out by members of Jones' research group at the University of Florida, there was only one report of the alpha-elimination of an alkyl group. Grubbs carried out mechanistic studies which implicated the ring contraction of the nickellacyclohexane



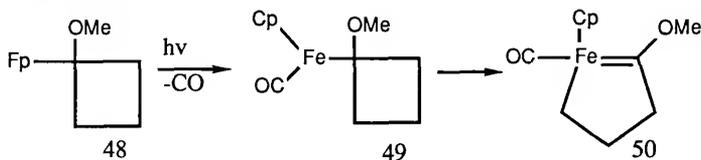
40 to the alkyl-carbene complex 41.<sup>37</sup> It should be noted that the carbene complex was not isolated or detected.

The first reported isolation of a carbene complex derived from the alpha-elimination of an alkyl group was that of Lisko and Jones in 1985.<sup>38</sup> Photolysis of the iron acyl complex 42 resulted in the isolation of the sigma complex 43 and the acyl-carbene complex 44. A mechanism was proposed in which the acyl complex 42 decarbonylated to give the sigma complex 43. Complex 43 then underwent photo-induced decarbonylation to give the 16e- coordinatively unsaturated intermediate 44 which went on to give the 18e- carbene complex 45 via the alpha-elimination of an alkyl group of the cyclopropane ring. Complex 47 was thought to be produced by ligand induced carbonylation of carbene complex 45 via the unsaturated acyl complex 46.

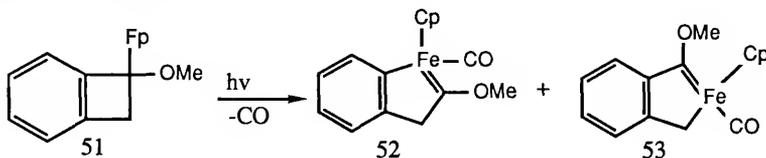


This initial report was followed by two other examples of such a rearrangement. The cyclobutyl sigma complex 48 produced the alkyl, carbene complex 50 presumably through

the unsaturated intermediate complex 49.<sup>39</sup> Two carbene complexes, 52 and 53, were isolated from the photolysis of

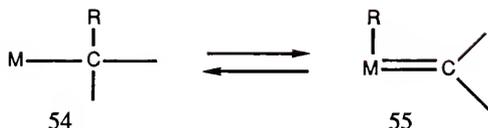


the benzocyclobutyl sigma complex 51.<sup>40</sup> The last result is interesting in that it includes the report of both the alpha-elimination of an alkyl and an aryl group.



It is perhaps surprising to note that the reports of alpha-eliminations of alkyl and aryl groups are less numerous than the occurrence of the elimination of hydrides. This may be the case simply because such rearrangements have not been actively sought in appropriate systems. However, at least one researcher believes the paucity of alkyl eliminations correlates with an innate thermodynamic difference between the migration of an alkyl group and that of a hydride.

Cooper and Green considered the equilibrium between a metal alkyl, 54, and a carbene resulting from an alpha-elimination, 55. In 1979, they noted the 1,1-eliminations

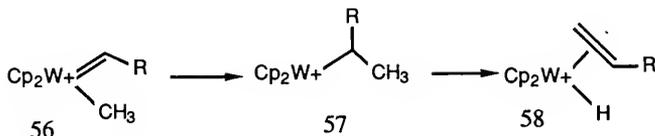


to produce carbenes had not been frequently observed. It was their opinion that the reason for this may be that the equilibrium normally lay toward the left-hand side.<sup>41</sup>

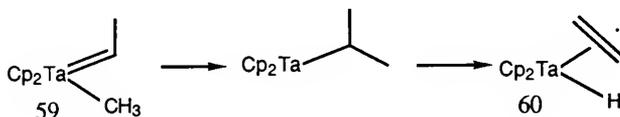
A simple way of evaluating this assertion would be to compare the bond strengths in 54 and 55. Whereas extensive tabulations of bond energies exist in the literature for organic compounds, there are no extensive nor reliable bond energies for applicable organometallic systems at this time.<sup>42</sup> A further difficulty is that in the typical process the species 54 is usually envisioned as a coordinatively unsaturated entity and 55 is not. Bond strengths in unsaturated species may be quite different from similar bonds in saturated species.<sup>43</sup> Other evidence must be sought to evaluate Cooper and Green's contention.

If one searches the literature, examples can be found where an alkyl-carbene complex spontaneously rearranges to an unsaturated metal alkyl which then undergoes further reaction to complete its coordination sphere. Cooper has reported a tungsten system in which the carbene complex 56 rearranges to give the unsaturated alkyl 57. This complex

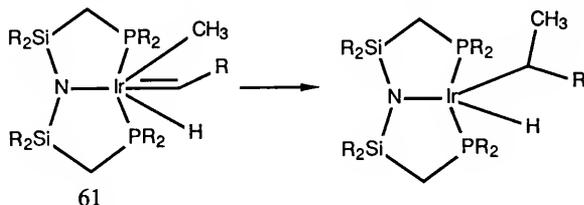
undergoes beta-hydride elimination to produce the olefin complex 58.<sup>10, 44</sup>



Schrock finds that his tantalum carbene complex 59 gives the hydrido-alkene complex 60. He proposes an alpha-elimination of the methyl group to explain the occurrence of



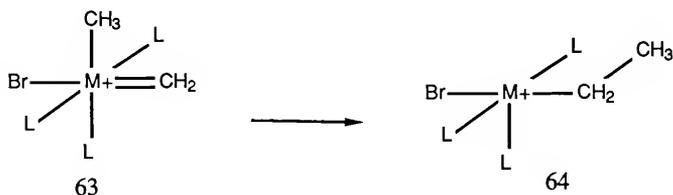
the product.<sup>45</sup> Fryzuk has proposed that complex 61 rearranges to give complex 62.<sup>46</sup> This result is quite



interesting since either the migration of a hydride or an alkyl group from the metal to the carbenic center can occur from 61. This implies, although not necessarily, that there may be a preference for the migration of the alkyl group over the hydride. If 61 and 62 are in equilibrium, this may

reflect a thermodynamic difference; if they are not, it may reflect a difference in the activation energy for the migration.

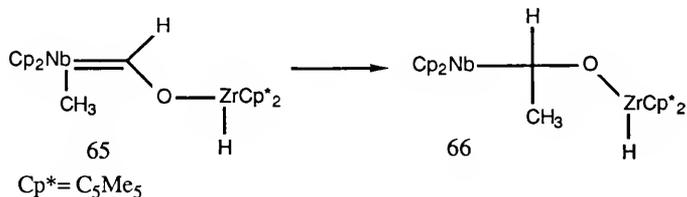
Thorn has reported spontaneous migration of alkyl groups upon generating carbenes in both iridium and rhodium systems.<sup>47</sup> When the carbene complex 63 is prepared from the corresponding methoxy substituted alkyl complex via



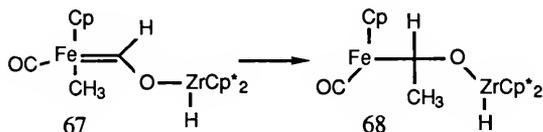
M= Ir, Rh

alkoxide abstraction, complex 64 is formed. The unsaturated 64 then completes its coordination sphere and quenches its positive charge by combining with bromide ion which is present in solution.

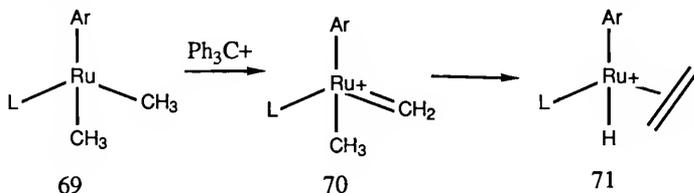
The migration of hydride, methyl or benzyl from the niobium carbene complex 65 was studied by Bercaw.<sup>48</sup> He



found the order of migratory aptitude to be  $H \gg CH_3 > CH_2Ph$ . He further extended the observed rearrangement to cobalt, rhodium, iron and ruthenium systems.<sup>49</sup> The conversion of 67 to 68 is representative.



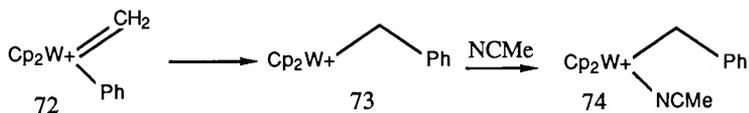
Finally, Werner published the results of the reaction of trityl cation with the ruthenium complex 69.<sup>50</sup> Instead of isolating the expected carbene complex 70, he reported the isolation and x-ray structure of the hydrido-alkene complex 71. He postulated a mechanism in which 70 is formed



but rearranges via migration of the methyl group to the newly formed methylenide to produce an unsaturated metal alkyl complex. This complex then beta-hydride eliminates to form 71.

The migration of an aryl group to a carbenic center has also been observed. Cooper has published reports in which the tungsten carbene 72 rearranges to produce the

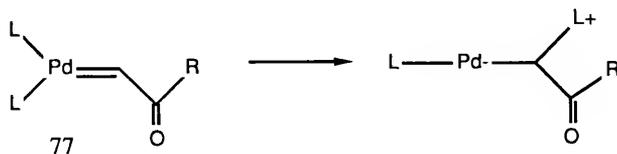
unsaturated alkyl complex 73. Complex 73 then adds acetonitrile to form the saturated alkyl complex 74.<sup>51</sup>



There are also cases in which non-alkyl groups migrate to carbenic centers. Mango reports the iridium carbene 75 rearranges to the stable alkyl 76.<sup>52</sup> This is an example of chloride migration.



The migration of triphenylphosphine was postulated by Collum. The palladium complex 77 undergoes phosphine migration to form an ylide which reacts further.<sup>53</sup>

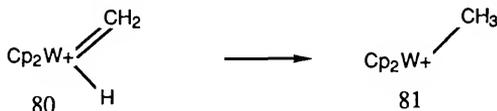


In contrast to the situation which exists for alpha-eliminations, there are far fewer reported examples of

hydride migrating from a metal to a carbenic center than there are when the migrating group is an alkyl. Tulip found that hydride spontaneously moves from the metal to the carbene in the iridium complex 78 to produce the methyl



complex 79 which goes on to acquire iodide.<sup>54</sup> Green observed the reversible migration of hydride in his tungsten system.<sup>12</sup> The rearrangement of the hydride from 80 to 81

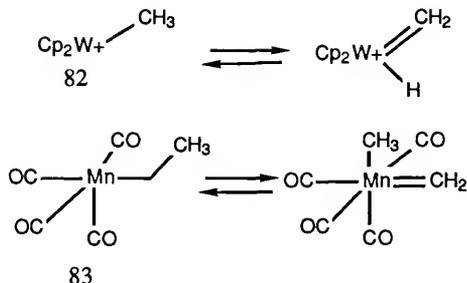


was shown to be rate-determining and a crossover experiment found the migration to be intramolecular.

Once again, definite conclusions based solely on the number of reports of phenomena are impossible. It does, however, provide the probable cause for the origin of Green's thermodynamic caveat against alkyl alpha-eliminations. Of course, it is not inconsistent with his argument.

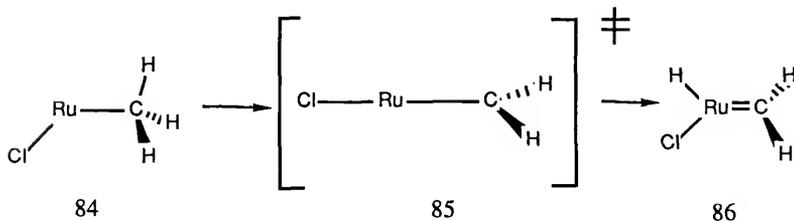
Since the alpha-elimination holds such a primal place in mechanistic organometallic chemistry, it is not surprising to find that the reaction has been the subject of theoretical study. Hoffmann has carried out extended Huckel

calculations for systems in which hydride 82 and methyl 83



alpha-eliminate. He found that the activation energy for converting the alkyl into the carbene to be very close to the thermodynamic difference between the two species.<sup>55</sup> With little activation energy (4.0 kcal°/mol) he predicted that, "one should expect an easy thermal equilibrium of this type." [J. Am. Chem. Soc. 1978, 100, p. 7232]

Goddard performed ab initio calculations, which should yield more reliable values regarding energy differences, on the ruthenium alkyl 84.<sup>56</sup> He found that the lowest energy pathway is concerted one involving a transition state such as 85. Although his system was simplified to expedite the



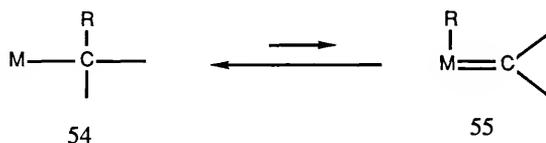
calculation, he came up with an activation barrier of 18.6 kcal/mol for the alpha-elimination of hydride. He posits that the barrier for the elimination of an alkyl is higher and that the process would be endothermic by 4.9 kcal/mol.

The evaluation of the results of these theoretical studies is complicated by two factors. Firstly, Hoffmann's use of EHMO methods leaves one uncertain about the reliability of the absolute magnitudes of the energy differences upon which he bases his conclusions. The similarity of the results in the alkyl and hydride system would certainly suggest that the processes are not wildly different, and the activation energies for both eliminations should be similar. Secondly, although Goddard uses ab initio methods which give more accurate energies, the system which he evaluates has not been studied experimentally: it is a model for extant systems which would be too cumbersome for facile calculation. Therefore while the activation energy calculated for this process should be more reliable than Hoffmann's, it is not clear whether this value would correlate meaningfully with an actually observable alpha-elimination.

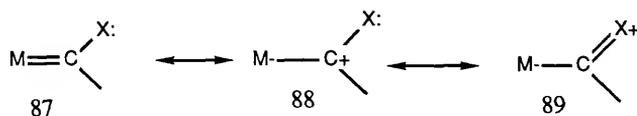
It may be said that these theoretical studies are not inconsistent with Green's contention that the alpha-elimination of an alkyl group is uphill thermodynamically. Indeed, Goddard found the metal alkyl to be favored by

nearly 5 kcal over the alkyl carbene. Whether or not there is a substantial activation barrier for the elimination can not be conclusively stated.

Green's postulate was accepted by Jones in the previously cited works. Jones reasoned that if the metal alkyl 54 and the alkyl-carbene 55 were in equilibrium, then

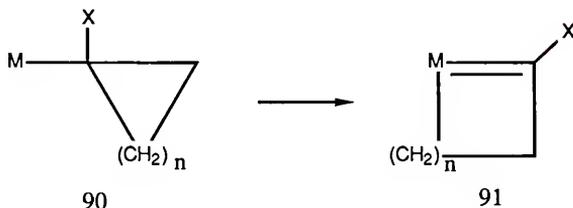


by appropriately perturbing the system the equilibrium could be displaced to favor the carbene 55. The choice was made to stabilize the carbene 55 by substituting at the carbenic center with an electron donating group. Mesomeric stabilization is afforded via the resonance interactions depicted in the canonical forms 87 through 89.



A second strategy was combined with the stabilization of the carbene, namely destabilizing the metal alkyl by the incorporation of ring strain. It was hoped that there would be less strain in the carbene form 91 than in the metal alkyl 90. Therefore, the alpha-elimination of an alkyl

group belonging to the small ring would lead to a certain amount of relief of strain in forming 91. This would drive the reaction toward the carbene.

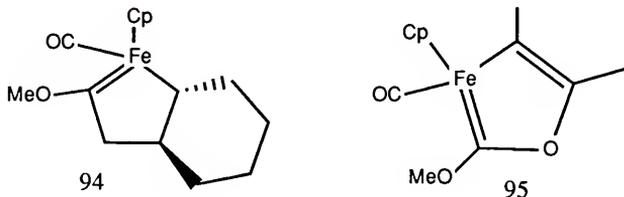


In evaluating this strategy, one cannot dispute that stabilization of an electrophilic, Fischer-type would displace the equilibrium as proposed. Whether the relief of strain energy sought in going from 90 to 91 would be actualized is not as certain. The strain energy incorporated into the metal alkyl can be reliably gauged as 28.3 kcal/mol for a cyclopropyl ring and 27.4 kcal/mol for a cyclobutyl ring.<sup>57</sup> The residual ring strain of the metallacyclobutene, 92, or metallacyclopentene, 93, can

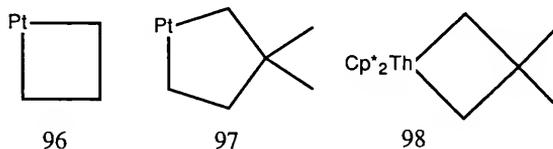


only be estimated. No reliable data exist in the literature concerning the ring strain of metallacyclic carbene complexes. Stable metallacyclic carbene complexes are

known. Compounds 94 and 95 are but two examples.<sup>58</sup> No estimate has been made as to any ring strain present in them.



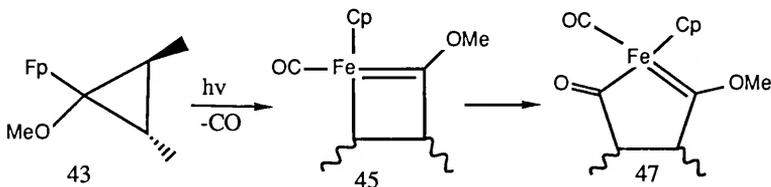
Various groups have estimated strain energies in saturated metallacycles. Puddephatt suggests a strain energy of 9 to 13 kcal/mol for the platinum(IV) metallacyclobutane 96.<sup>59</sup> Whitesides estimates that the



platinacyclobutanes are much less strained than cyclobutane itself. He further found that the ring strain of a platinum(II) metallacyclopentane 97 is less strained than a corresponding metallacyclobutane by no more than 5 kcal/mol.<sup>60</sup> Marks used anaerobic batch-titration calorimetry to calculate the strain energy of the thorium(IV) metallacyclobutane 98.<sup>61</sup> The value he determined by this method was 16 kcal/mol.

The strain energy for 92 should be at least 9-16 kcal/mol. It is not known with certainty whether the incorporation of the metal carbon double bond into the ring would lead to a greater strain energy than this, but that result is not at all unlikely. Extending Whitesides reasoning to this system, 92 should be no more strained than cyclobutene (30.6 kcal/mol).<sup>62</sup> Therefore the rather bloated bound of 9-31 kcal/mol can be set for the strain energy of the metallacyclobutene 92. The possibility therefore exists for strain relief in going from 43 to 45.

Though a definite judgement cannot be made on the magnitude of the strain relief (if any) which accompanied the conversion of 43 to 45, it was the belief of Lisko and



Jones that residual strain in 45 provided the impetus for the carbonylation of the metallacyclobutene to afford the ferracyclopentenone 47. Since carbene stabilization was operant in this case, no estimate was made as to the relative contribution of strain relief versus carbene stabilization in driving the reaction forward. Evidence exists that alkoxy stabilization of a carbene alone will not

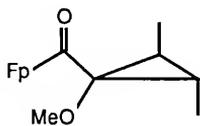
prevent the migration of a methyl group from the metal to the carbenic center.<sup>47c</sup> Furthermore, Grubbs's previously cited work shows that a ring contraction can also occur in the course of an alkyl alpha-elimination.<sup>37</sup>

Therefore, it was the purpose of this research to investigate the rearrangement of dicarbonyl( $h^5$ -cyclopentadienyl)iron cyclopropyl sigma complexes to their corresponding ferracyclopentenones. The mechanism of the rearrangement was probed as to the relative importance of ring strain and carbene stabilization. An attempt was made to obtain evidence for the existence of the intermediates in the mechanism proposed by Lisko and Jones. Furthermore, the chemistry of the novel ferracyclopentenones was also investigated.

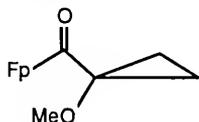
## CHAPTER II

### ALKOXY-CYCLOPROPYL SYSTEMS

The rearrangement of the acyl-cyclopropyl complex 42 to the acyl-carbene complex 46 was the first of its kind reported. It was therefore deemed wise to reproduce the rearrangement by using an acyl-cyclopropyl system which was quite similar to 42. The acyl complex 99 was chosen since



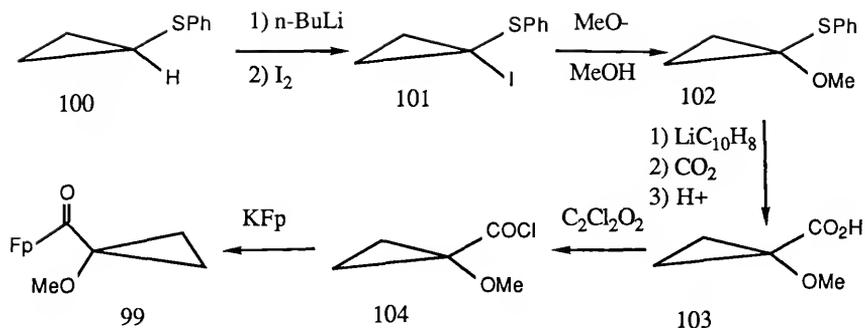
42



99

it differed from 42 only by being sans methyl groups on the beta carbon atoms of the cyclopropyl ring. The effect that beta alkyl substitution on the cyclopropane has on the rearrangement would also be investigated in studying the photolysis of 99.

The synthesis of 99 proceeded via the route shown below. Compounds 101 and 102 were formed in good yield and in a straightforward manner from cyclopropylphenyl sulfide by adapting the procedure reported by Lisko.<sup>63</sup>



However, the carboxylic acid **103** was obtained by reaction of **102** with lithium naphthalenide and carbon dioxide at low temperatures, and this reaction produced the acid in yields ranging from 0 to 70%. Other researchers have reported similar problems with this reaction.<sup>64</sup>

The preparation of **99** was accomplished by reacting the acid chloride **104** with potassium(dicarbonyl)(h<sup>5</sup>-cyclopentadienyl)ferrate (KFp). The yellow crystalline solid was purified by column chromatography and analytical samples were prepared using low temperature recrystallizations from hexanes. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **99** are presented in Figures 1 and 2 respectively.

The photolysis of **99** was carried out in an NMR tube containing carborundum chips and fitted with a rubber septum. The acyl complex was dissolved in C<sub>6</sub>D<sub>6</sub> so that the

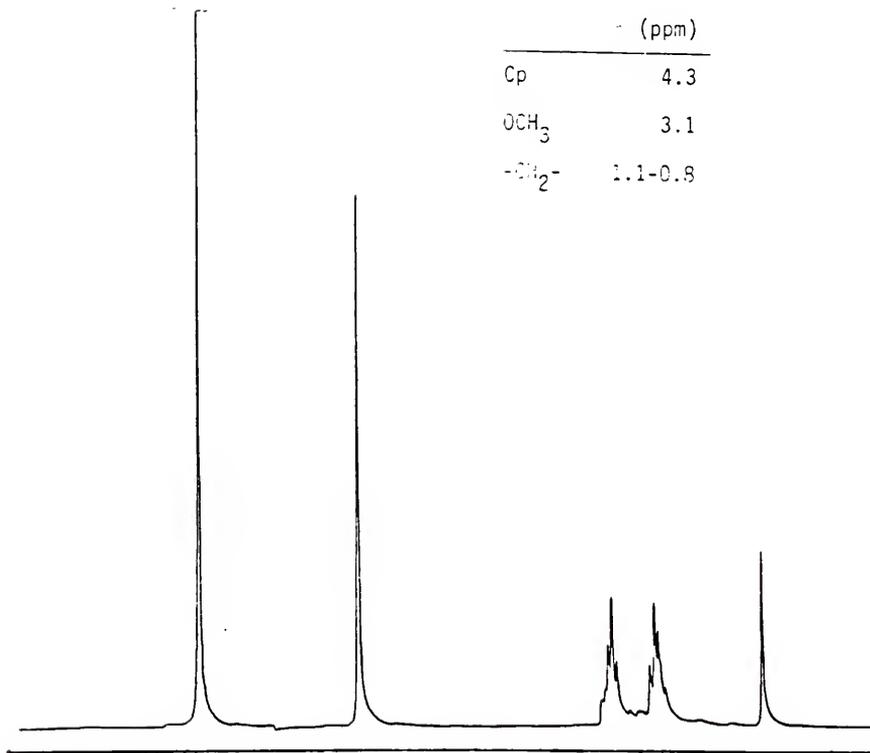
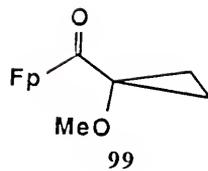


Fig. 1. <sup>1</sup>H NMR spectrum of compound 99 in C<sub>6</sub>D<sub>6</sub>.

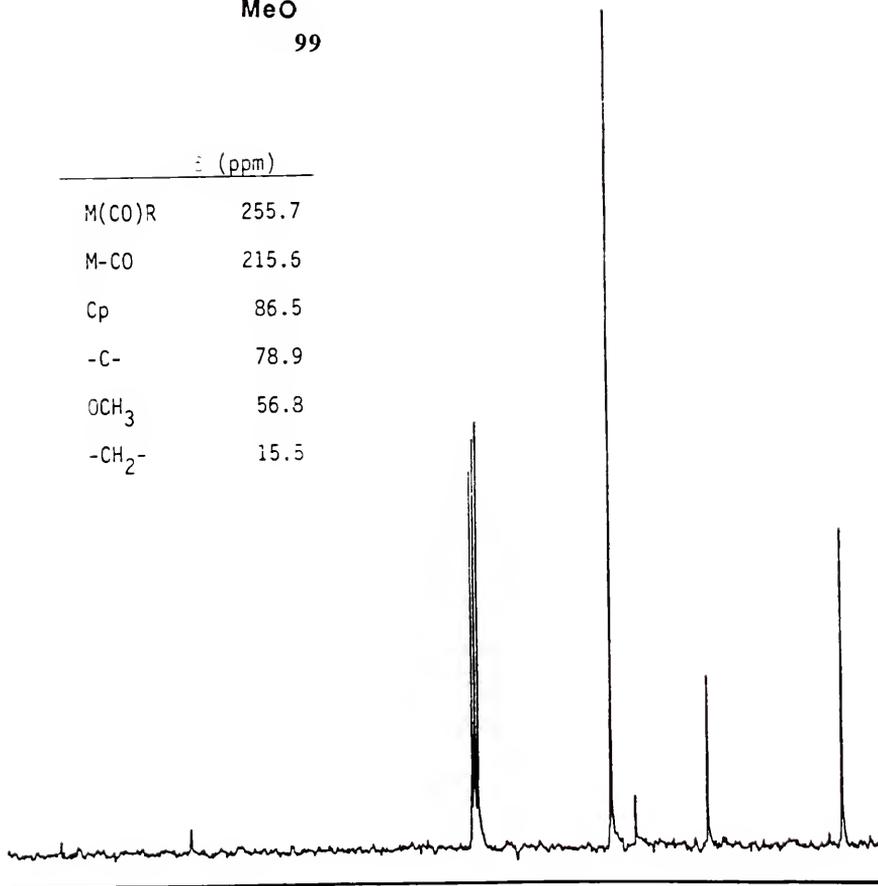
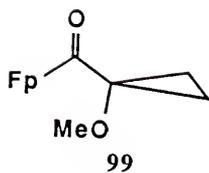
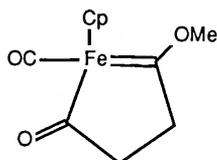


Fig. 2.  $^{13}\text{C}$  NMR spectrum of compound **99** in  $\text{C}_6\text{D}_6$ .

reaction could be monitored by NMR methods. The irradiation was carried out under an  $N_2$  blanket in the cell of a sonicator using a 350 watt medium pressure Hg lamp as the ultraviolet source. Bubbling commenced upon irradiation and the solution's bright yellow color gave way to a dark red. All of these conditions mirrored the original experimental procedures of Lisko.

After 6 hours of photolysis, the contents of the tube were subjected to column chromatography and the acyl-carbene complex 105 was isolated as a red crystalline solid. The proton and carbon NMR spectra of 105 are displayed in



105

Figures 3 and 4 respectively. Mass spectral and elemental analysis data are consistent with the structure 105. The IR spectrum shows two carbonyl stretches at  $1955$  and  $1650\text{ cm}^{-1}$ : one in the terminal and one in the acyl region. Perhaps the most telling evidence for assigning the compound's structure as 105 is the  $^{13}\text{C}$  NMR data.

The carbenic carbons of Fp carbene complexes have distinctive chemical shifts in the  $^{13}\text{C}$  spectrum. They can appear from 314 to 419 ppm downfield from TMS.<sup>65</sup> Though

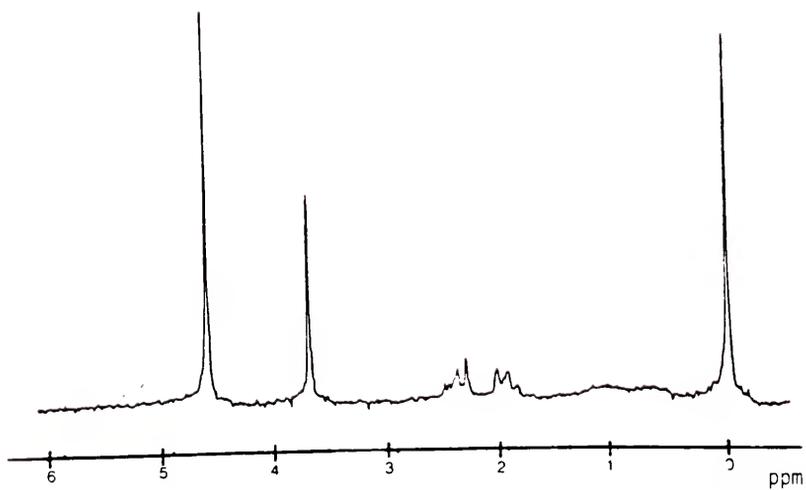


Fig. 3.  $^1\text{H}$  NMR spectrum of compound 105 in  $\text{C}_6\text{D}_6$ .

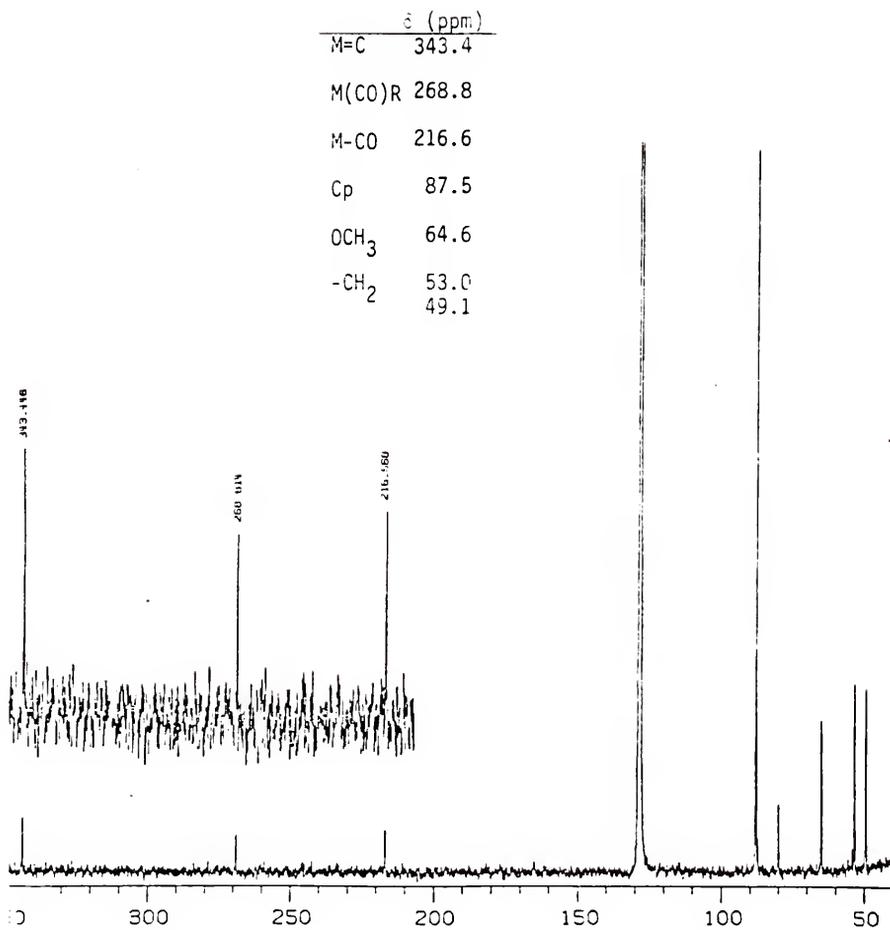
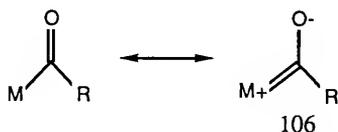


Fig. 4.  $^{13}\text{C}$  NMR spectrum of compound 105 in  $\text{C}_6\text{D}_6$ .

many CpFe carbene complexes bear a positive charge, it appears that the downfield shift of this carbon is inherent to the carbene character of the carbon atom and not due solely to its charge.<sup>66</sup> The chemical shift of 343.4 ppm found for 105 correlates nicely with that of Lisko's acyl-carbene 47 which had a carbenic carbon with a shift of 348.1 ppm.

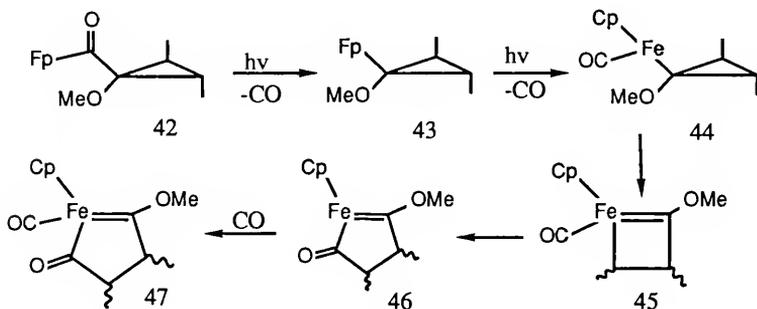
Further confirmation of the structure is afforded by the other resonances in the <sup>13</sup>C NMR spectrum. The chemical shifts of the terminal and acyl carbonyl carbon atoms occur in rather narrow and distinctive ranges. Compound 105 has a resonance at 268.8 ppm which can be assigned to the acyl carbon; the resonance at 216.6 can be assigned to the terminal carbonyl. The downfield shift of the acyl carbon is a result of the contribution of the resonance form depicted in 106 to the electronic constitution of the acyl complex.<sup>67</sup>



The rearrangement brought to light by Lisko was reproduced. The absence of the methyl groups did not prohibit the formation of the acyl-carbene complex 105. A comparison of <sup>1</sup>H NMR spectra acquired at hourly intervals

during the photolyses of 42 and 99 indicates that the absence of the beta methyl groups neither retarded nor accelerated the formation of the corresponding acyl-carbene complex. Qualitatively, the rates of formation of the acyl-carbenes were comparable.

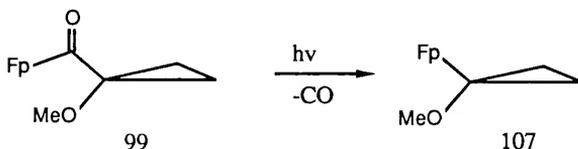
The mechanism proposed by Jones and Lisko to account for the photolytic production of the acyl-carbene 47 from the acyl complex 42 is reproduced below.<sup>38</sup> Lisko isolated



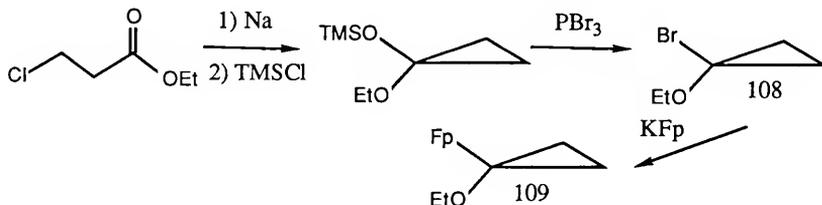
the sigma complex 43 from the photolysis mixture by column chromatography. Subsequent photolysis of pure 43 also yielded the acyl-carbene 47 thus supporting their contention that the first step in the mechanism was the photo-induced decarbonylation of the acyl to produce the sigma complex. Indeed, such decarbonylations have been used as synthetic methods for preparing Fp sigma complexes.<sup>68</sup> However, no further work was done by Lisko to determine the validity of

the steps which followed the formation of the sigma complex in the proposed mechanistic scheme.

In order to investigate the fate of the sigma complex upon photolysis, a reliable method of making an appropriate Fp-alkoxy sigma complex was needed. The difficulties encountered in producing compound 103 made it highly desirable to find an alternative to obtaining the Fp-alpha methoxycyclopropyl sigma complex 107 from the photolytic decarbonylation of the acyl 99.

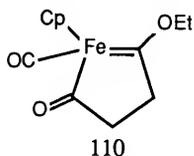


An excellent method for preparing such a sigma complex was found by reacting KFp with 1-bromo-1-ethoxycyclopropane (108). This reaction produced the sigma complex 109 in yields averaging 38.8%, and analytical samples were obtainable via column chromatography. Compounds 108 and 109 could be obtained in large quantities from the synthetic route shown below.



The  $^{13}\text{C}$  NMR spectrum of 109 is shown in Figure 5. The terminal carbonyl resonance at 217.6 is characteristic of a sigma complex. The IR spectrum also shows the diagnostic doublet in the terminal CO stretching region for the symmetric and asymmetric stretching modes of the two end-bound carbonyls.

It was not anticipated that the change of a methoxy group to an ethoxy group would greatly affect the rearrangement; indeed, the photolysis of 109 in benzene produced the red crystalline acyl-carbene 110 which was



isolated by column chromatography. The proton and carbon NMR spectra are presented in Figures 6 and 7. The carbenic carbon was detected at a chemical shift of 342.0 ppm. Resonances characteristic of acyl and terminal carbonyls were found at 270.0 and 216.9 ppm respectively. With a readily available source of the sigma complex 109 which gave the acyl-carbene 110 upon photolysis, the investigation of the proposed mechanism for the conversion of the sigma to the acyl-carbene was begun.

The first step in the mechanistic scheme is the photo-induced decarbonylation of the sigma complex to form a 16e-

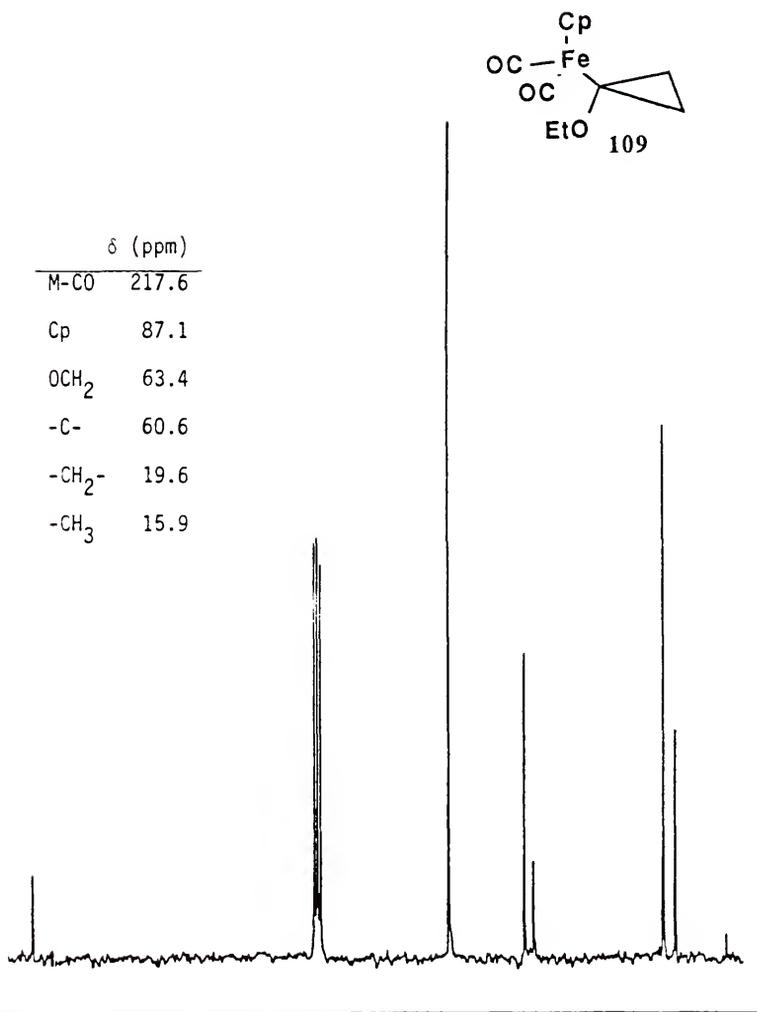


Fig. 5.  $^{13}\text{C}$  NMR spectrum of compound 109 in  $\text{C}_6\text{D}_6$ .

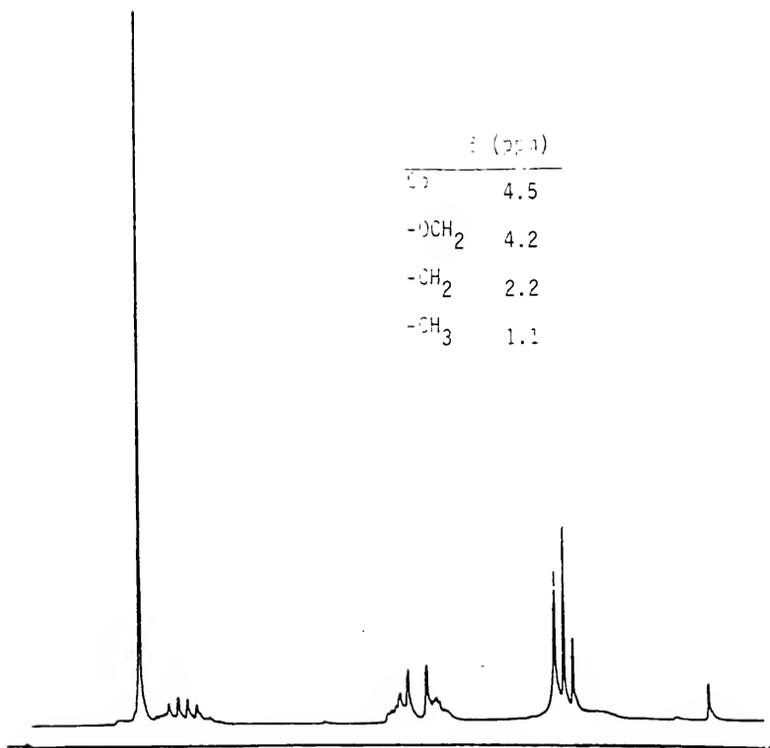
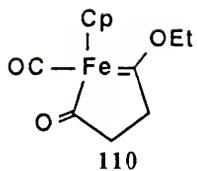


Fig. 6.  $^1\text{H}$  NMR spectrum of compound **110** in  $\text{C}_6\text{D}_6$ .

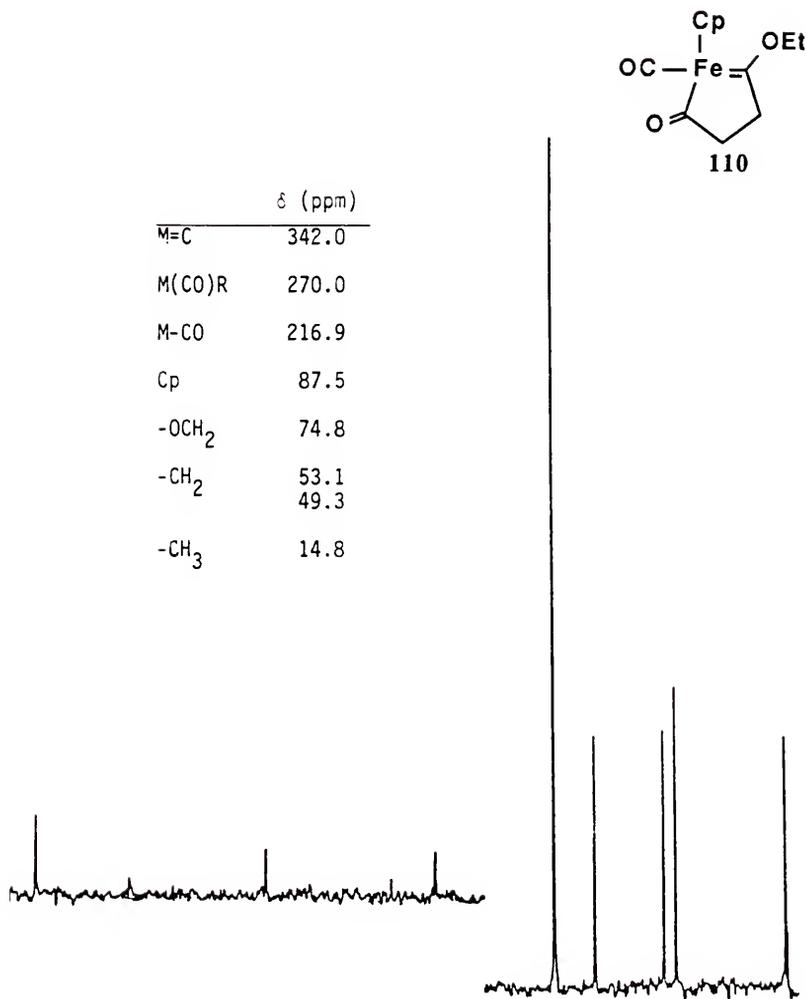
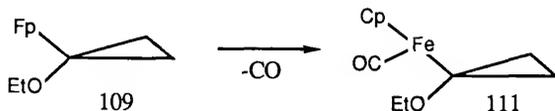


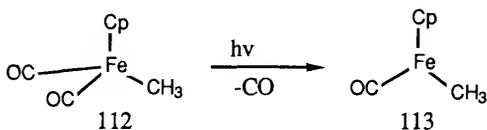
Fig. 7.  $^{13}\text{C}$  NMR spectrum of compound 110 in  $\text{C}_6\text{D}_6$ .

coordinatively unsaturated intermediate 111. There is much literary precedence for such a reaction. Specifically for



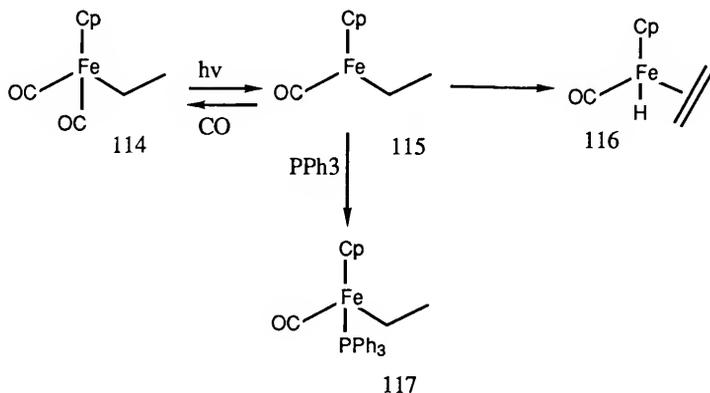
Fp sigma complexes, many authors have found that their products could be rationalized from photo-ejection of CO.<sup>6,9</sup>

Wrighton has extensively studied the photochemistry of Fp sigma complexes. He has determined that the loss of CO from these compounds can occur at temperatures as low as  $-90^{\circ}\text{C}$ .<sup>7,0</sup> Another group has observed CO loss at 10K.<sup>7,1</sup> Loss of carbon monoxide occurs thermally from a photo-excited state of the sigma complex due to a ligand field (LF) transition.<sup>7,2</sup> That the loss of CO upon irradiation of FpMe 112 produces 113 has been confirmed by direct spectroscopic



observation of 113 at low temperatures.<sup>7,3</sup> Fortunately, evidence for unsaturated intermediates such as 113 can be obtained without the use of elaborate experimental apparatus.

By using a combination of low temperature and flash/time-resolved techniques Wrighton has demonstrated that 16e- unsaturated intermediates, such as 113, can be intercepted with phosphine ligands. When FpEt 114 is



irradiated, CO is lost and the unsaturated intermediate 115 is formed. This can back react with CO to reform 114 or undergo an intramolecular rearrangement (beta hydride elimination) to form the hydrido-alkene complex 116. In the presence of triphenylphosphine, the only product formed is the phosphinalated sigma complex 117 FppEt.<sup>70</sup>

To determine if the unsaturated complex 111 was formed upon irradiation of 109, the sigma complex was photolyzed in the presence of 1 equivalent of triphenylphosphine. The course of the photolysis was monitored by NMR methods and is depicted in Figure 8. A red crystalline solid was isolated

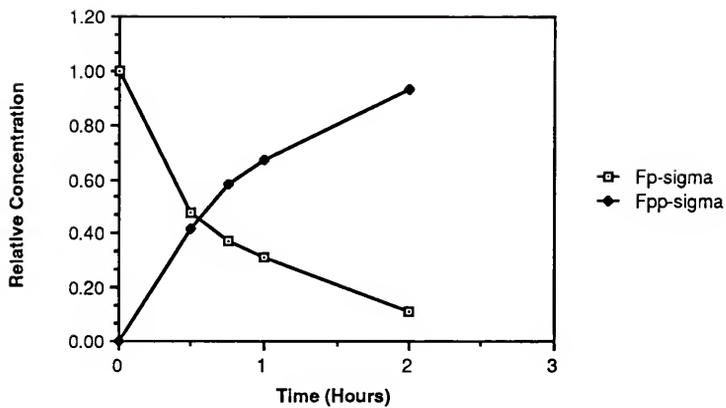
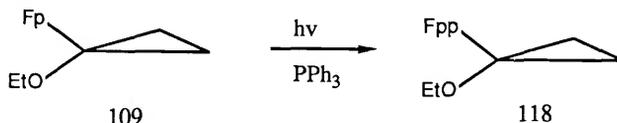


Fig. 8. Photolysis of compound 111 with  $\text{PPh}_3$  in  $\text{C}_6\text{D}_6$ .

by low temperature column chromatography ( $-50^{\circ}\text{C}$ ). It was determined to be the phosphine substituted sigma complex 118. The IR of 118 reveals a single carbonyl stretch at



1911  $\text{cm}^{-1}$  characteristic of Fpp sigma complexes. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the compound are shown in Figures 9 and 10 respectively. The proton spectrum exhibits two features characteristic of Fpp sigma complexes: the Cp resonance is split into a doublet by three-bond coupling to the phosphorus attached to the iron and the methylene protons of the ethoxy group appear as a multiplet because they are rendered diastereotopic by the now chiral iron center. The carbon spectrum also shows P-C splitting of the Cp, -CO, aryl and -C-OEt carbon atoms. The  $-\text{CH}_2$  carbon atoms appear individually as they are now diastereotopic by virtue of the chiral iron center.

Another experiment was performed in order to gain evidence for the unsaturated complex 111. A 1.9M benzene solution of the sigma complex 109 was photolyzed in the presence of 2 atm of isotopically labelled carbon monoxide. The photolysis was monitored by proton and carbon NMR. After 3 hours the unreacted sigma complex was isolated by

Chemical Shift (ppm)

|                    |         |
|--------------------|---------|
| PPh <sub>3</sub>   | 7.7-7.1 |
| Cp                 | 4.3     |
| -OCH <sub>2</sub>  | 3.2     |
| -CH <sub>3</sub>   | 1.0     |
| -CH <sub>2</sub> - | 0.5-0.2 |

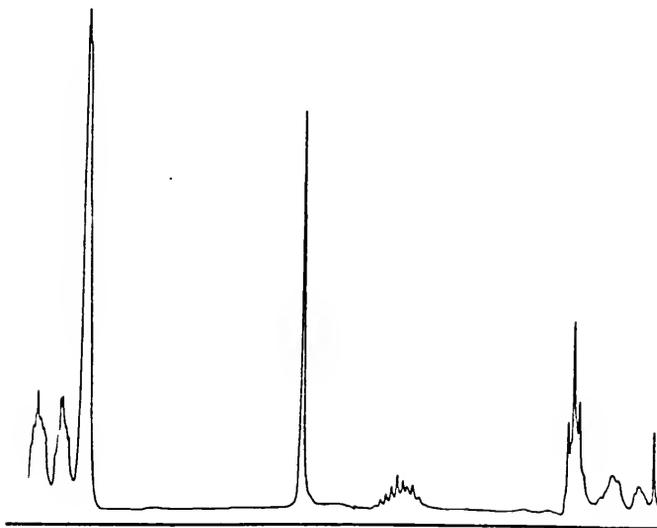
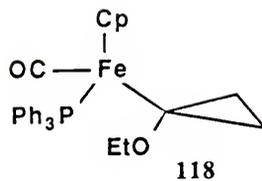


Fig. 9. <sup>1</sup>H NMR of compound 118 C<sub>6</sub>D<sub>6</sub>.

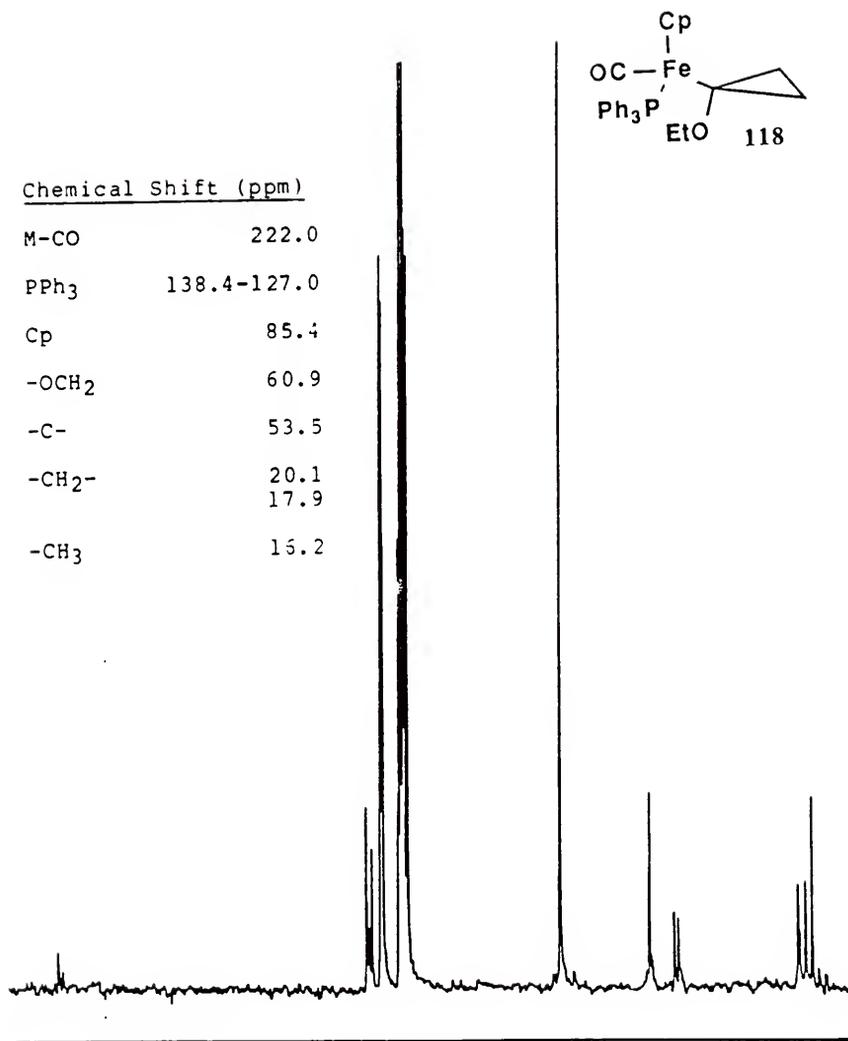
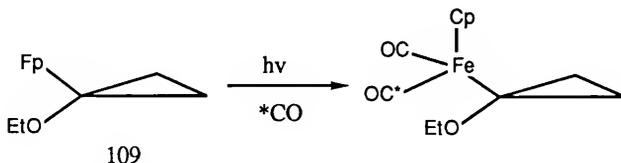


Fig. 10.  $^{13}\text{C}$  NMR spectrum of compound 118 in  $\text{C}_6\text{D}_6$ .

column chromatography. The percent incorporation of  $^{13}\text{C}$  in the unreacted sigma complex was determined from integrals obtained by  $^{13}\text{C}$  NMR and mass spectrometry. The data from both methods agreed that there was a small amount of labelled CO taken up by the sigma complex (less than 1%).



Although the reaction was run under an external CO pressure, the course of the photolysis was not greatly affected: the rate at which 109 disappeared and the rate at which 110 appeared were not very different from the corresponding rates in the photolysis without added CO. Figures 11 and 12 depict this graphically. The relative concentrations were determined by  $^{13}\text{C}$  NMR integrations against an internal standard (vide infra). It is not surprising that such a low percentage of incorporation was observed. Wrighton found that external CO pressure suppresses photodissociation to a very small extent.<sup>72</sup> Although the concentration of photo-released CO ( $10^{-2}\text{M}$ )<sup>80</sup> should be comparable to the concentration of CO in solution due to external CO pressure ( $10^{-2}\text{M}$ )<sup>74</sup>, escape of photo-ejected CO from the solvent cage is inefficient.<sup>70</sup> Back reaction of 111 occurs primarily with CO which has not left the solvent cage; this reason has

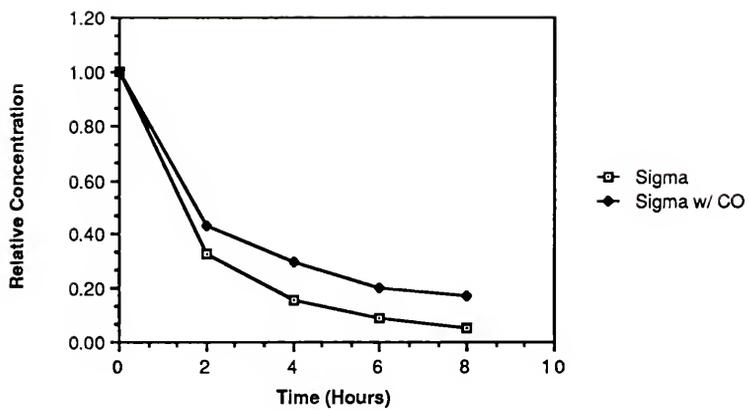


Fig. 11. Photolysis of compound 109: effect of CO.

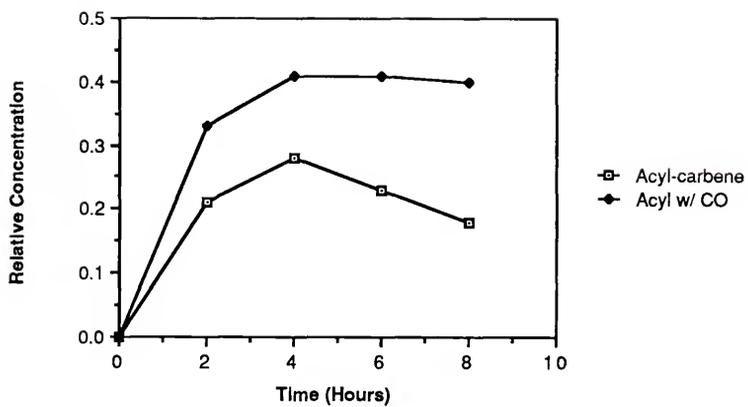


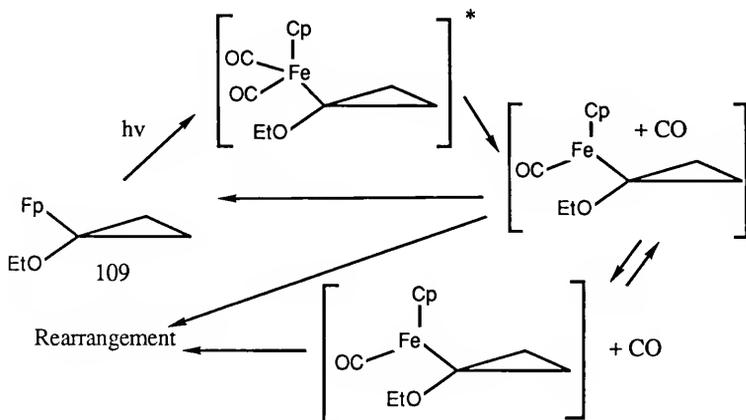
Fig. 12. Photolysis of compound 109: effect of CO.

been used to rationalize the extremely large apparent rate constants which have been measured for the CO recombination reaction of  $16e^-$  coordinatively unsaturated complexes ( $k=10^7-10^{10}$ ).<sup>75</sup> Coupled with this bias for recombination with photo-ejected CO is the observation that the apparent rate of intramolecular rearrangements, such as beta hydride elimination, and subsequent completion of the complex's coordination sphere is much greater than back reaction with CO in these Fp systems.<sup>70</sup>

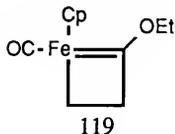
What appears to be the case is that the complex 111 undergoes rearrangement faster than it can back-react with CO; it preferentially recombines with CO originating from the coordination sphere of compound 109 rather than any externally added CO. Triphenylphosphine is much more efficient in trapping 111 than added CO so that the phosphine adduct is obtained rather cleanly when an equivalent of triphenylphosphine is present. This may be due to the greater relative concentration of the phosphine present in solution, the greater donicity of the phosphine relative to CO ( $k_1 \gg k_{CO}$ ) and/or the ability of the phosphine to displace the photo-ejected CO from the metal's solvent cage. It is therefore significant that the recovered sigma complex had incorporated the tagged CO at all.

These two experiments establish the intermediacy of the  $16e^-$  complex 111. Furthermore, the CO study demonstrates

that a small amount of the intermediate frees itself from its photodissociated CO in its solvent cage and can combine with external CO which has migrated into its solvent sphere. Since in this free state the intermediate has nearly the same probability of picking up a tagged or untagged CO, the low percentage of incorporation implies that 111 either rearranges much faster than it can reincorporate CO into its cage and recombine and/or 111 may undergo rearrangement while photo-ejected CO is still in its solvent cage.



The next step in the proposed mechanism was the alpha elimination of the methylene moiety of the cyclopropane ring from 111 to form the 18e- alkyl-carbene complex 119. If the



proposed mechanistic scheme were correct, 119 should be an intermediate on the way to the acyl-carbene complex 110. As an intermediate its concentration should rise from zero to some maximum level during the photolysis and then should give way as the concentration of 110 builds up. Since the length of the irradiation period was 6 hours, it was hoped that 119 could be spectroscopically detected and perhaps even isolated if the reaction were curtailed at the appropriate time.

Lisko monitored his reactions using proton NMR. Because many of the new resonances overlapped with existing ones, very little information was gleaned from these experiments regarding the relative concentrations of any species formed during the reaction. It was hoped that following the photolysis by using  $^{13}\text{C}$  NMR and comparing the integrals found in the Cp region of the spectrum against a photostable internal standard would give a qualitative picture of the evolution and fate of the CpFe containing compounds in the reaction vessel.

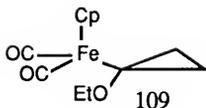
In order to acquire accurate integrations using an FT-NMR instrument, the  $T_1$  relaxation times of the nuclei to be monitored must be determined. This will allow adequate pulse delays to be set (usually 5X longer than the  $T_1$ 's of the carbons of interest) so that different carbon atoms spin states can relax to their equilibrium populations

before another exciting pulse is applied.  $T_1$  studies were performed on compounds 109 and 110 using the inversion-recovery method. The results of these studies are listed in Figure 13. From this a pulse delay of 35 seconds was thought to be adequate as the Cp carbon atoms had relaxation times under 7 seconds.

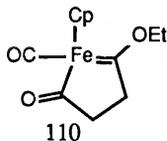
To see if ferrocene would be a suitable standard, it was irradiated for 20 hours. No change in its proton or carbon spectra occurred over this period.

A sample of 109 was prepared in which ferrocene was added. A carbon spectrum was recorded before photolysis commenced in order to determine the initial ratio of 109 to ferrocene present. The sample was photolyzed in  $C_6D_6$  and a  $^{13}C$  NMR was taken at two hour intervals for a total of 8 hours. The results proved to be quite exciting.

After 2 hours resonances were found in the Cp region which corresponded to the sigma complex 109,  $Fp_2$ , the acyl-carbene 110, the pi-allyls (which will be more fully treated later) and a resonance at 82.8 ppm which was not seen in carbon spectra taken of previous reaction mixtures after 6 hours of photolysis. As can be seen in Figure 14, this resonance was accompanied by peak found far downfield in the carbene region at 334.9 ppm and a peak in the terminal carbonyl region at 224.8 ppm. Indeed four other peaks were



| <u>Nucleus</u>      | <u>T<sub>1</sub> (sec)</u> | <u>Error (sec)</u> |
|---------------------|----------------------------|--------------------|
| Cp                  | 6.9                        | 0.3                |
| Fe-CO               | 17.7                       | 0.8                |
| -C-                 | 28.3                       | 1.3                |
| -CH <sub>2</sub> -  | 2.7                        | 0.4                |
| -OCH <sub>2</sub> - | 2.4                        | 0.3                |
| -CH <sub>3</sub> -  | 1.3                        | 0.1                |



| <u>Nucleus</u>      | <u>T<sub>1</sub> (sec)</u> | <u>Error (sec)</u> |
|---------------------|----------------------------|--------------------|
| Cp                  | 6.2                        | 0.8                |
| Fe=C                | 10.8                       | 3.0                |
| Fe(CO)R             | 6.6                        | 3.3                |
| -CO                 | 19.0                       | 4.0                |
| -OCH <sub>2</sub> - | 1.7                        | 0.3                |
| -CH <sub>2</sub> -  | 3.7                        | 2.1                |
|                     | 1.2                        | 0.3                |
| -CH <sub>3</sub>    | 2.6                        | 1.0                |

Fig. 13. <sup>13</sup>C T<sub>1</sub> relaxation times of compounds 109 and 110 in C<sub>6</sub>D<sub>6</sub>.

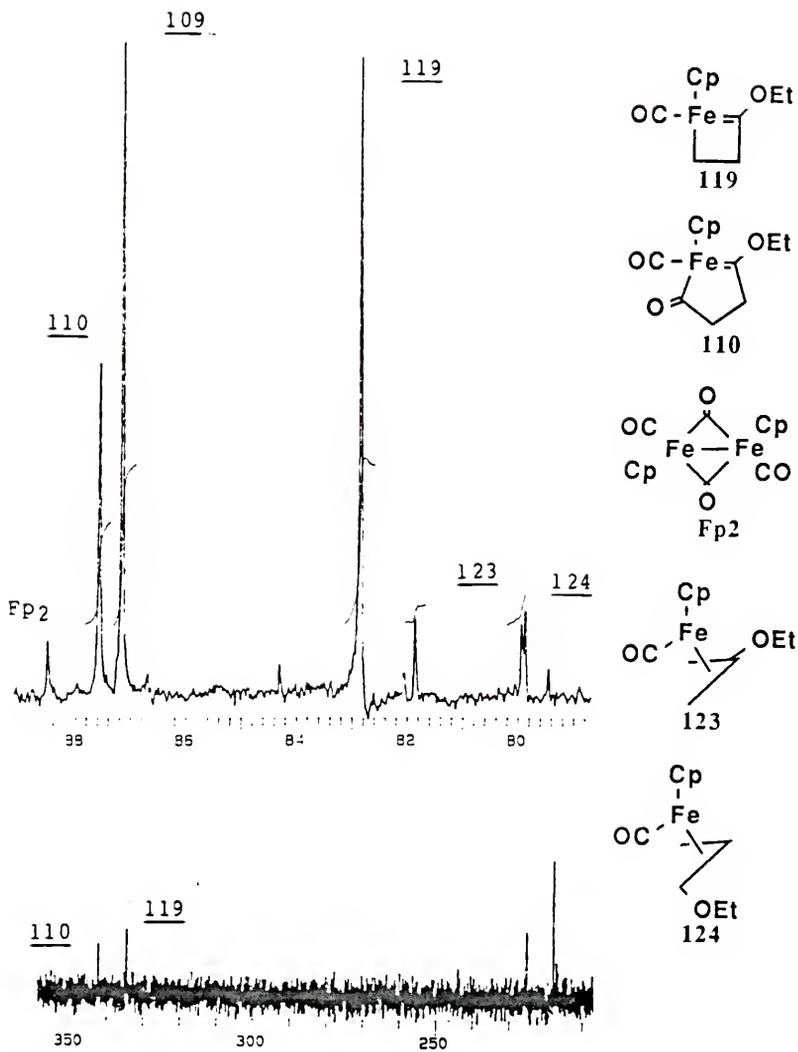
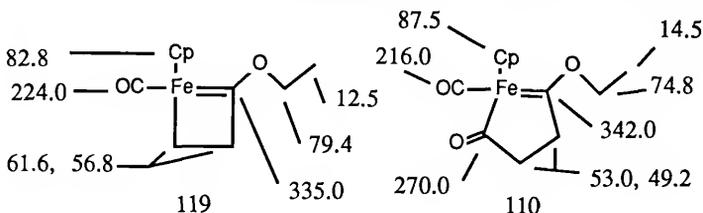


Fig. 14.  $^{13}\text{C}$  NMR spectrum of the photolysis of 109 in  $\text{C}_6\text{D}_6$  after 2 hours.

found which were unassignable to any previously isolated material from the reaction mixture. These resonances were presumed to belong to the alkyl-carbene complex 119. A comparison of the  $^{13}\text{C}$  assignments for compounds 119 and 110



is shown here. It should be noted that the carbene resonance of 119 is 8.9 ppm upfield from the carbene resonance for compound 110. This is in agreement with Schubert's observation that sterically strained carbenes experience an upfield shift in the carbon spectrum;<sup>76</sup> one would certainly expect 119 to be more strained than 110.

Upon continued photolysis, the Cp resonance assigned to 119 decreased as 110 grew in relative concentration. Figure 15 graphically demonstrates the situation. This behavior is consistent with that expected for the true intermediate 119. After 4 hours, only a small steady concentration of 119 remained.

If indeed the intermediate 119 had truly been observed in the carbon spectrum of the reaction mixture, according to the proposed mechanism, it should be quite reactive towards CO. Therefore a sample of the sigma complex 109 was

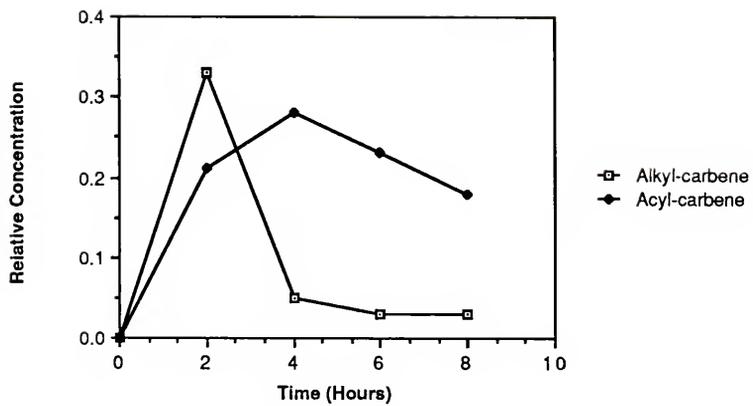
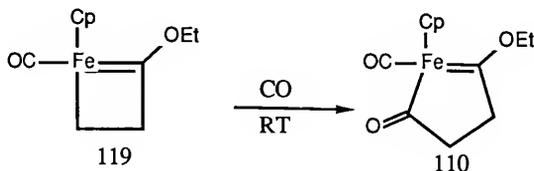
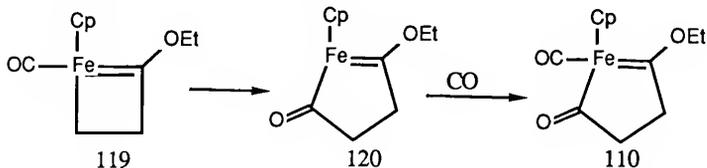


Fig. 15. Photolysis of compound 109.

photolyzed in benzene for 30 minutes. A  $^{13}\text{C}$  NMR spectrum revealed only one peak in the carbene region, that occurring at 334 ppm: the alkyl-carbene 119. Carbon monoxide was then bubbled through the solution for 1 hour. The peaks at 334, 224 and 82.8 ppm completely disappeared and new resonances appeared at 342, 270, 216 and 87.5 ppm. These correspond to the acyl-carbene 110. By observing the disappearance of the



other peaks in the spectrum, the assignments made for the other carbon atoms of 119 were seen to be correct. Figure 17 shows the carbon spectra before and after the treatment with CO. This constitutes excellent evidence not only for the detection of the alkyl-carbene complex 119 but also for the next proposed mechanistic step: conversion of 119 to 110 via the migratory insertion of CO.



An attempt was made to isolate compound 119. Though most four-membered ring cyclic carbene complexes are quite

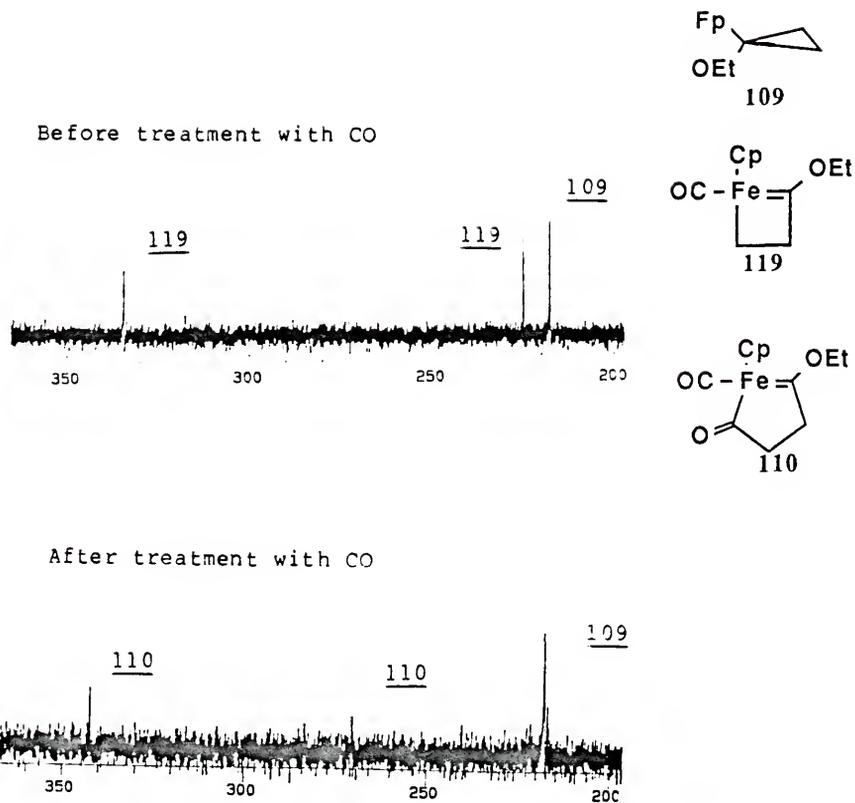
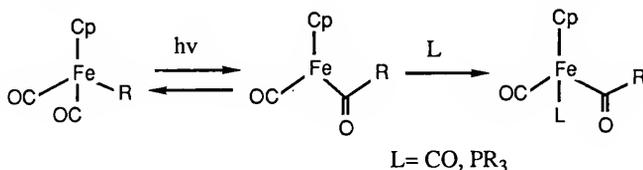


Fig. 16.  $^{13}\text{C}$  NMR of compound 119 in  $\text{C}_6\text{D}_6$  when treated with CO.

reactive<sup>77</sup> several are stable enough to isolate and obtain X-ray quality crystals.<sup>78</sup> An exceptionally large quantity (1g) of the sigma complex 109 was photolyzed to produce a maximal amount of 119. The contents of the reaction tube were run down a silica gel column at -50C. A very small amount of a red solid was recovered. The <sup>1</sup>H NMR spectrum of this solid is presented in Figure 17. The spectrum is consistent with the structure of 119. The amount of material recovered was insufficient for obtaining a good carbon spectrum. The sample also decomposed in solution over a span of 30 minutes; no IR spectrum, mass spectrum nor elemental analysis was obtained. Not too surprisingly,<sup>79</sup> 119 appeared to be badly decomposed by the silica gel column. Perhaps trace amounts of these decomposition products present in the sample completed the destruction of the compound in solution.

With sound evidence for the preceding steps' validity, the question of the migratory CO insertion of 119 to form 110 was addressed. Such carbonylation reactions for Fp-alkyl sigma complexes have been thoroughly studied by various groups.<sup>80</sup> Kinetic studies indicate that the



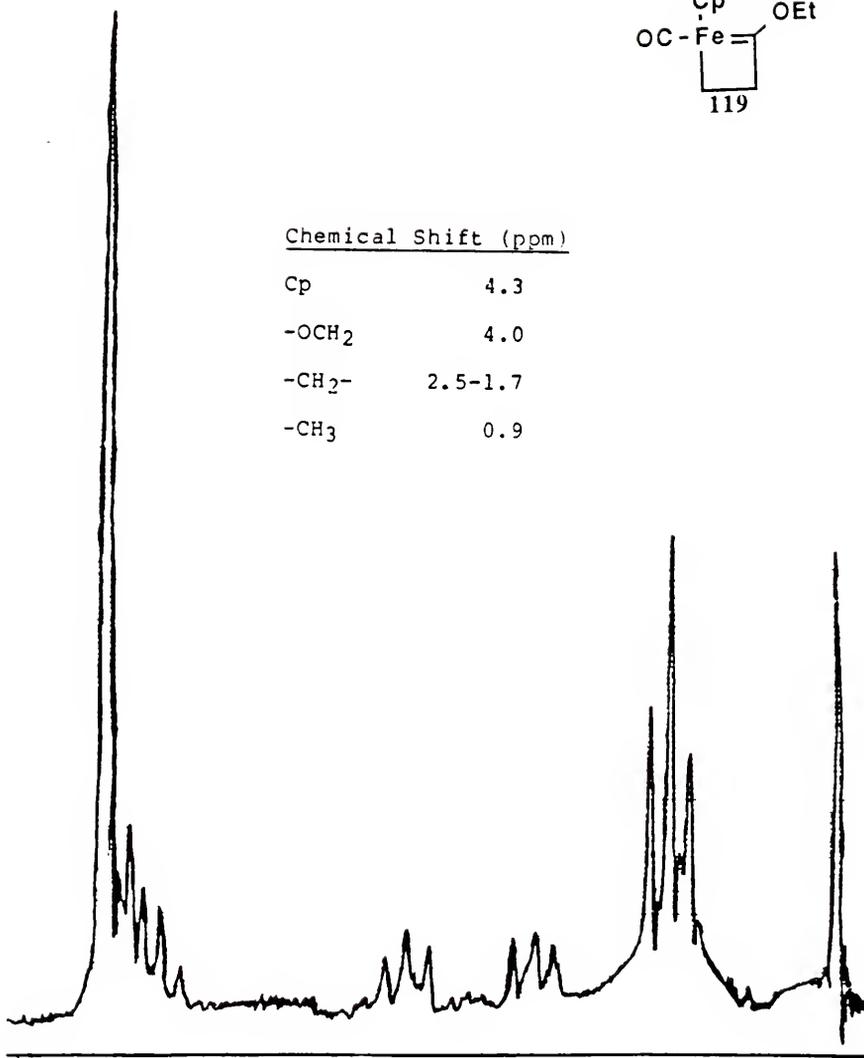
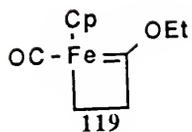
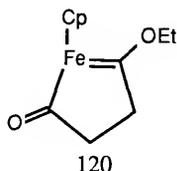


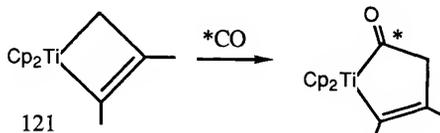
Fig. 17. <sup>1</sup>H NMR spectrum of compound **119** in C<sub>6</sub>D<sub>6</sub>.

reaction of an Fp sigma complex with an externally added ligand, such as a phosphine or CO, proceeds through a distinct intermediate.<sup>81</sup> Rosenblum has determined from his trapping experiments that the intermediate is a 16e-coordinatively unsaturated species which can be intercepted by phosphine, CO or by solvents of high coordinating ability.<sup>82</sup>

In the mechanism proposed by Jones and Lisko, the alkyl-carbene 119 undergoes migratory insertion to form the unsaturated species 120. This complex then completes its

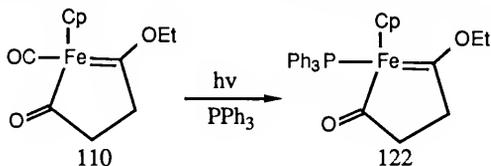


coordination sphere by scavenging CO from the solution to form compound 110. The carbonylation of metallacyclobutanes has been reported by several groups;<sup>83</sup> it has also been reported by Grubbs for the metallacyclobutene 121.<sup>84</sup>



Therefore, the step proposed by Jones and Lisko is not without literature precedent.

In order to gather evidence for the existence of 120, the strategy of entrapment of it with triphenylphosphine was employed. This was done by photolyzing the acyl-carbene 110 in the presence of the added ligand. The phosphine substituted acyl-carbene 122 was isolated from the

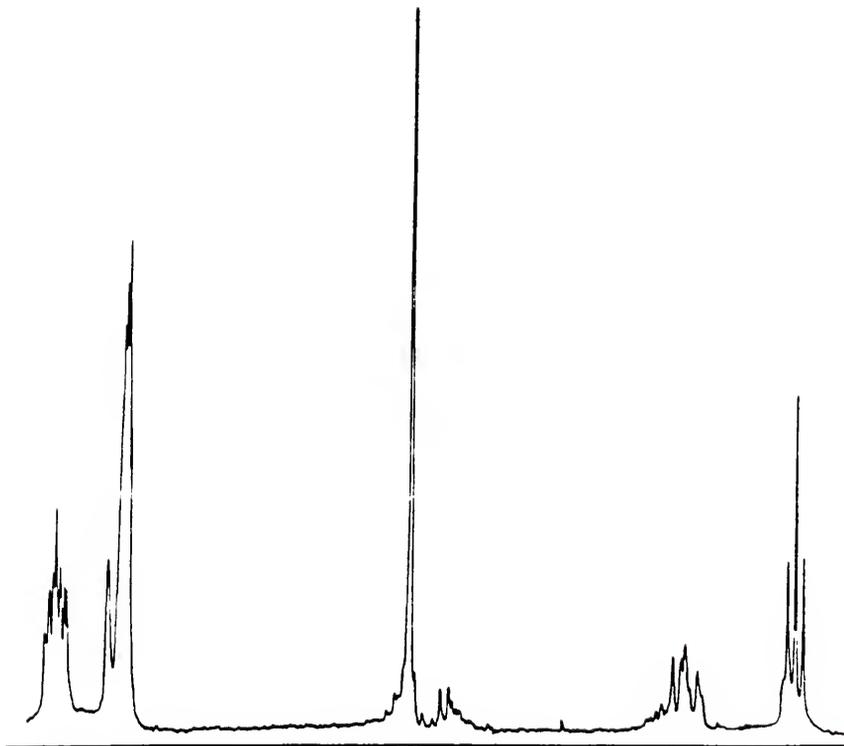
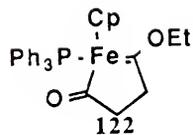


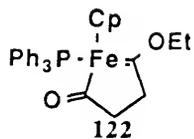
reaction mixture by means of low temperature column chromatography. Figures 18 and 19 respectively contain the proton and carbon spectra of the material. The  $^{13}\text{C}$  NMR spectrum is noteworthy in two respects. First, the carbene and acyl carbon atoms show phosphorus coupling. Second, the acyl resonance occurs at 293 ppm: 23 ppm downfield from the acyl resonance in the carbonyl substituted acyl-carbene 110. This shift is consistent with those of phosphine substituted acyl complexes.<sup>85</sup>

The isolation of 122 is consistent with the presence of 120 during the photolysis of the acyl-carbene 110. It does not require that 120 is present during the conversion of 119 into 110. Therefore 119 was induced to form 122 directly. This was accomplished by treating a benzene solution of 119, generated from 109 after 2 hours of photolysis, with triphenylphosphine. Upon standing at room temperature for

Chemical Shift (ppm)PPh<sub>3</sub>      7.6-6.9

Cp            4.5

-OCH<sub>2</sub>      4.1-CH<sub>2</sub>-      1.6-1.0-CH<sub>3</sub>        0.3Fig. 18. <sup>1</sup>H NMR spectrum of compound 122 in C<sub>6</sub>D<sub>6</sub>.



| Chemical Shift (ppm) |             |
|----------------------|-------------|
| M=C                  | 341.0       |
| M(CO)R               | 293.3       |
| PPh <sub>3</sub>     | 138.4-128.3 |
| -OCH <sub>2</sub>    | 71.2        |
| -CH <sub>2</sub>     | 50.7        |
| -CH <sub>3</sub>     | 49.2        |

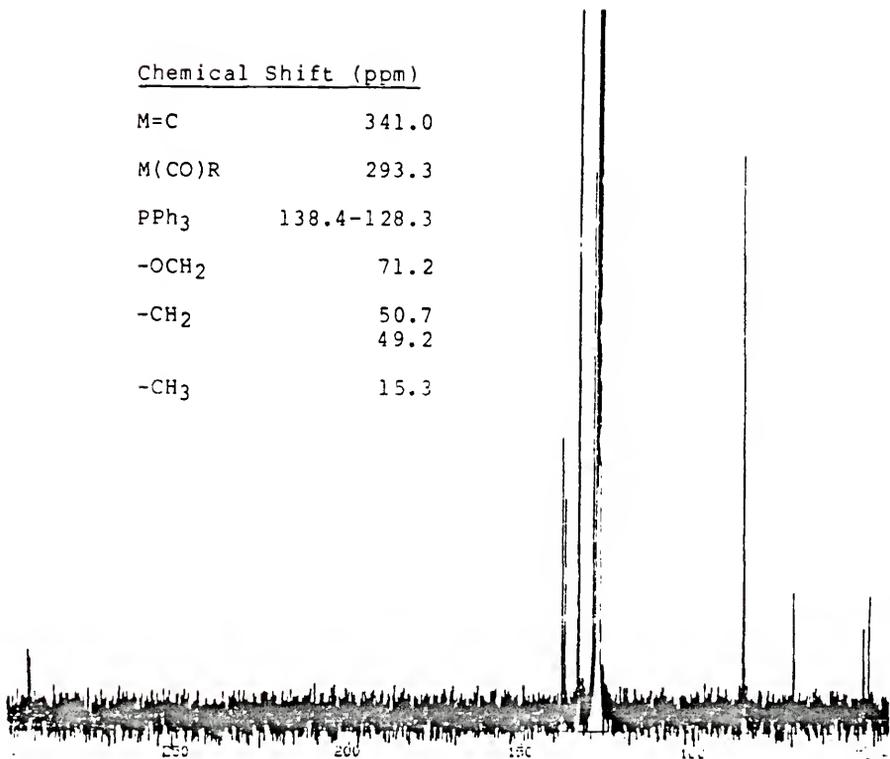
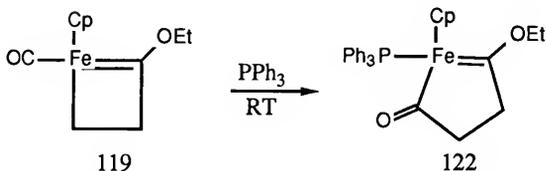


Fig. 19. <sup>13</sup>C NMR spectrum of compound 122 in C<sub>6</sub>D<sub>6</sub>.

five minutes, the  $^{13}\text{C}$  NMR indicated that 119 had been quantitatively transformed into 122. This result is in

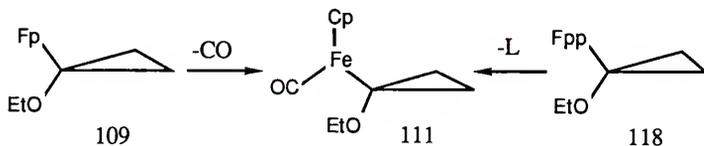


agreement with the oft reported observation that phosphine induced migratory insertions are much faster than CO induced processes.<sup>80a</sup>

These last two results, along with the previously mentioned conversion of 119 into 110 via exposure to CO strongly suggest that Jones and Lisko were correct in proposing that their acyl-carbene complex results from a CO induced migratory insertion. Therefore, the mechanistic scheme that they proposed to account for the generation of the acyl-carbene 47 from the acyl complex 42 appears to be valid based on the experiments performed in this work.

All of the alkyl alpha elimination reactions reported by Jones and co-workers resulted from the photolytic generation of a coordinatively unsaturated metal complex. It is well known that Fpp sigma complexes lose a phosphine ligand upon heating to generate 16e- iron species.<sup>86</sup> Photolysis of 109 or the thermolysis of 118 should therefore generate the same unsaturated intermediate. If so, one

should expect to see the same type of alkyl alpha elimination reaction upon heating 118 as from the photolysis of 109.



Complex 111 would be expected to be in its electronic ground state if generated by the thermolysis of 118. Should rearrangement occur, the result would imply that the intermediate 111 generated from the photolysis of 109 was also in its electronic ground state. This would be consistent with compound 109 absorbing a photon to produce an excited state species which then ejected CO to form the ground state complex 111. The thermal rearrangement was found to occur.

A benzene solution of 118 was heated to 75°C. The progress of the reaction was monitored by  $^{13}\text{C}$  NMR spectroscopy. As Figure 20 demonstrates 118 was rather cleanly converted into the phosphine substituted acyl-carbene complex 122 over the course of 47 hours. This is the first reproducible, thermally induced sigma to carbene rearrangement reported in the Jones research group.

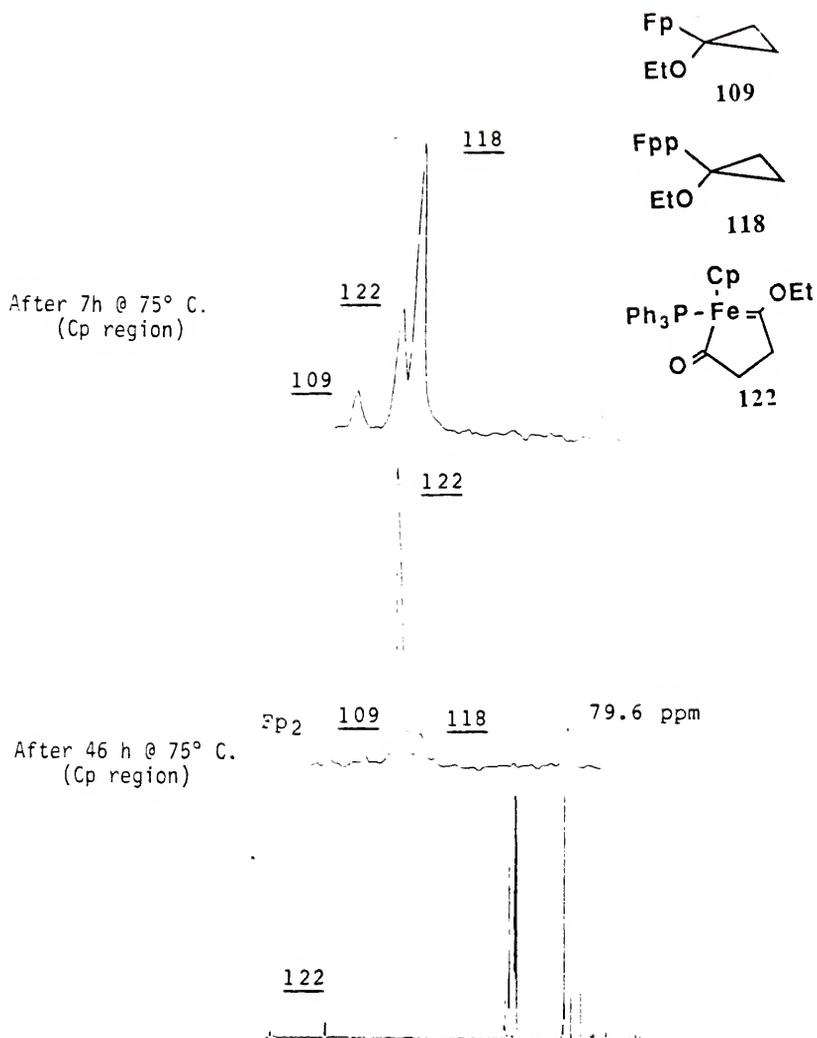
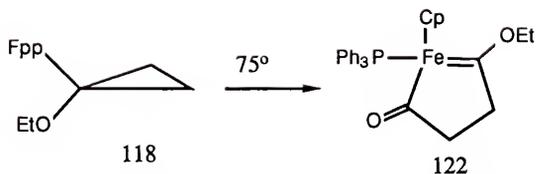


Fig. 20. <sup>13</sup>C NMR spectra of the thermolysis of 118 in C<sub>6</sub>D<sub>6</sub>.



It should be noted that at no time in the thermolysis reaction was there any spectroscopic evidence for the formation of the alkyl-carbene complex 119. This is not unexpected since triphenylphosphine is known to induce migratory CO insertion much more efficiently than carbon monoxide.<sup>80a</sup> It would therefore not be at all unexpected if 119 was converted into 122 before it had a chance to build up to a detectable concentration.

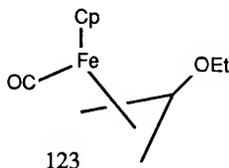
The thermal rearrangement of the phosphine substituted sigma complex 118 was almost completely suppressed when run in the presence of an excess (10-fold) of triphenylphosphine. This result further secures the involvement of 111 as an intermediate in the rearrangement to the acyl-carbene.

Earlier, brief mention was made of the isolation of pi-allyl products from the photolysis of the sigma complex 109. This will now be more fully presented.

While following the photolysis of 109 by carbon NMR spectroscopy, the growth of two new resonances was observed

in the Cp region of the spectrum after 4 hours of irradiation. As can be seen in Figure 21, the peaks appear at 79.9 and 79.5 ppm. These resonances were accompanied by others, most notably ones at 222, 221, 134 and 100 ppm. The peaks continued to grow in at the expense of the sigma, alkyl-carbene and acyl-carbene resonances as the irradiation continued through 8 hours.

Careful and repeated column chromatography of the final photolysis mixture yielded two yellow solids corresponding to compounds never before found by Lisko or others investigating such rearrangements. Each was fully characterized as an ethoxy substituted pi-allyl complex. Figures 22 and 23 present the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for complex 123 (pi-c), the centrally substituted pi-allyl.



This complex was responsible for the resonances at 221, 134 and 79.5 ppm in the photolysis mixture.

Figures 24 and 25 depict the proton and carbon NMR spectra of complex 124 (pi-t), the terminally substituted pi-allyl. The  $^{13}\text{C}$  NMR spectrum shows that this compound produced the peaks at 222, 100 and 79.9 ppm found in the

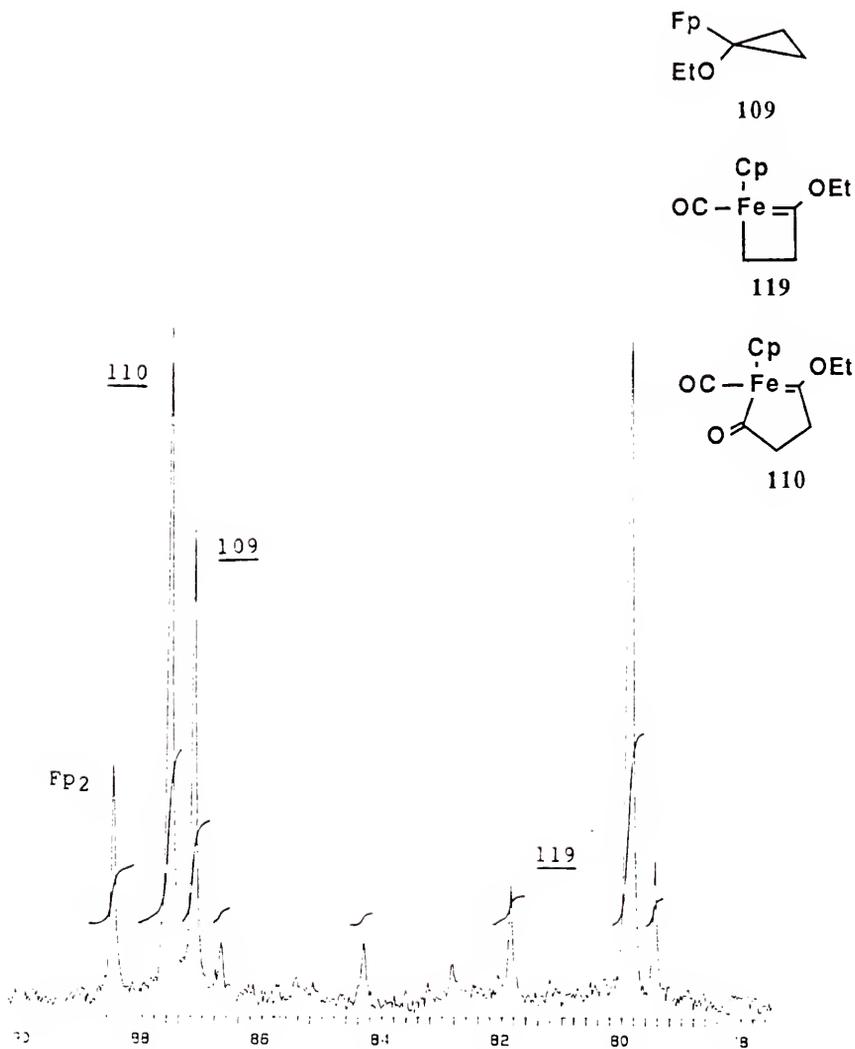


Fig. 21.  $^{13}\text{C}$  NMR spectrum of the photolysis of 109 in  $\text{C}_6\text{D}_6$  (4 h).

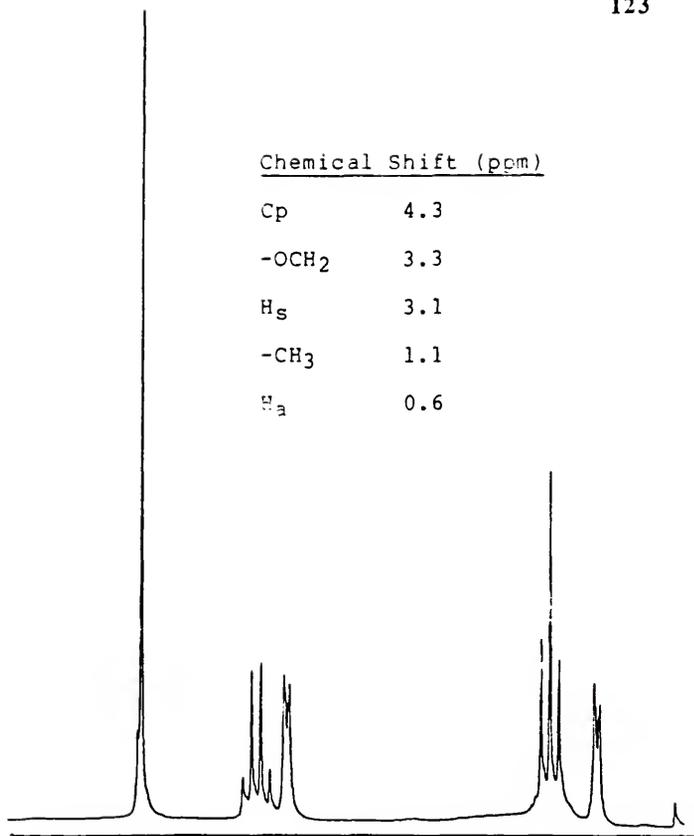
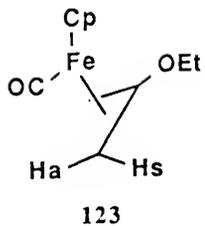
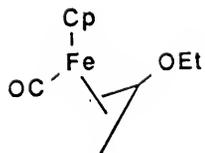


Fig. 22. <sup>1</sup>H NMR spectrum of compound **123** in C<sub>6</sub>D<sub>6</sub>.

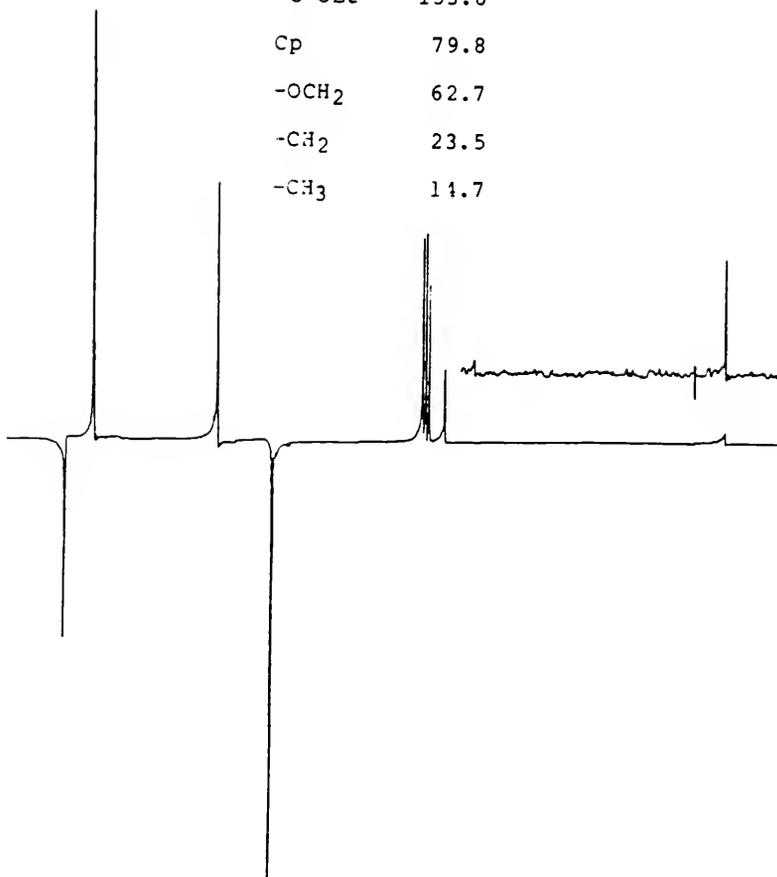
-C-, CH<sub>2</sub> ↓CH, CH<sub>3</sub> ↑Chemical Shift (ppm)

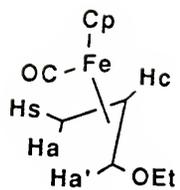
M-CO      221.3

**123**

-C-OEt    133.8

Cp        79.8

-OCH<sub>2</sub>   62.7-CH<sub>2</sub>     23.5-CH<sub>3</sub>     14.7Fig. 23. <sup>13</sup>C NMR spectrum of compound 123 in C<sub>6</sub>D<sub>6</sub> (APT).



124

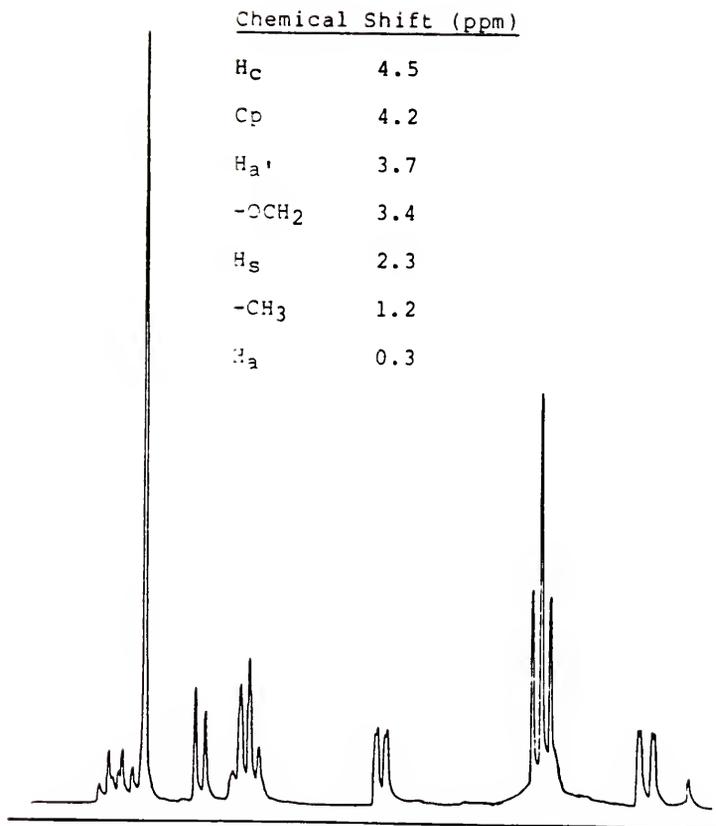
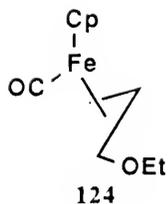


Fig. 24.  $^1\text{H}$  NMR spectrum of compound 124 in  $\text{C}_6\text{D}_6$ .

-C-, CH<sub>2</sub>     ↓  
 CH, CH<sub>3</sub>     ↑



Chemical Shift (ppm)

|                   |       |
|-------------------|-------|
| M-CO              | 222.2 |
| CH                | 99.9  |
| Cp                | 79.8  |
| -OCH <sub>2</sub> | 67.8  |
| HC-OEt            | 61.0  |
| -CH <sub>2</sub>  | 22.4  |
| -CH <sub>3</sub>  | 15.1  |

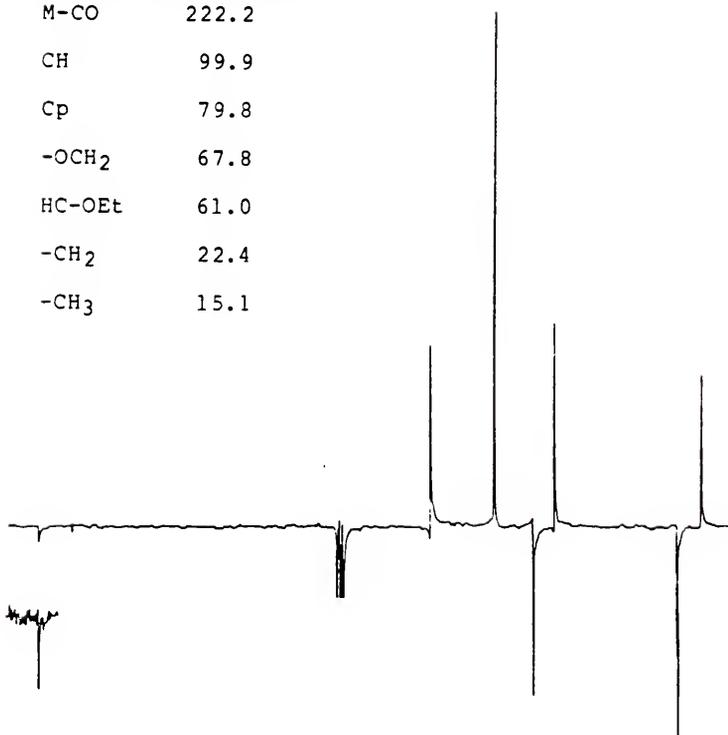
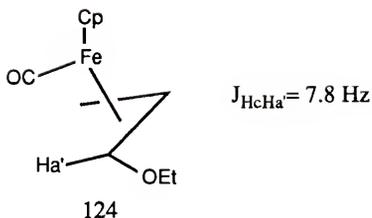
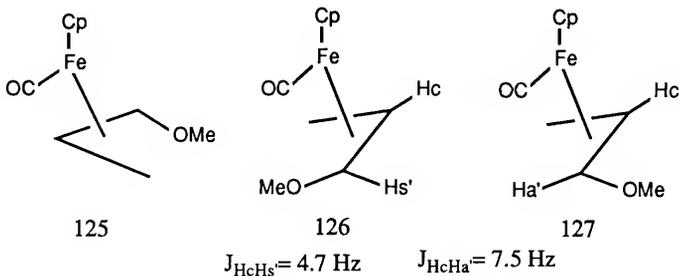


Fig. 25. <sup>13</sup>C NMR spectrum of compound 124 in C<sub>6</sub>D<sub>6</sub> (APT).



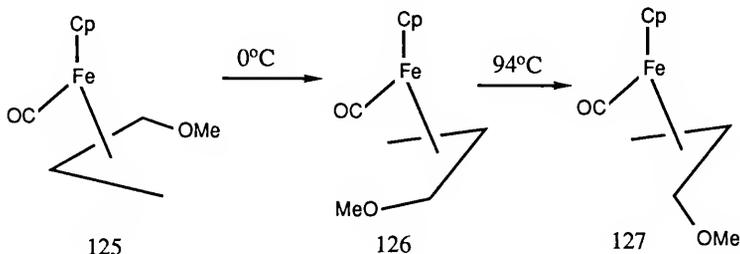
photolysis mixture. Compound 124's structural assignment was made on the basis of its  $^1\text{H}$  NMR coupling data.

Rosenblum has prepared compounds 125, 126 and 127 via an

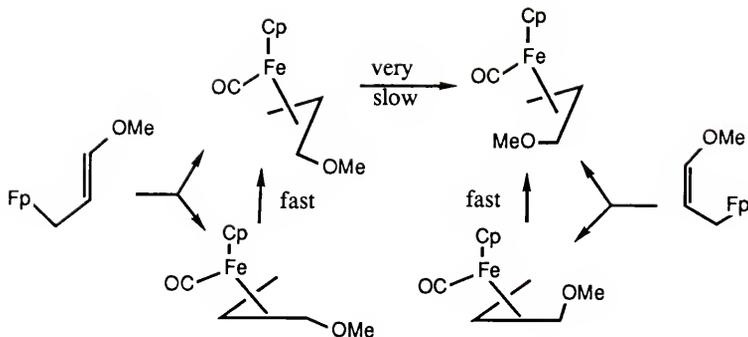


alternate synthesis.<sup>87</sup> He has determined the magnitudes of the coupling constants for the syn and anti protons when coupled to the central proton: these are distinctive and were used to assign the ethoxy group to the syn position on the allyl moiety. It was further determined from correlations of the  $^1\text{H}$  NMR chemical shifts of 123 and 124 with 125 and 127 that the allyl groups in both 123 and 124 were arranged in the exo orientation.

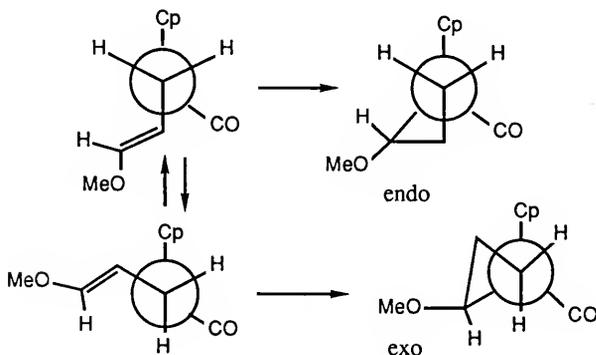
Rosenblum's results also throw some light onto the formation of these complexes from the photolysis of 109. It was discovered that the endo compound 125 rearranged quickly and completely at 0°C. to give the exo complex 126 (half-life at -10°C. of <30 min.). The anti orientation of the methoxy group was retained during this process. It was not until anti 126 was heated to 94°C. that isomerization to the syn compound 127 (half-life at 94°C. of 360 min.) occurred.



The exo, syn complex 127 was found to be the thermodynamically most stable isomer. Furthermore, though photolysis of  $h^1$ -allyl complexes produced both exo and endo pi-allyls, the cis-trans configurations of the sigma complexes were retained in the respective pi-allyl complexes: the reaction was stereospecific with respect to the configuration orientation of substituents on the double bond. The results were rationalized in the scheme shown below.



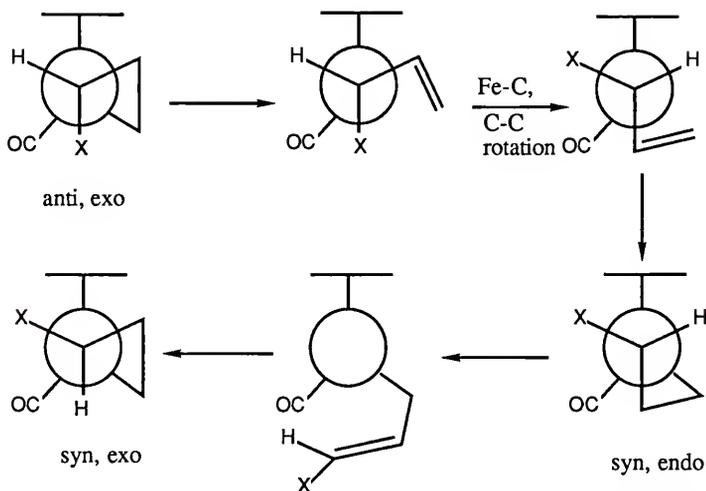
The exo, endo mixture obtained upon photolysis reflects the relative populations of the two conformations of the 16e- intermediates which collapse to give the pi-allyls.



Futhermore, since endo-exo isomerization is much more facile than syn-anti isomerization, decomplexation of a C=C bond ( $h^3-h^1$  rearrangement) and collapse back to the pi-allyl must be faster than the Fe-C and C-C bond rotations which convert

the anti allyl ligand into the syn allyl ligand.

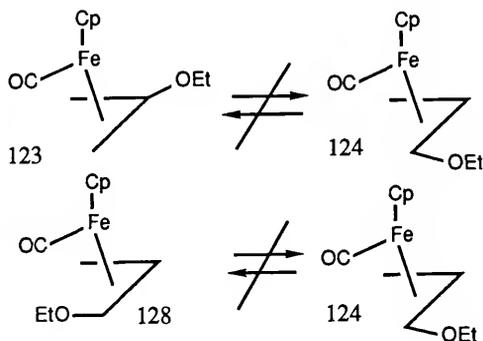
Decomplexation, Fe-C and C-C bond rotations, and



recomplexation may be accompanied by inversion at the iron center. A point of interest is that the syn-anti isomerization is not brought about by irradiation.

A mixture of the compounds 123 and 124 was photolyzed for 3 hours. Proton and carbon NMR spectra taken at intervals were unchanged with respect to the ratio of the two compounds. A small amount of  $Fp_2$  was detected after 3 hours of irradiation. This result is in agreement with Rosenblum's experiments; he did not find any interconversion of centrally and terminally substituted pi-allyl complexes. This precludes one pi-allyl as being the source of the other. It also appears safe to conclude, based

on Rosenblum's experiments, that 124 does not arise from the photolytically induced isomerization of 128.



The next point to address is the compound from which either or both 123 and 124 originate. The results of the thermolysis of compound 118 offer a clue. It will be remembered that the conversion of 118 to the acyl-carbene 122 occurred quite cleanly. A glance at Figure 20 shows that there is only a very small, broad resonance at 79.6 ppm. This could be indicative of the presence of a small amount of the pi-allyl complexes (the Cp resonances of 123 and 124 are 79.5 and 79.9 ppm) but, clearly, only trace amounts of material could be present at best. The point is that pi-allyl formation has been suppressed in the thermolysis of 118 relative to the photolysis of 109.

The obvious reason is that the intermediates responsible for the formation of the pi-allyls were directly or indirectly scavenged by the released triphenylphosphine.

Unsaturated complexes are known to be intercepted preferentially by phosphines when CO is also present. If a pi-allyl precursor was unsaturated, it would be directly scavenged by the phosphine; if it was in rapid equilibrium with an unsaturated species which reacted with phosphine, it would be indirectly scavenged. As long as the rearrangements which produce the pi-allyls are slow compared to the trapping of a 16e- intermediate with phosphine, their concentrations would be suppressed. Unsaturated complexes could therefore be candidates for pi-allyl precursors.

Complexes 111 and 119 both have one terminal CO, a Cp ring and a mono or bidentate ligand which has the same empirical formula as the pi-allyl ligands in 123 and 124. Complex 111 is unsaturated and complex 119 has been shown to be carbonylated by the addition of triphenylphosphine or CO by a process most likely involving an equilibrium between 119 and the unsaturated species 120. Therefore, 111 and 119 are obvious choices for the progenitors of the pi-allyls 123 and 124.

The photolysis of 109 in the presence of added CO provides another clue to the origin of the pi-allyl complexes. When the concentration profiles of the sigma complex 109 and the acyl-carbene complex 110 are compared during photolysis with and without the presence of added carbon monoxide, a very slight decrease in the rate at which

109 disappears can be detected. The rate at which 110 is formed is accelerated to a greater extent. This is consistent with a minimal effect of added CO on the rate of back reaction of intermediate 111 and an increase in the rate of the migratory insertion of 119 in the presence of externally added CO. The effect of the carbon monoxide is most dramatic in its impact on the concentration profiles of the alkyl-carbene complex 119 and the terminally substituted pi-allyl 124.

Figure 26 shows the effect of added CO on the concentration profile of the alkyl-carbene. The initial concentration build-up is attenuated, and the overall effect is that only a small, steady concentration is ever present during the experiment. Figure 27 shows that added CO has exactly the same effect on the reaction profile of the terminal pi-allyl complex 124. Only a small concentration which steadily builds is found. These two results imply that the source of 124 is 119. The effect of CO on the concentration of the central pi-allyl is also enlightening.

As can be seen from Figure 28, the concentration profile of the centrally substituted pi-allyl 123 is impacted differently than those of 119 or 124. Although the overall concentration present at any given time is decreased, the extent to which the concentration is decreased is not as great. Taken together these data are

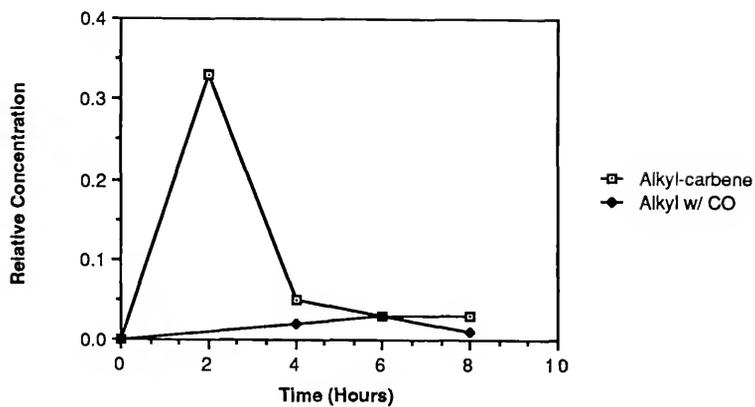


Fig. 26. Concentration profile of 119 during photolysis: effect of CO.

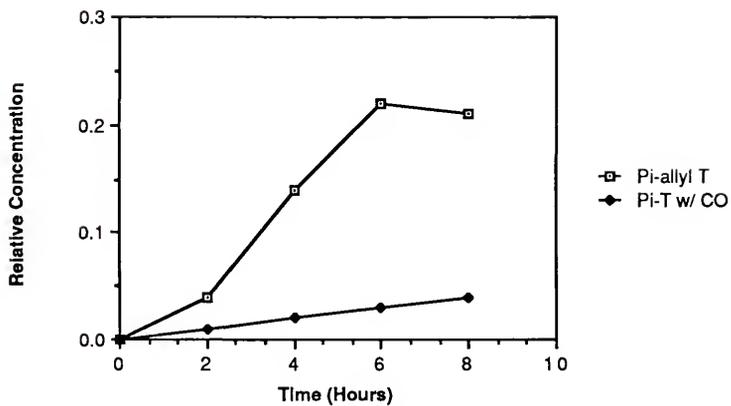


Fig. 27. Concentration profile of 125 during photolysis: effect of CO.

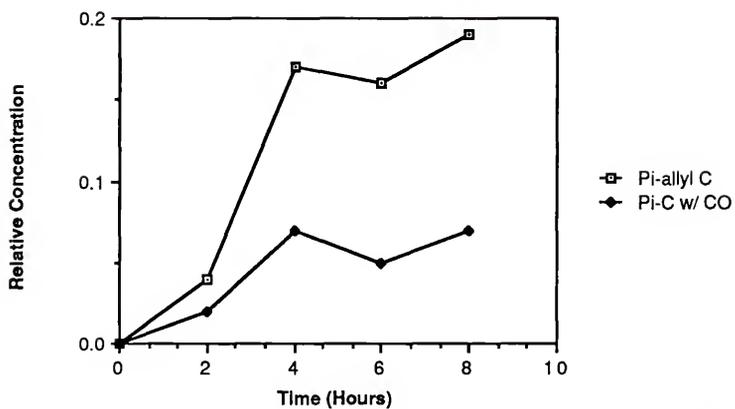


Fig. 28. Concentration profile of 124 during photolysis: effect of CO.

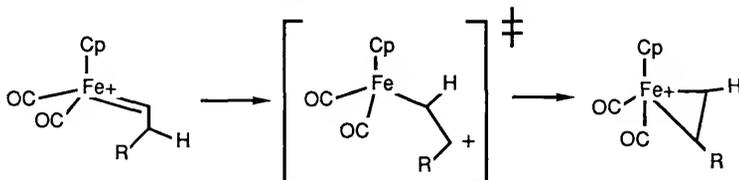


complex may form 123 or rearrange to give 119. Complex 119 then rearranges to give 124, undergoes migratory insertion to form 120 which is trapped as the acyl-carbene or reverses to give 111. Adding CO has little effect on the production of 111 or its conversion to 123 or 119; however, the rate at which 120 is trapped increases thereby depleting 119 with which it is in equilibrium. Since 123 forms in nearly the same quantity as in the unadulterated photolysis, reversal of 119 to 111 does not greatly contribute to the formation of 111: reversal of 119 to 111 is relatively slow compared to the other reactions which are occurring. When phosphine is present, not only is 119's concentration suppressed by enhancement of the migratory insertion pathway, but 111 is also trapped much more efficiently than is the case when added CO is present. Therefore, the thermolysis of 118 produces 111 which either rearranges to 119 which is then converted into 122, or which is trapped by phosphine before it has a chance to form 123.

In summation, during the photolysis of 109, rearrangement of 111 to 123 and that of 119 to 124 competes favorably with the back reaction of 111 to form 109 and the migratory insertion of 119 to produce 110. When CO is added, the reactions of 111 are not greatly affected, but the rearrangement of 119 to 124 can no longer compete with the conversion of 119 to 110. When triphenylphosphine is

present the rearrangement of 111 to 123 can no longer compete with the back reaction to form 118 or the rearrangement to form 119 which goes on to produce 122.

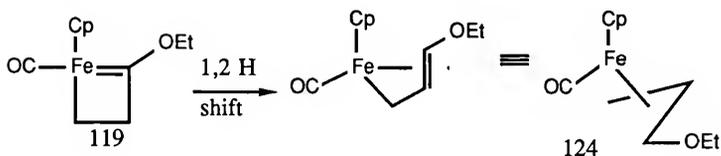
The question of the mechanism of the conversion of 119 to 124 will now be addressed. Many researchers have found that Fp-carbene complexes can rearrange to pi-complexes of the corresponding alkenes.<sup>88</sup> Such rearrangements can be spontaneous at low temperatures or require heating.<sup>89</sup> The mechanism of the reaction has been studied and described as a 1,2 hydride shift.<sup>90</sup> Brookhart has shown that the rearrangement involves a transition state in which substantial positive charge builds up on the beta carbon



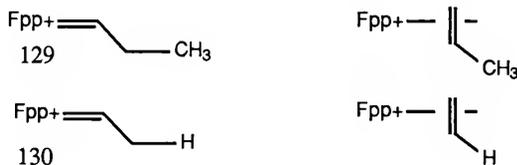
atom. The presence of a carbocation stabilizing substituent, such as an alkoxy group, on the carbon atom developing the positive charge greatly facilitates the rearrangement.<sup>91</sup> This acceleration was postulated to arise from a lowering of the activation energy of the rearrangement by delocalization of the developing positive charge in the activated complex.<sup>92</sup>



As shown below, the product of such a carbene rearrangement from the alkyl-carbene 119 would be a pi-allyl complex.



This is due to the metallacyclic structure of 119. The presence of alkyl substitution on the beta carbon atom, such as the alpha methylene group in 119, greatly facilitates such a rearrangement. Brookhart found that the methyl substituted carbene 129 rearranges much more easily (half-life at  $-40^{\circ}\text{C}$  of 1 hour) than the unsubstituted carbene 130 (half-life at  $25^{\circ}\text{C}$  of 3 hours).<sup>90a</sup>



In a further attempt to determine if compound 119 is indeed the progenitor of 124, a sample of 109 was photolyzed to obtain a quantity of the alkyl-carbene 119. This sample was then heated for 1 hour at  $75^{\circ}\text{C}$ . Figure 29 shows  $^{13}\text{C}$  NMR spectra taken before and after the thermolysis. The amounts of sigma 109 and acyl-carbene 110 did not change during the thermolysis; however, the alkyl-carbene all but disappeared

Before thermolysis

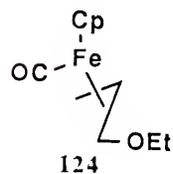
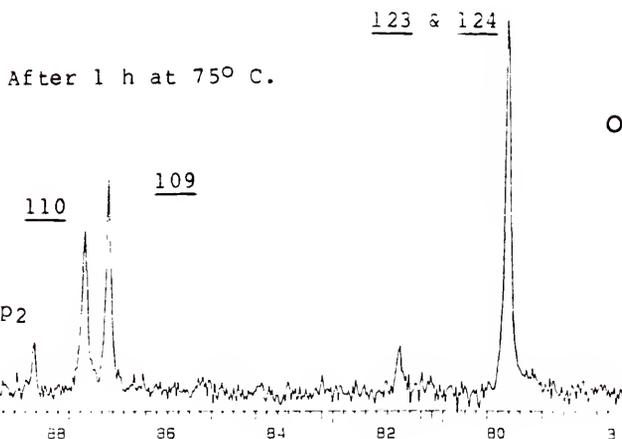
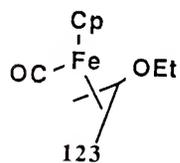
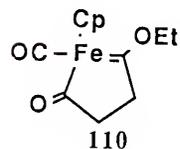
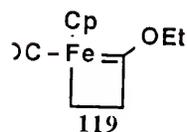
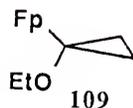
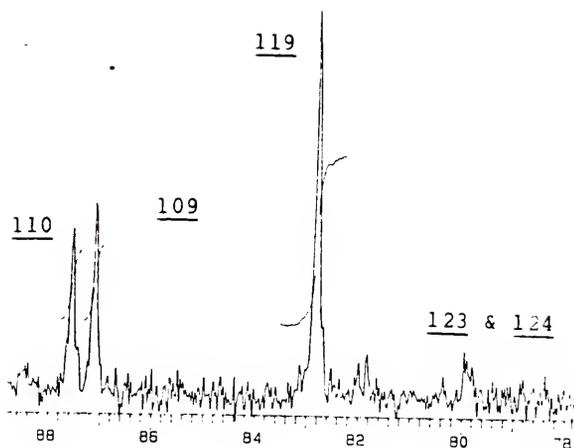
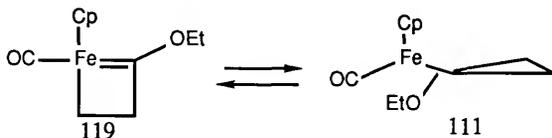


Fig. 29. Thermolysis of compound 119 in  $C_6D_6$ .

and in its place a mixture of the pi-allyls 123 and 124 was found. Figure 30 graphically displays these results. The outcome of this experiment gives rise to three very interesting probabilities: first, that the alpha elimination of the cyclopropyl alkyl group is reversible;



second, that the pi-allyl 125 is thermally accessible from the alkyl-carbene 119; third, that the anti configured pi-allyl is the kinetic product of the carbene rearrangement of 119.

The direct observation of a reversible alpha elimination of an alkyl group has never been reported.<sup>5b</sup> If 124 originates from 119 and 123 from 111 the observation of both 123 and 124 implies that the alkyl-carbene 119 may be thermally induced to undergo a 1,1-alkyl insertion into



the iron-carbon double bond. As was previously stated, this is a well known reaction for systems in which the reactant and product are acyclic. Reversible alpha eliminations for metallacycles have been proposed in gas-phase reactions.<sup>93</sup>

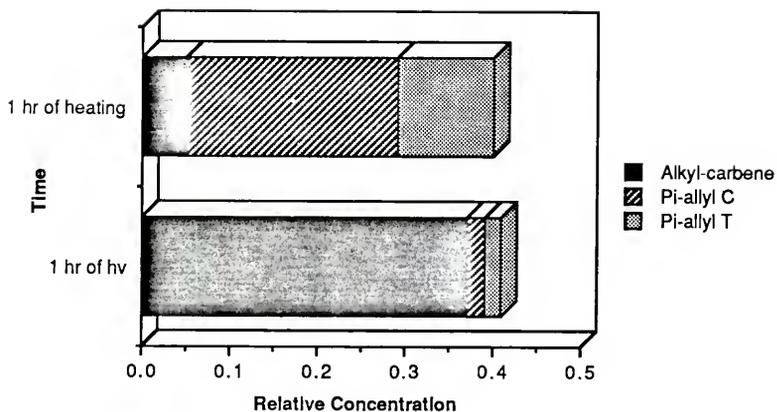
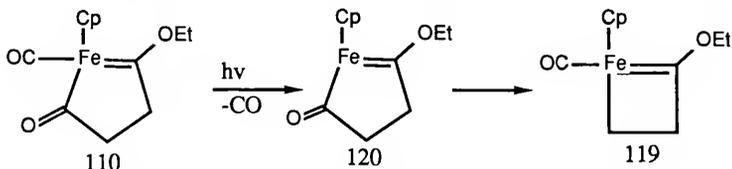


Fig. 30. A comparison of the relative concentrations of compounds 119, 123 and 124 after 1 h of photolysis and after 1 h of irradiation followed by heating at 75°C. for 1 h in C<sub>6</sub>D<sub>6</sub>.

Aside from Grubbs's previously stated reaction, few researchers have reported metallacyclic ring contraction reactions involving proposed reversible alkyl alpha eliminations.<sup>82</sup>

To explore this possibility further, the acyl-carbene complex 110 was photolyzed in a benzene solution. Previously, the phosphine substituted acyl-carbene 122 had been recovered from the photolysis of 110 in the presence of triphenylphosphine. Therefore it was hoped that the unsaturated complex 120 formed by loss of CO from 110 would rearrange to give the alkyl-carbene 119. Compound 119



could then undergo the reverse alkyl elimination (1,1 insertion) to form 111. The presence of photo-ejected CO in solution would allow for the interception of some of 111 as the sigma complex 109.

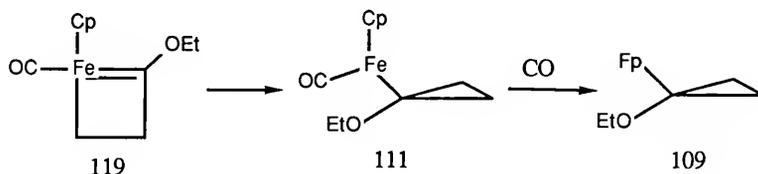
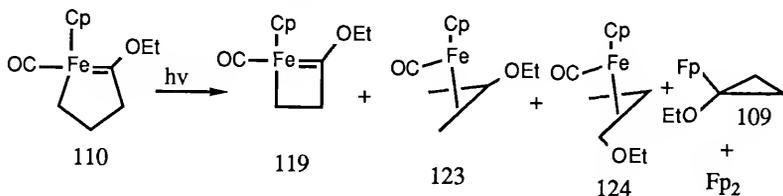
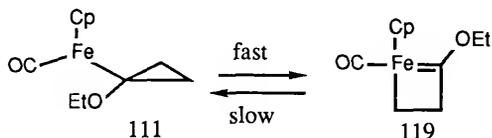


Figure 31 shows a  $^{13}\text{C}$  NMR spectrum of the Cp region of the reaction mixture after 2 hours of photolysis. Resonances due to the  $\text{Fp}_2$ , the alkyl-carbene 119, the pi-allyls 123 and 124 and the sigma complex 109 are all present.



After 6 hours the concentration of the acyl-carbene has decreased significantly while the concentration of all other peaks save the alkyl-carbene had increased: the alkyl-carbene's concentration remained fairly constant throughout the photolysis.

Inspection of Figure 31 shows that conversion of 110 back to 109 is much slower than the formation of 110 from 109 during the photolysis of the sigma complex. Furthermore, the amount of 124 present is greater than that of 123. Also, 119 is the dominant species present. These facts are



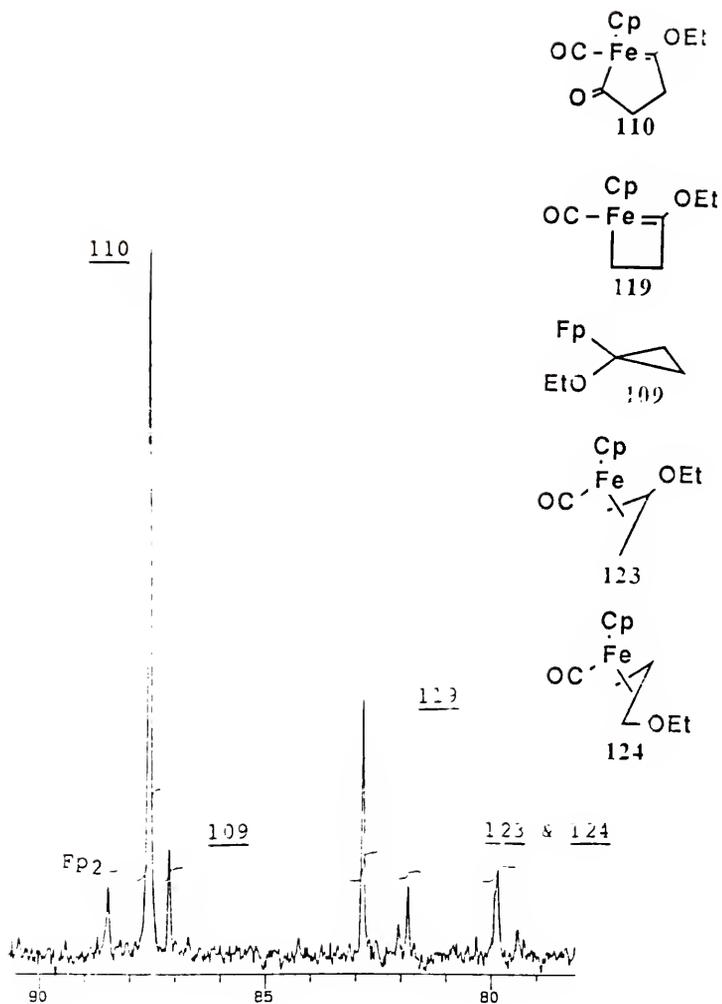
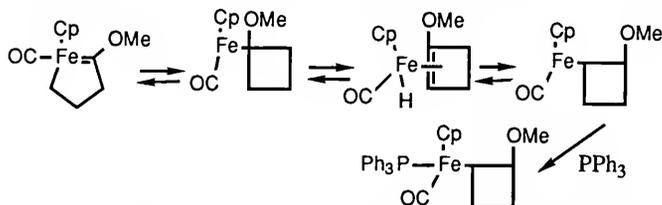


Fig. 31.  $^{13}\text{C}$  NMR spectrum of the photolysis of compound 110 after 2 hours of irradiation in  $\text{C}_6\text{D}_6$ .

consistent with a slow conversion of 119 to 111. It is likely that the increase in strain energy encountered in the reaction is responsible to some degree for this fact.

The result of the above experiment coupled with those from the thermolysis of the alkyl-carbene provides strong evidence for the reversibility of all the steps in the mechanism proposed by Jones and Lisko for the reaction. The most significant implication is that the reversibility of an alpha elimination of an alkyl group has been established. Stenstrom proposed such a step in the phosphine induced rearrangement of his alkyl-carbene complex to a beta-



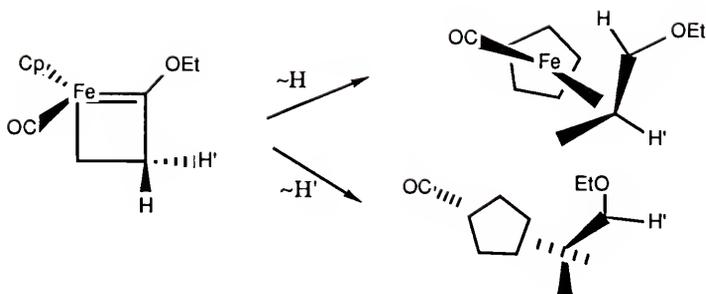
substituted sigma complex. Interestingly enough, the exhaustive photolysis of the acyl-carbene (over 20 hours) implies that the formation of the pi-allyls 123 and 124 is not reversible under photolytic conditions. The fact that the ratio of 123 and 124 does not change (vide supra) upon continued heating of the thermolysis of products 119 is consistent with the premise that the formation of the pi-allyl complexes is irreversible.

The formation of the pi-allyl complexes under thermal conditions coupled with the reversibility of the

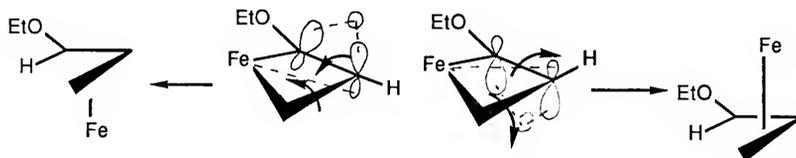
rearrangements implies that the photolysis of 109 has "light" and "dark" components. The "light" phase serves as a pathway for the production of the 16e- unsaturated intermediates 111 and 120 by the photo-ejection of CO. The "dark" phase involves the thermal equilibration of 111, 119, and 110. It also includes the apparently irreversible rearrangements of 111 to the pi-allyl 123 and that of 119 to 124.

The fact that Rosenblum found that the anti pi-allyl 126 does not isomerize to the syn pi-allyl 127 photolytically or until heated to 94°C shows that there is a considerable thermal barrier to the rearrangement. Since the anti pi-allyl should have a half-life at 94°C of 6 hours, if any had formed during the thermolysis (which lasted only 1 hour) of 119 it should have been detected: it was not. It appears that the thermal rearrangement of 119 produces the syn pi-allyl exclusively.

The above conclusion is in complete accord with Brookhart's mechanism for the carbene to pi-complex rearrangement. It can be seen upon inspection of models that the syn pi-allyl 124 can be produced from the alkyl-carbene 119 upon migration of either beta hydrogen so long as the iron complexes to the opposite face of the developing allyl ligand. This can be accounted for by a mechanism in which there is some bonding between the iron and the beta



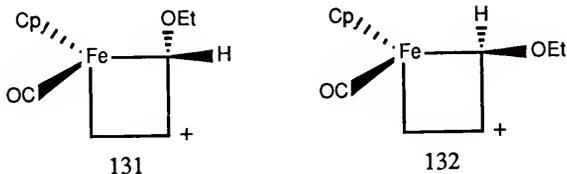
carbon atom in the transition state. The iron begins bonding with the lobe of the developing p-orbital opposite to that from which the hydride is departing.



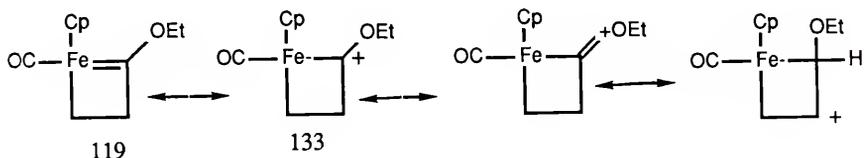
The orientation of the ethoxy group is determined by the rotation of the C-C bonds to form the allyl moiety. The 100% stereoselective nature of the rearrangement is consistent with the view of the rearrangement as concerted although not necessarily synchronous; as the hydride departs and positive charge develops on the beta carbon atom, the iron assists from the backside and bonding begins. The sigma orbitals on the alpha atoms of the allyl moiety follow

the iron and become the p-orbitals of the allyl ligand. This rotation puts the ethoxy group in the syn position no matter which beta hydrogen migrates.

If the pair of free zwitterions 131 and 132 were formed, both syn and anti isomers would form unless steric



effects precluded rearrangement to only the observed syn isomer. This would require that only one of the beta hydrogens migrate to produce the product. Furthermore, the conversion of the resonance form 133 of 119, which has a tertiary iron and alkoxy stabilized cationic center, to 131 or 132, which possesses secondary cationic center lacking



iron or alkoxy stabilization, should be unfavorable energetically. A concerted mechanism in which bond formation to the beta carbon occurs while charge builds

would help to offset the energy required for the migration of the hydride.

In order to determine whether the solvent used in the photolysis of 109, benzene, plays an important role in the reactions, the photolysis of the sigma complex was carried out in two other solvents. The non-coordinating solvent cyclohexane and the oxygen donor tetrahydrofuran (THF) were used. The photolyses were carried out in a merry-go-round apparatus along with a sample which had benzene as the solvent. Ferrocene was used as a standard and the relative concentrations of the various compounds were determined by a comparison of integrals obtained by  $^{13}\text{C}$  NMR spectroscopy.

The results obtained from this experiment showed no great dependence on the solvent used. The concentration profiles for the sigma complex, the alkyl- and acyl-carbenes,  $\text{Fp}_2$ , and the pi-allyls were very similar. The impact these three solvents have on migratory CO insertions in Fp systems has been shown to be small.<sup>82</sup> Figure 32 shows the concentration profiles of the alkyl-carbene in the three different solvents. It appears that the role of solvent in the alpha elimination of an alkyl group is minimal: the concentrations as a function of time do not deviate greatly from one another in the different solvents.

The results of the above experiments provide a sound basis of evidence for the mechanism proposed by Jones and

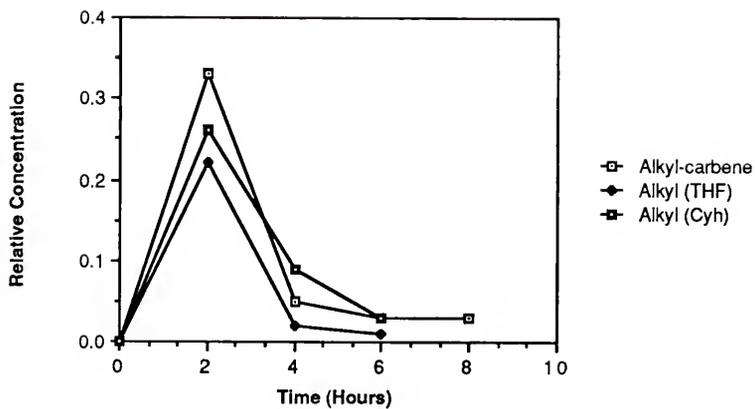
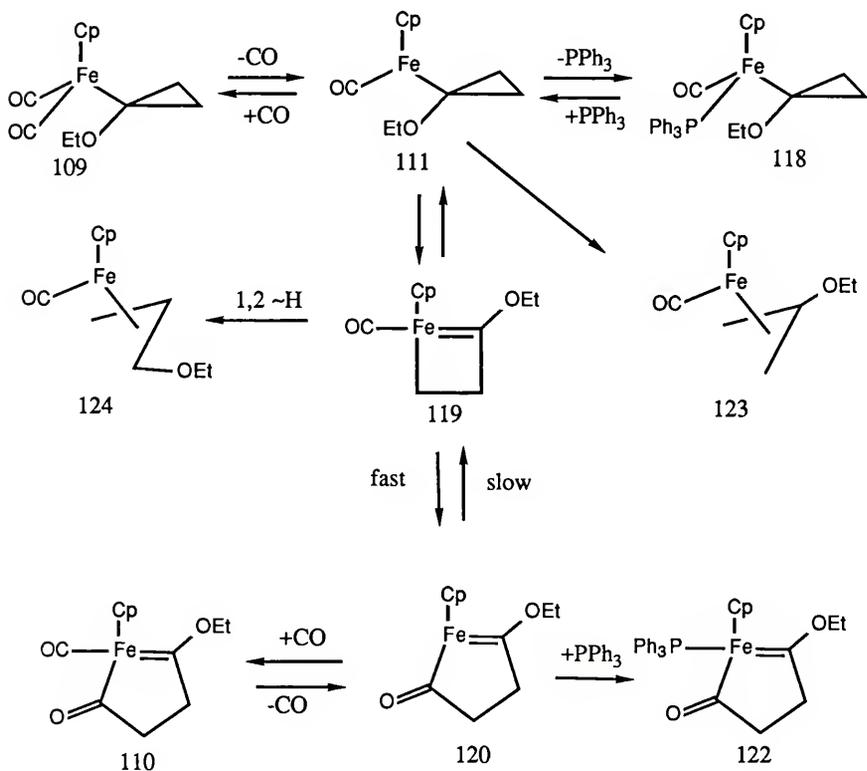
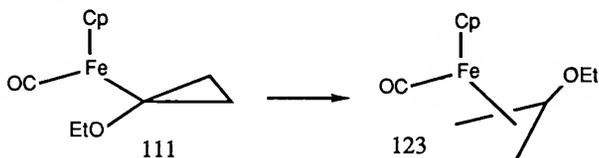


Fig. 32. Concentration profiles of compound 119 during irradiation in benzene, THF and cyclohexane.

Lisko. Along with this, it was found that the alpha elimination of the methylene group of the cyclopropane is reversible with the forward reaction proceeding at a greater rate than the reverse. Two new products from the photolysis of the compound 109 were isolated and characterized, namely the pi-allyls 123 and 124. Evidence was given that 123 and 124 arise from different precursors: it is likely that 123



arises from a rearrangement of the unsaturated intermediate 111; 124 most likely arises from a carbene rearrangement of compound 119. The formation of the pi-allyls appears to be irreversible. Both photolytic (reactions occurring from excited states) and thermal reactions occur during the photolysis. The scheme given above depicts the transformations thought to occur during the photolysis of complex 109.



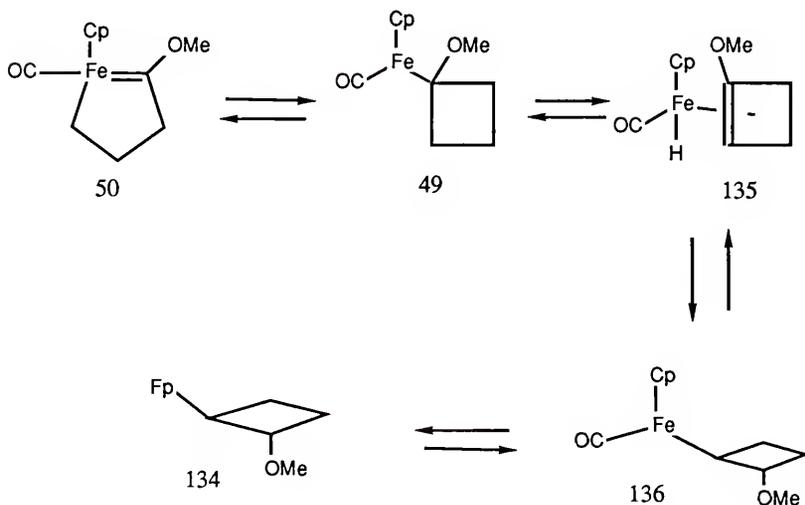
The question of how 111 rearranges to form 123 is a thorny one. This problem will be addressed in the following chapter. Experiments which were proposed in order to shed some light on this question proved interesting in their own right. They will also be discussed.

CHAPTER III  
THIOPHENYL, FLUORO AND UNSUBSTITUTED  
CYCLOPROPYL SYSTEMS

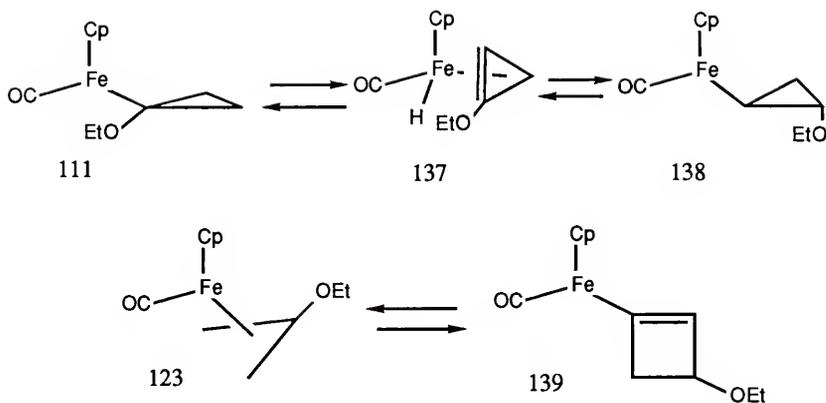
In the previous chapter it was suggested that a rearrangement of the unsaturated complex 111 was responsible for the production of the centrally substituted pi-allyl complex 123. Attention is now turned to possible mechanisms which account for the formation of 123 from 111. Four mechanistic schemes which are grounded in literary precedent will be evaluated. The behavior of Fp cyclopropyl sigma complexes during photolysis and thermolysis will be discussed as well as the photo-reaction of an acyclic Fp sigma complex.

It has been argued that the terminally substituted pi-allyl 124 owes its existence to a 1,2 hydride migration from the alkyl-carbene complex 119. Based upon this suggestion and the work of Stenstrom, a similar rearrangement from an isomeric alkyl-carbene complex can be proposed to account for the formation of 123. Stenstrom found that treatment of his alkyl-carbene complex 50 with carbon monoxide led to the isolation of the beta substituted sigma complex 134. The origin of the sigma complex was rationalized by the

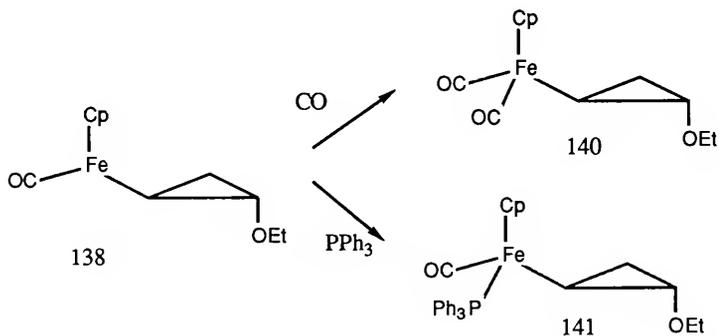
following scheme. The reversibility of the reactions was demonstrated by the photolysis of 134; it produced the alkyl-carbene 50.



If the unsaturated intermediate 111 were to undergo a beta hydride elimination to produce the hydrido pi-complex 137, a 1,2 insertion reaction in which the hydride is delivered to the carbon bearing the ethoxy group would produce the 16e<sup>-</sup> species 138. This intermediate would form the alkyl-carbene complex 139 upon alpha-elimination of a methylene group. A 1,2 hydride carbene rearrangement would then give the pi-allyl 123 directly.

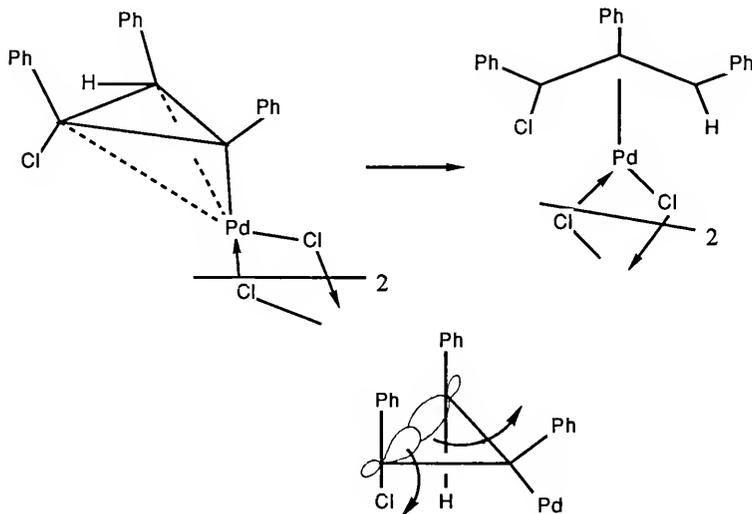


It is highly unlikely that this mechanism is responsible for the formation of 123. At no time during the photolysis of 109 or the thermolysis of 118 (which would generate the same reactive intermediate, 111) were the beta substituted sigma complexes 140 or 141 detected; neither

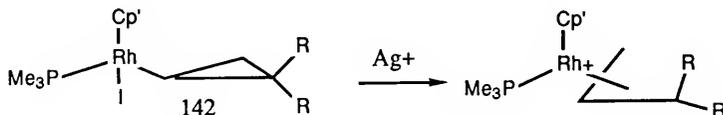


complex was isolated from the final reaction mixtures. It is to be expected that complex 138 should be as readily trappable with CO or triphenylphosphine as 111. Since it has been clearly demonstrated that 111 can be generated and trapped with both CO and phosphine, it is unlikely that 138 is present during the photolysis of 109.

A second pathway for the conversion of 111 into 123 involves insertion of the metal into the C-C bond between the two ring methylene groups. Such reactions have been proposed for other metal systems. Battiste used such an insertion to explain the results of his investigations of a palladium system.<sup>95</sup> The stereochemistry of the product

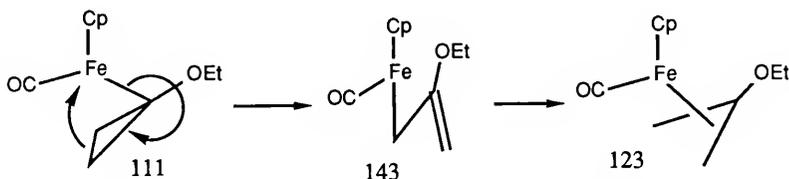


indicates that insertion involving direct attack of the metal center on the bond with the orbital motion as shown does not occur. Bergman was able to generate a pi-allyl complex via halide abstraction from the rhodium complex 142.<sup>96</sup> The substitution of the resulting pi-allyl

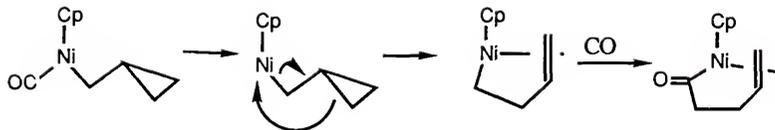


is consistent with an attack upon the C-C bond of the two beta carbon atoms.

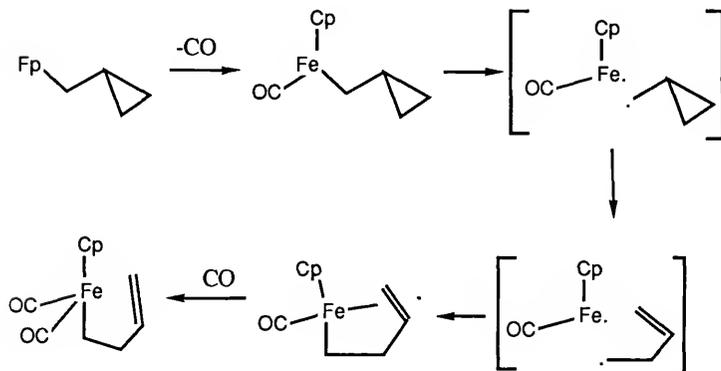
The beta-elimination of a ring methylene group from 111 would produce the species 143. Coordination of the resulting double bond leads to the pi-allyl 123. Green has



shown that unsaturated h<sup>1</sup>-allyl CpFeCO complexes form h<sup>3</sup>-allyl complexes very readily.<sup>97</sup> The complexation of the olefin could also occur concomitantly with the beta-elimination. Such eliminations have been proposed for cyclopropyl carbonyl sigma complexes. Brown postulated that such a reaction was concerted for his nickel system which

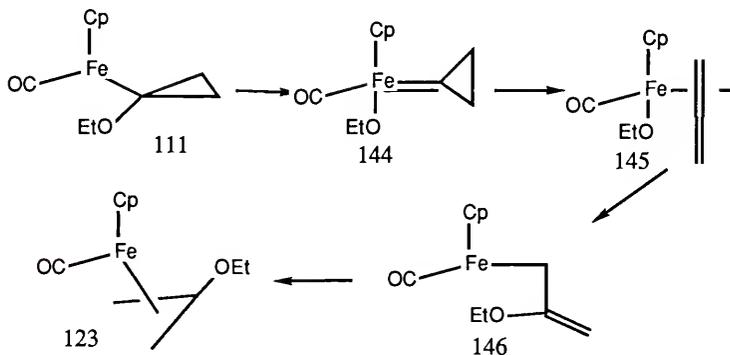


then underwent a migratory CO insertion.<sup>98</sup> Pannell prefers a stepwise radical mechanism to rationalize the beta-elimination he observes in the analogous iron



system.<sup>99</sup> It should be noted that the ethoxy group of complex 111 should facilitate the beta-elimination of the ring methylene group. It has been found that ethoxy substituted olefins complex preferentially to iron centers over unsubstituted alkenes.<sup>100</sup> This has been attributed to an electronic effect of the ethoxy group.

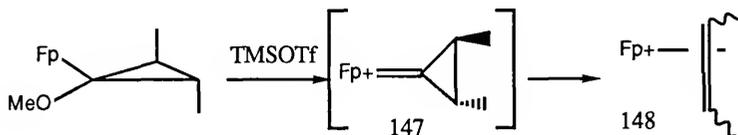
Finally, the following scheme also accounts for the conversion of 111 into 123. This mechanism involves the



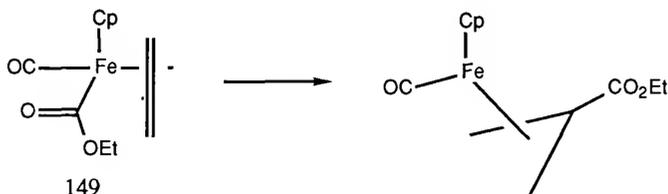
alpha-elimination of the ethoxy group of the cyclopropyl ligand to form the alkoxy cyclopropylidene 144. The cyclopropylidene then undergoes ring opening to form the allene complex 145. Migration of the alkoxy group to the central atom of the allene yields the unsaturated complex 146 which completes its coordination sphere to form the pi-allyl complex 123.

As was previously stated, alpha-eliminations of alkoxy groups resulting in carbene formation have been postulated by Semmelhack and Wulff. Jones and Lisko have demonstrated that alkoxy abstracting reagents can be used to convert the sigma complex 43 into the cationic allene complex 148 presumably via the cyclopropylidene complex 147.<sup>101</sup> In 111 the abstracting agent would be the unsaturated metal center.

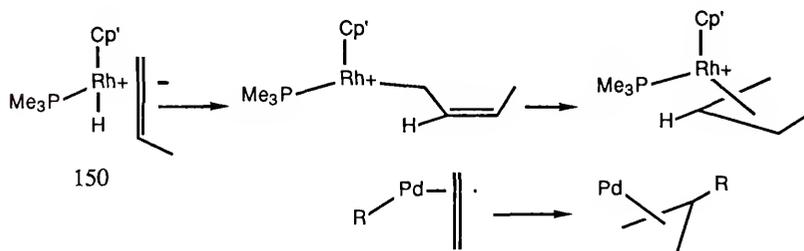
Though the resulting alkoxy cyclopropylidene complex 144 bears no charge, openings of neutral cyclopropylidenes to



allenes are known for both uncomplexed<sup>102</sup> and complexed species.<sup>103</sup> Finally, intramolecular migrations of moieties on metal species have been demonstrated to yield pi-allyl complexes. Wojcicki has found this to be the case for the iron species 149<sup>104</sup> and Werner has reported such a migration



for the rhodium complex 150.<sup>105</sup> Similar rearrangements are also known for palladium species.<sup>106</sup>

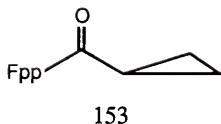


The results reported in the previous chapter are consistent with the beta C-C insertion, the beta alkyl elimination and the alkoxy alpha-elimination mechanisms described above. Preference for one mechanism over the others would be based on speculation rather than experimental results. The chemistries of differently substituted cyclopropyl Fp complexes were examined; it was hoped that the data gleaned from these experiments would shed some light on the problem of the conversion of 111 to 123. Furthermore, the nature and requirements of the alkyl alpha-elimination which produces the alkyl-carbene 119 from 111 could also be probed.

The first system studied was the unsubstituted cyclopropyl complex 151. Both the acyl and sigma complexes

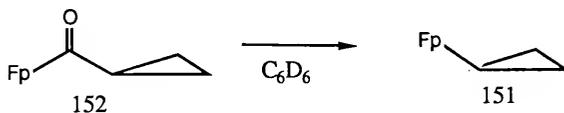


are known. Stone prepared the acyl complex 152 and found that he could not decarbonylate the compound thermally or photochemically to generate the sigma complex.<sup>107</sup> The photolysis was carried out both in light petroleum ether and neat. Conversion of the acyl to the phosphine substituted acyl complex 153 occurred in cyclohexane solution in the presence one equivalent of triphenylphosphine. Manganiello found that the acyl complex could be decarbonylated to give

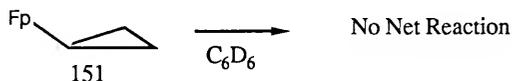


the sigma complex if acetone was used as the solvent.<sup>6a</sup>  
 Rosenblum prepared the sigma complex directly from NaFp and cyclopropyl bromide.<sup>8a,b</sup>

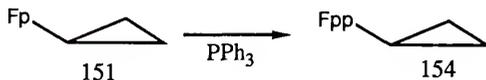
The acyl complex 152 was prepared via a modification of Stone's procedure. It was found that the compound could be smoothly decarbonylated photolytically in benzene solution.



The sigma complex 151 was also prepared from the cyclopropyl bromide. Photolysis of the sigma complex for 6 hours in benzene led to no net reaction. When a benzene solution of the sigma complex was irradiated in the presence of one equivalent of triphenylphosphine, the phosphine substituted sigma complex 154 was formed quantitatively in 2 hours as

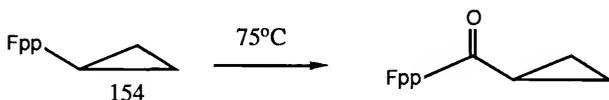


determined by NMR methods. Figure 33 depicts the  $^{13}\text{C}$  NMR spectrum of 154. The peaks corresponding to the carbonyl



and alpha carbon atoms show characteristic phosphine couplings (222.5 ppm;  $J^2_{\text{PC}}=31.4$  Hz and -11.0 ppm;  $J^2_{\text{PC}}=27.2$  Hz respectively).

The phosphine substituted sigma complex 154 was heated to 75° C. in benzene for 10 days. As was previously stated, these conditions are known to induce dissociation of the phosphine ligand to generate a coordinatively unsaturated intermediate. NMR analysis of the reaction mixture at the end of this time period showed the presence of the starting sigma complex and a small amount of the phosphine substituted acyl complex 153. Apparently phosphine



dissociation did occur which induced a migratory insertion of the cyclopropyl ligand in 154. Another resonance in the carbon spectrum was detected in the Cp region at 78.9 ppm. Such a value would be expected for the Cp ring carbons of a pi-allyl complex, but no corroborating data were present to

Chemical Shift (ppm)

|                    |             |
|--------------------|-------------|
| M-CO               | 222.5       |
| PPh <sub>3</sub>   | 137.8-127.8 |
| Cp                 | 85.5        |
| -CH <sub>2</sub> - | 11.7<br>9.9 |
| -CH-               | -11.0       |

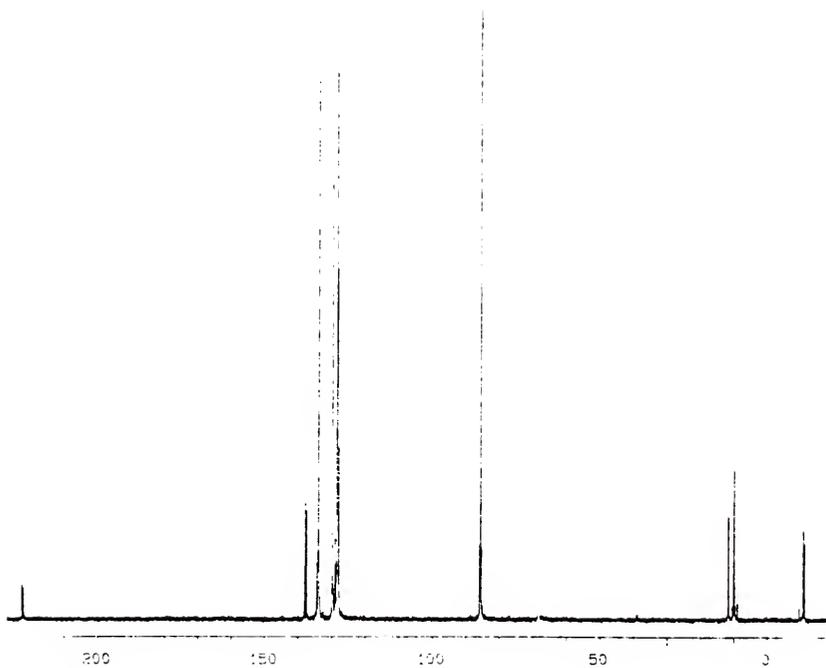
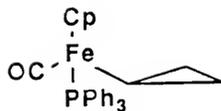
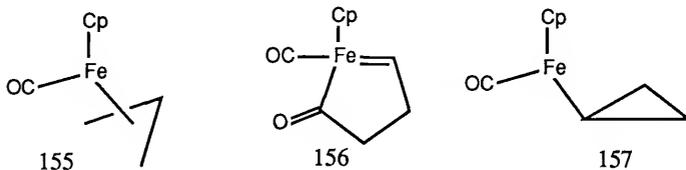


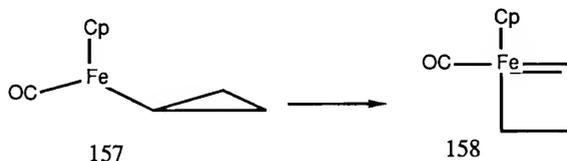
Fig. 33. <sup>13</sup>C NMR spectrum of compound 154 in C<sub>6</sub>D<sub>6</sub>.

support such an assignment. A brown, intractable solid which resisted characterization was also isolated from the reaction mixture.

The interesting observations in the above experiments are that the pi-allyl complex 155 and the acyl-carbene complex 156 were not found, yet the 16e- intermediate 157



was intercepted by triphenylphosphine. If the unsaturated species 157 was indeed produced in the photolysis or thermolysis, the fact that no carbene species was detected could be evidence for the requirement of a group present on the alpha carbon atom of the cyclopropyl ring to stabilize the forming carbenic center during the alpha-elimination of a ring methylene group. In other words the strain relief encountered upon the formation of 158 from 157 is not of sufficient magnitude to drive the reaction forward.



The above results are also consistent with a scheme in which the free  $16e^-$  species 157 never actually forms; the absence of products is also consistent with the absence of the alleged reactive species. It could be the case that the

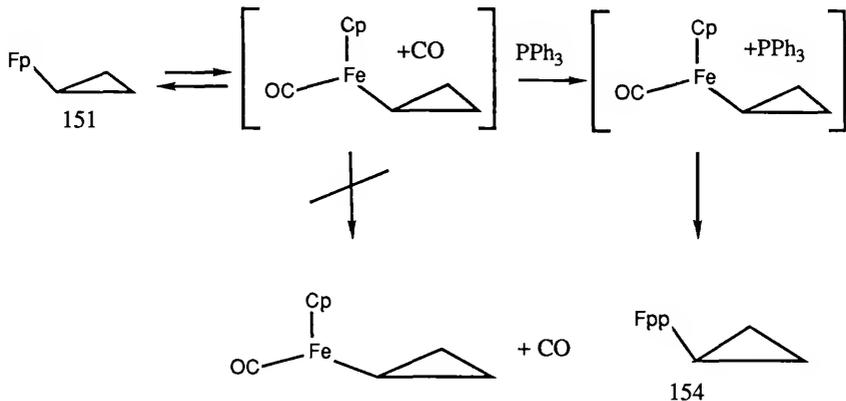
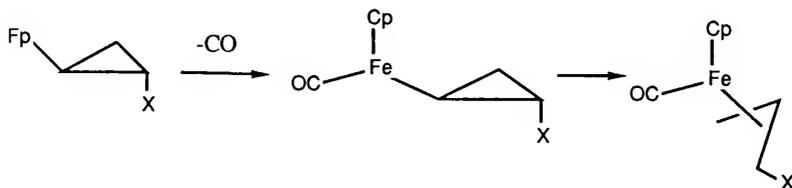


photo-ejected CO never leaves the solvent cage unless the phosphine ligand is present to aid in its displacement. If rearrangement to 155 and 158 occurs only from 157 once it frees itself from the photo-ejected carbon monoxide, no net photochemistry would be observed unless the nucleophilic phosphine were present. The rearrangement of 111 proceeds because the oxygen lone pair can take the place of the phosphine in displacing the photo-ejected CO from the solvent cage of 111; the alpha alkoxy substitution is necessary only to free 111 from photo-ejected CO. Two experimental results are in conflict with this line of reasoning.

Photolysis of the sigma complex 151 in the highly coordinating solvent tetrahydrofuran (THF) produced no net reaction other than the slow production of  $Fp_2$ . It seems likely that THF in such a high concentration would be able to displace CO from the solvent cage of an unsaturated species, especially if this is the role played by the alpha alkoxy group in 111, allowing for the formation 157 free of CO; however, it could also be the case that the THF-solvated 157 may simply sit around in solution until back reaction with CO could occur. Ligation of carbon monoxide would be favored thermodynamically over that of THF since backbonding with the metal center is possible only for the former.

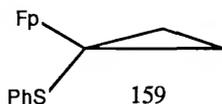
It will be briefly mentioned here that the photolysis of a beta substituted cyclopropyl complex produced a pi-allyl compound. A full account of the experiment will be



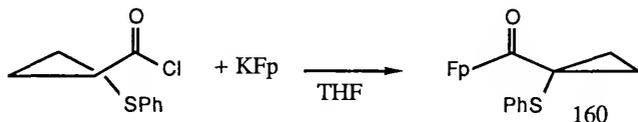
given later (vide infra), but it should be noted that no donor group is present on the alpha carbon atom which can displace photo-ejected CO from the solvent cage of the unsaturated intermediate in the manner suggested above: the alpha substituent is a hydrogen atom just as in complex 151.

This result implies that the role of the alpha alkoxy group is not simply to free 111 from carbon monoxide.

Though it was suggested above that displacement of CO via chelation is not the lone role of the alpha alkoxy group during the photolysis of 109, the next system studied did provide compelling evidence that oxygen coordination through the alkoxy group's lone pair may indeed occur. This conclusion was based on the results of the chemistry of the thiophenyl substituted sigma complex 159.



The alpha thiophenyl substituted acyl complex 160 was prepared by the reaction of the appropriate acid chloride



with KFc. Figures 34 and 35 display the proton and carbon NMR spectra of 160 respectively. The photolysis of a benzene solution of 160 was followed via  $^{13}\text{C}$  NMR. The Cp ring carbons of 160 appear at 86.5 ppm, an acyl carbonyl peak is detected at 250.3 ppm and a terminal carbonyl at 215.3 ppm. After 2 hours of irradiation, a new singlet at

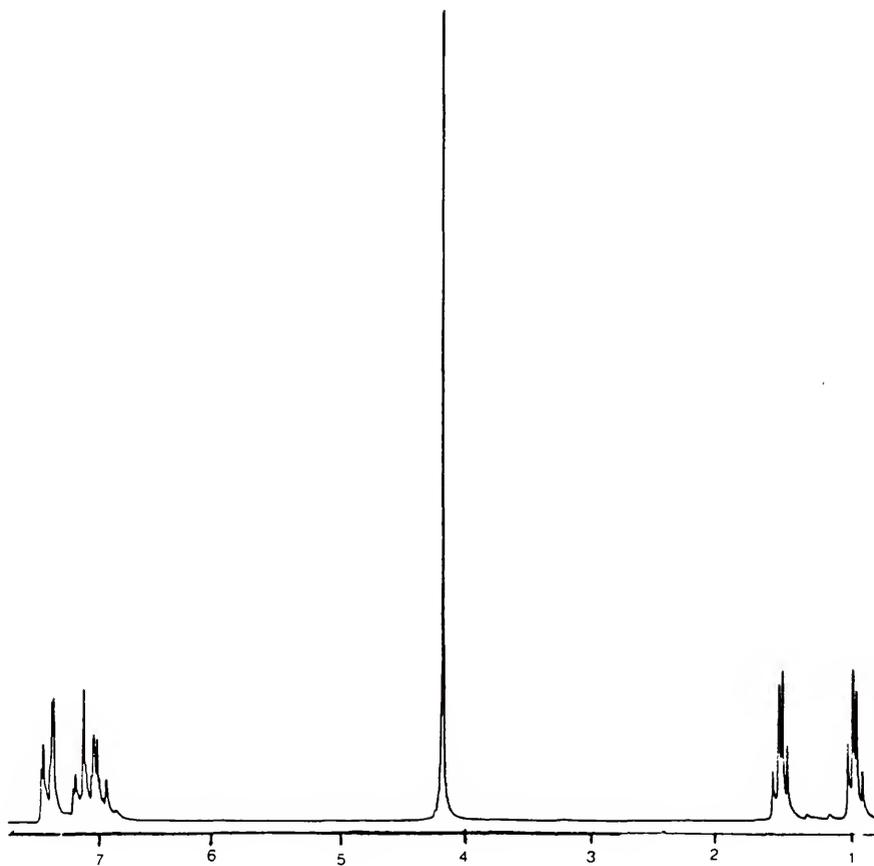
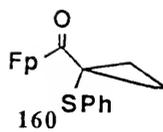


Fig. 34.  $^1\text{H}$  NMR spectrum of compound 160 in  $\text{C}_6\text{D}_6$ .

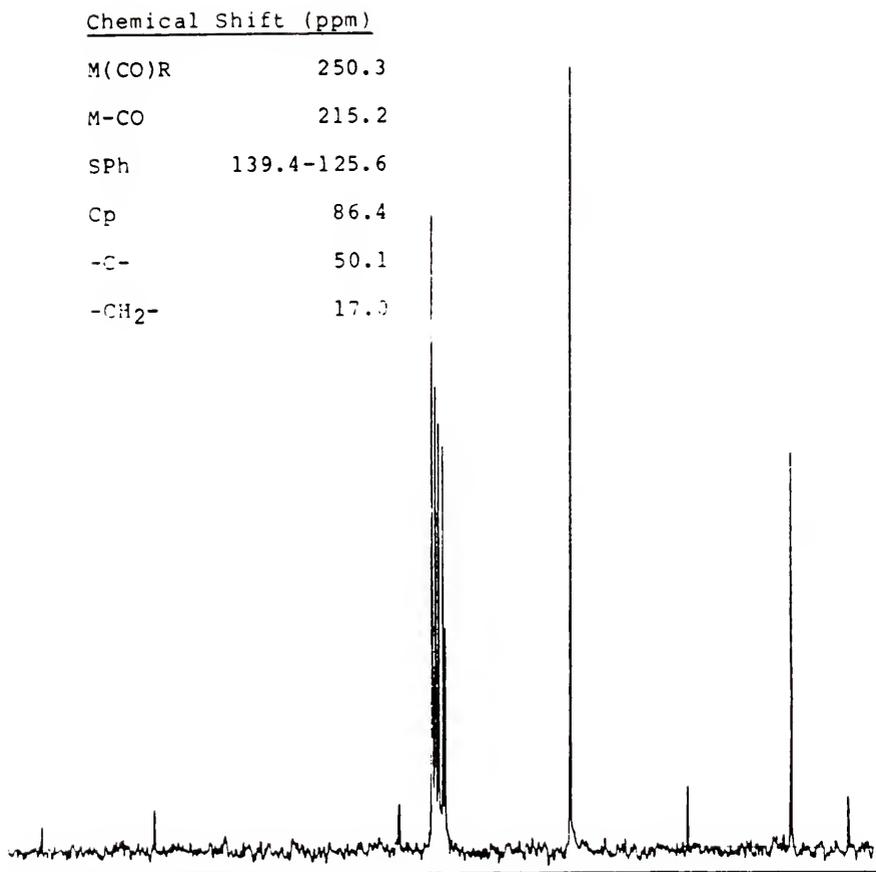
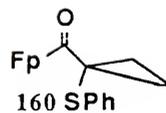
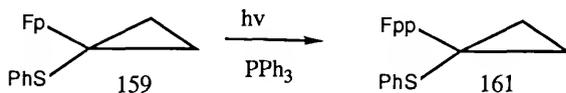


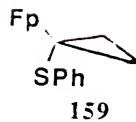
Fig. 35.  $^{13}\text{C}$  NMR spectrum of compound 160 in  $\text{C}_6\text{D}_6$ .

87.8 ppm is present and the peak corresponding to the Cp of the acyl complex has all but disappeared. The sigma complex 159 may be isolated by column chromatography as a yellow oil. Figure 36 depicts the carbon NMR spectrum of the sigma complex. This same sigma complex was also prepared directly via the reaction of 1-iodo-1-thiophenylcyclopropane with K<sub>2</sub>Fp.

In order to establish the presence of an unsaturated intermediate during the photolysis of 159, the sigma complex was irradiated in the presence of one equivalent of triphenylphosphine. The yellow solution gave way to a deep red color. Evaporation of the solvent produced a red oil which gave a red solid upon recrystallization from hexanes at low temperature. The red solid was assigned the structure of the phosphine substituted sigma complex 161 on



the basis of all spectroscopic and chemical data collected. Figure 37 displays the <sup>13</sup>C NMR spectrum of the complex. Both the terminal carbonyl peak at 222.7 ppm and the alpha carbon atom of the cyclopropyl ring at 7.7 ppm are coupled to phosphorus by 32.1 and 21.5 Hz respectively. The Cp ring appears at 86.3 ppm, and the ring methylene carbons are



Chemical Shift (ppm)

|                    |             |
|--------------------|-------------|
| M-CO               | 216.4       |
| SPh                | 139.6-126.4 |
| Cp                 | 87.8        |
| -CH <sub>2</sub> - | 20.6        |
| -C-SPh             | 10.7        |

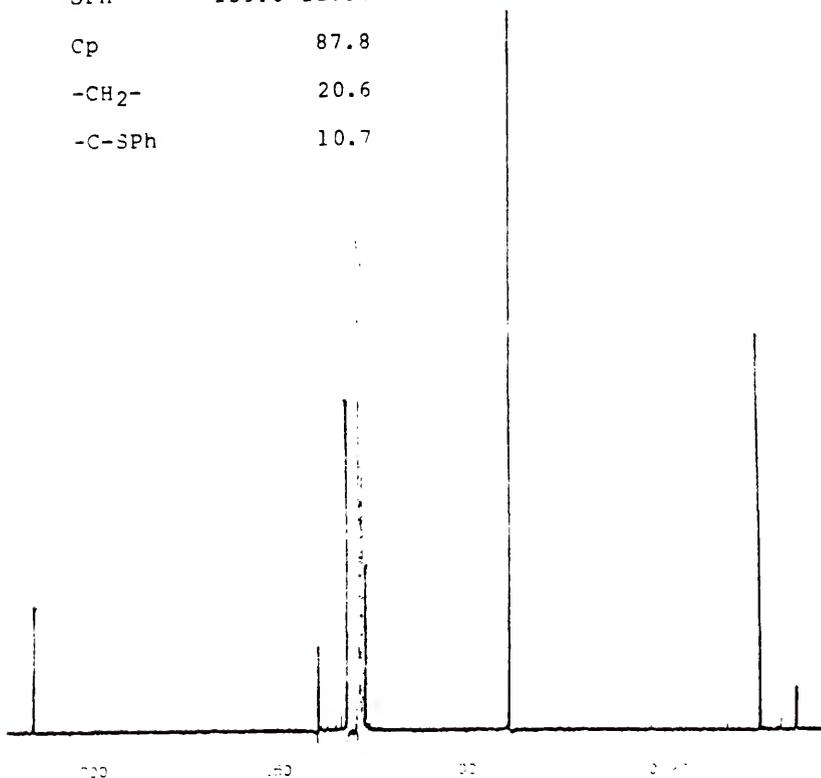


Fig. 36.  $^{13}\text{C}$  NMR spectrum of compound 159 in  $\text{C}_6\text{D}_6$ .

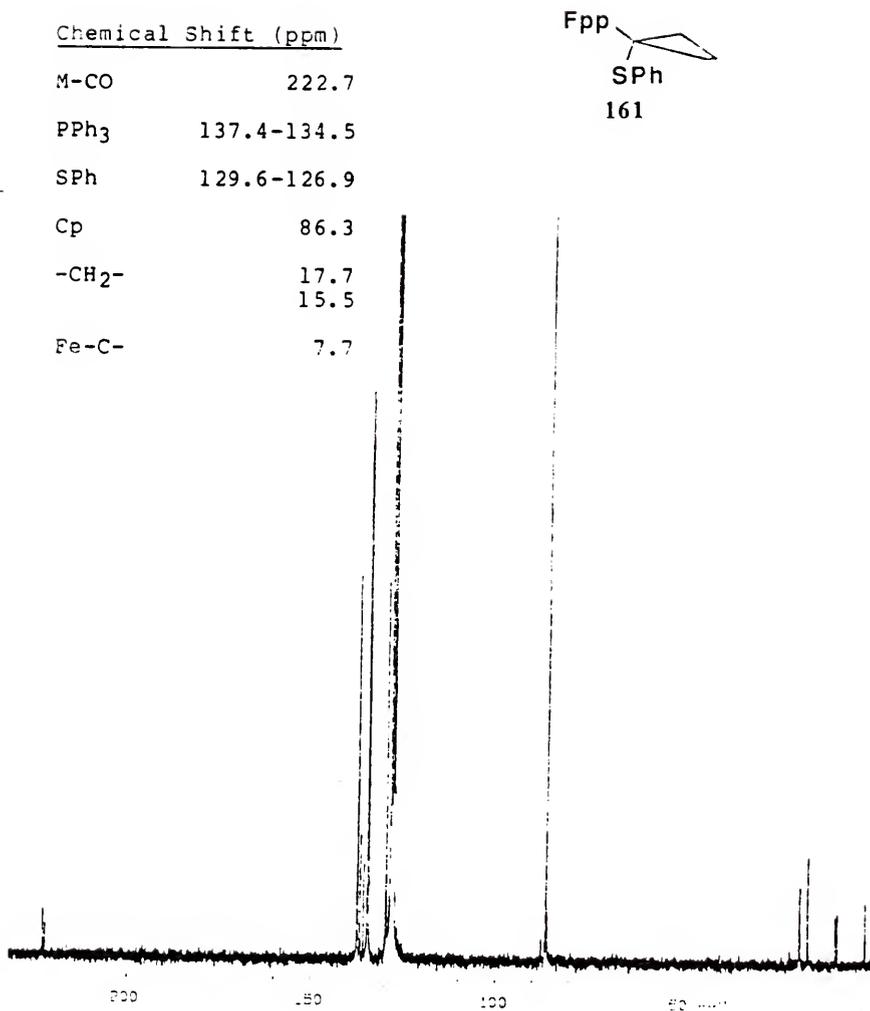
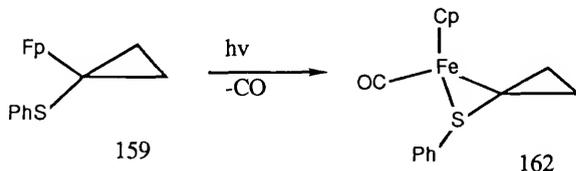


Fig. 37.  $^{13}\text{C}$  NMR spectrum of compound 161 in  $\text{C}_6\text{D}_6$ .

rendered diastereotopic by virtue of the now chiral iron center: they appear individually at 17.7 and 15.5 ppm.

Continued photolysis of the acyl complex 160 or irradiation of the sigma complex 159 produces a yellow solid which can be isolated by evaporation of the solvent from the reaction mixture and slow, undisturbed recrystallization from hexanes. Figure 38 depicts the carbon NMR spectrum of this compound. It possesses a terminal carbonyl peak at 218.6 ppm, a resonance in the Cp region at 79.8 ppm, a quaternary carbon atom which appears at 49.6 ppm and two peaks at 14.7 and 10.9 ppm which correspond to distinctive ring methylene groups along with resonances in the aromatic region (133.2-126.8 ppm). The IR spectrum of this material reveals that it has a single terminal carbonyl stretch at  $1921.8\text{ cm}^{-1}$ . This data along with the results of an elemental analysis and mass spectroscopic studies (vide infra) are consistent with a structure in which the sulfur atom of the thiophenyl group coordinates to the iron center as in 162.



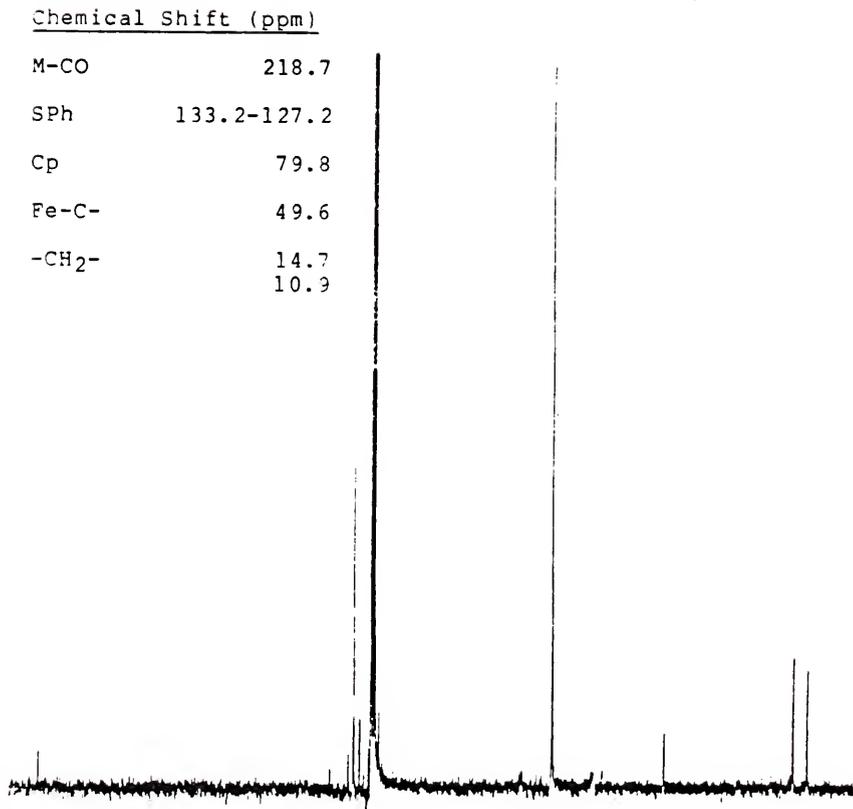
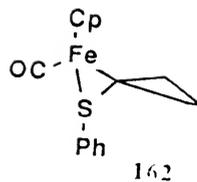
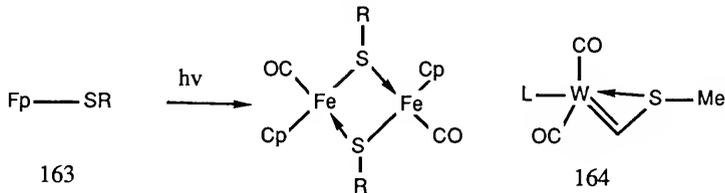
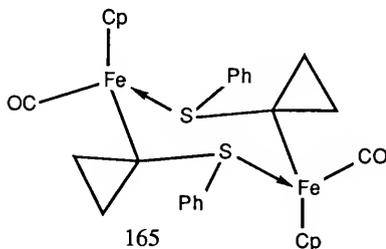


Fig. 38.  $^{13}\text{C}$  NMR spectrum of compound 162 in  $\text{C}_6\text{D}_6$ .

It is well known that Fp sulfide complexes such as 163 form dimeric sulfur bridges complexes upon photolysis.<sup>108</sup> The sulfur chelated carbene complex 164 has been isolated by



Angelici.<sup>109</sup> It is therefore not surprising that a complex such as 162 should form upon irradiation of the sigma complex 159, but based on the reactivity of compounds such as 163 one must ascertain whether the true nature of the photo-product of 159 is the monomeric 162 or the dimeric



165. A study of the photo-product by mass spectrometry sheds some light on this question.

When the sigma complex 159 is fragmented via chemical ionization, an M + 1 peak of 327 mass units is obtained (the actual mass of 159 is 326 mass units) along with peak

at 298 resulting from the loss of CO from 159. Chemical ionization characteristically produces the M+1 peak of the molecule. The photo-product of 159 was similarly fragmented resulting in a spectrum which contained peaks at 299 and 271 mass units. These would correspond to the M + 1 peak for structure 162 (actual mass of 298 mass units) and the ion resulting from the loss of CO from 162. In both cases there are no significant peaks above 500 mass units; the molecular ion of the dimeric 165 would have a value of 596 mass units.

Though no molecular ion for 165 was detected, it could be the case that a dimeric species such as 165 would be thermally unstable. The temperature required to introduce the photo-product of 159 into the ionization chamber of the mass spectrometer may have caused the dimer to cleave yielding the monomeric 162. Evidence for the monomeric nature of the photo-product may be inferred from the mass spectra obtained when the photo-product was scanned at various times during the ionization process.

A plot of the relative ion current of the sigma complex 159 as the volatilization chamber was heated from 60° to 200° C. during a 2 minute period revealed three relative maxima at temperatures of approximately 100, 140 and 160° C. The peak at 140° C. was of the greatest relative intensity. A scan of the peak at 100° C. gave a spectrum corresponding to that of the sigma complex 159 (327, 298 and 271). The

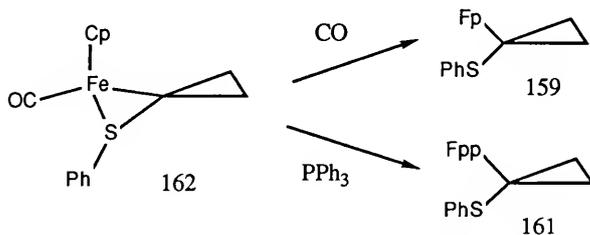
peak at 140° C. yielded a spectrum which matched that of the one obtained for the photo-product of 159 (299 and 271). Neither spectrum contained peak higher than 500 mass units. The scan of the peak at 160° C. did contain mass peaks above 500 mass units, in fact, a peak at 596 mass units was detected which corresponds to the molecular ion of the dimeric species 165.

When the same experiment was performed on the actual photo-product of 159, only two relative maxima were found in the plot of relative ion current versus temperature with the lower temperature peak being of much greater relative intensity than the peak which occurred at the higher temperature. They appear approximately at 135° C. and 170° C. The scan of the former revealed peaks at 299 and 271 mass units; the latter contained a faint peak at 596 mass units.

These results are consistent with a thermal conversion of the monomeric species 162 into the dimer 165 as the chamber was heated. Furthermore, it also appears that these species can be produced when the sigma complex 159 is heated in the volatilization chamber of the mass spectrometer. Cases where organometallic species have undergone thermally induced rearrangements in mass spectrometers due to heating have been reported.<sup>99</sup> Although the results are consistent with the assignment of the monomeric structure 162 to the

photo-product of 159, the assignment is not completely unambiguous since such a study cannot determine whether chamber heating quickly converts the dimer to the monomer. Attempts to grow crystals of quality suitable for an x-ray structure, which would show if the structural assignment of the monomer for the photo-product were correct in the solid state, failed. For the sake of brevity, the photo-product of 159 will be assumed to have the monomeric structure in the body of this work, but the limitations of this assumption are recognized.

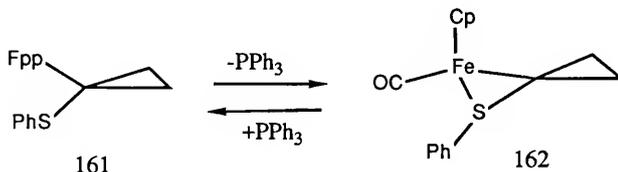
The chemistry of the photo-product was also investigated. When carbon monoxide was bubbled through a benzene solution of 162, the sigma complex 159 was cleanly produced. Likewise, treatment of a benzene solution of 162 with an equivalent of triphenylphosphine yielded the phosphine substituted sigma complex 161. Phosphine ligands



and carbon monoxide apparently replace the sulfur ligand on the metal. It cannot be stated with certainty whether this

displacement involves an associative, dissociative or intermediate mechanism.

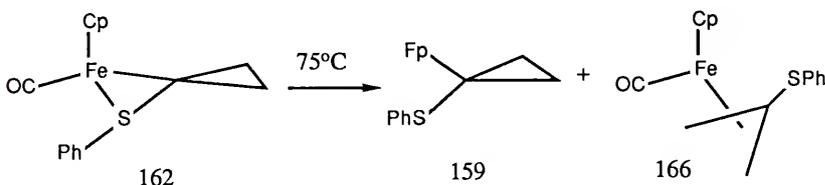
When the phosphine substituted sigma complex 161 is heated to 75° C. in benzene, no net reaction occurs. The most obvious explanation of this result is that the sulfur adduct 162 formed upon phosphine dissociation quickly back reacts with the liberated phosphine to re-form the starting sigma complex 161.



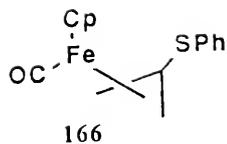
The most interesting aspect of the chemistry of 162 is what occurs upon heating a benzene solution of it at 75° C. The reaction was monitored over the course of 20 hours by both  $^{13}\text{C}$  NMR and FTIR spectroscopy. IR spectra taken of aliquots withdrawn at various times during the thermolysis revealed that the concentration of the sulfur adduct 162 decreased with time. Three new stretches increased during the reaction. Two of these (at 2010.5 and 1955.3  $\text{cm}^{-1}$ ) correspond to the sigma complex 159. Another peak grew in at 1945.9  $\text{cm}^{-1}$ . Such a terminal CO stretch is in the region expected for pi-allyl complexes.

The carbon spectra obtained over the same time period confirmed that the sulfur adduct 162 decreased in concentration as the sigma complex 159 and another CpFeCO containing species grew in concentration. This new compound had a resonance in the terminal CO region at 222.3 ppm. A peak in the Cp region was observed at 80.9 ppm as well as a peak at 42.1 ppm. Aromatic resonances were found between 133.7 and 125.8 ppm. Most interesting was the presence of quaternary carbon at 142.2 ppm. This resonance is in the region expected for hetero atom substituted central carbon atoms of CpFeCO pi-allyl complexes.

A brown, insoluble solid was filtered from the reaction mixture. Column chromatography of the remaining solution resulted in the isolation of two compounds: one being the sigma complex 159, the other being a yellow solid which was identified as the centrally substituted pi-allyl complex 166



based on spectroscopic, elemental and mass spectroscopic analysis. Figures 39 and 40 depict the proton and carbon NMR spectra of the compound.



| <u>Chemical Shift (ppm)</u> |         |
|-----------------------------|---------|
| SPh                         | 7.3-6.8 |
| Cp                          | 3.97    |
| H <sub>S</sub>              | 2.77    |
| H <sub>a</sub>              | 0.78    |

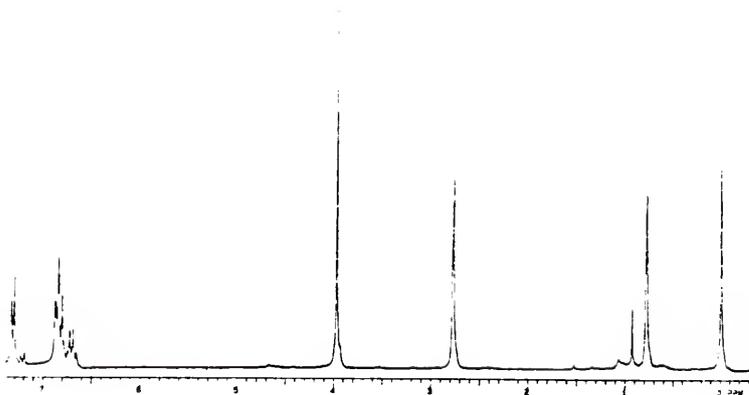


Fig. 39. <sup>1</sup>H NMR spectrum of compound 166 in C<sub>6</sub>D<sub>6</sub>.

Chemical Shift (ppm)

|                    |             |
|--------------------|-------------|
| M-CO               | 222.3       |
| -C-SPh             | 142.2       |
| SPh                | 129.1-125.8 |
| Cp                 | 80.9        |
| -CH <sub>2</sub> - | 42.1        |

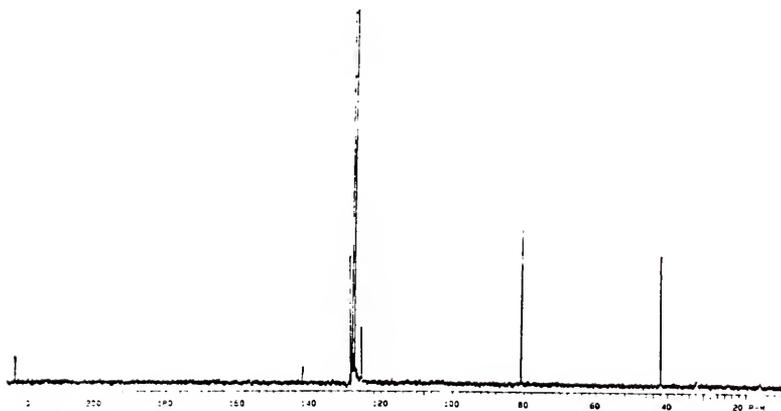
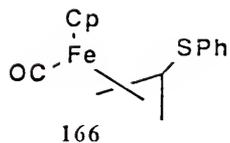
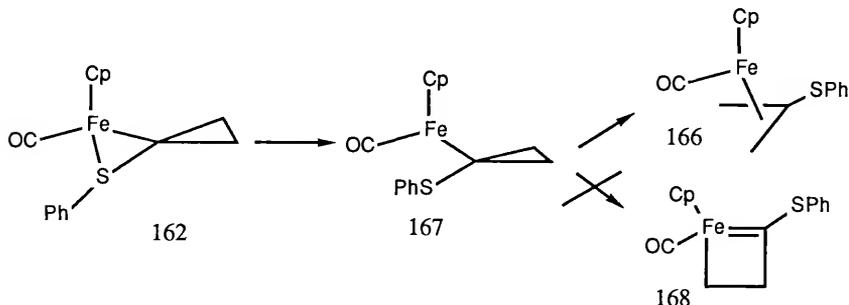


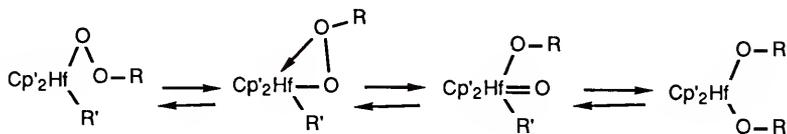
Fig. 40. <sup>13</sup>C NMR spectrum of compound 166 in C<sub>6</sub>D<sub>6</sub>.

At no time during the reaction was there any evidence of any carbene species being present. No terminally substituted pi-allyl species were detected. If it is the case that heating 162 disrupts the Fe-S bond to form the intermediate 167, then the relief of ring strain in going from 167 to the alkyl-carbene 168 plus the electronic stabilization of the carbene by the thiophenyl group does not provide the driving force necessary for effecting the alpha-elimination of the ring methylene group: the unfavorable equilibrium has not been displaced toward 168 as is the case when an ethoxy group resides on the alpha carbon of the cyclopropyl group. The thiophenyl group does allow for the rearrangement of 167 to the pi-allyl 166.

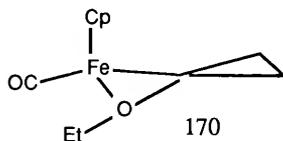


It could also be the case that the intermediate 167 is not formed upon heating the sulfur adduct 162. Systems are known where the coordination of a hetero atom precedes the cleavage of another bond to the coordinated hetero atom. Bercaw has reported the rearrangement of the hafnium

peroxide complex 169 which proceeds via coordination of an oxygen atom followed by O-O bond cleavage.<sup>110</sup> One of the



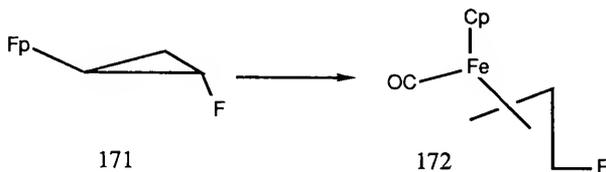
mechanisms proposed for the conversion of 111 to 123 involved the alpha-elimination of the ethoxy group. It seems likely that a species such as 170 could form during



the photolysis of 109. That 170 should not be detected whereas 162 can be isolated and characterized is not unexpected. Oxygen chelation in iron species is known to be more labile than that for sulfur ligands.<sup>111</sup> It could be the case that intermediates such as 162 and 170 precede the alpha-elimination of the thiophenyl and ethoxy groups respectively. This alpha-elimination is then responsible for the formation of the centrally substituted pi-allyl species. Once again the aforementioned rearrangement of the beta substituted cyclopropyl complex is at odds with this contention.

It is likely the case that the sigma complex results from a cannibalistic scavenging of CO from other iron species in solution. Reaction of the unsaturated intermediate 167 with CO would produce the sigma complex. The brown solid found in the reaction vessel could account for the iron species which sacrificially provided the CO to 167 for production of the sigma complex.

To further probe the mechanism of the rearrangement which produces the pi-allyl species, a beta fluoro substituted Fp cyclopropyl complex was prepared and photolyzed. The photolysis of 171 produced the pi-allyl species 172. Since the rearrangement of this sigma



complex could not occur via the alpha-elimination of the fluorine (since it is in the beta position), it seems unlikely that such eliminations of thiophenyl and alkoxy groups are required to form the pi-allyl species 123 and 166.

The stereochemical outcome of the photolysis of 171 is significant. The course of the reaction was followed by  $^{19}\text{F}$  NMR spectroscopy. The major product isolated from the

mixture was the pi-allyl complex 172. The fluorine occupies the syn position on the allyl moiety. This was determined from the magnitudes of the F-H coupling constants of the compound. The fluorine spectrum which is shown in Figure 41 contained a doublet of doublets at -172.9 ppm with couplings of 71.1 and 11.9 Hz. These correspond to  $J^{2,F_H}$  coupling and  $J^{3,F_H}$  cis-olefinic coupling respectively. A typical  $J^{3,F_H}$  trans-olefinic coupling would be on the order of 40 Hz.<sup>112</sup> Figure 42 depicts the carbon spectrum of 172 and Figure 43 displays the proton spectrum of the compound. The proton coupling constant of the proton residing on the fluorine substituted carbon atom supports the structural assignment. It has a coupling constant of 6.4 Hz; Rosenblum found a coupling of 7.8 Hz for the analogous hydrogen in the syn-chloro pi-allyl and 5.0 Hz for the anti-chloro pi-allyl.

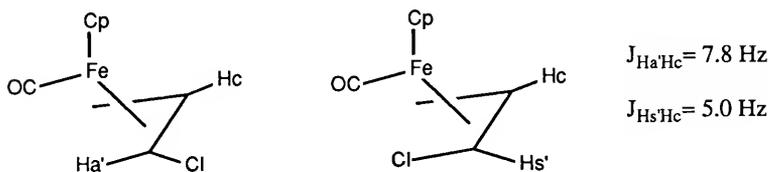
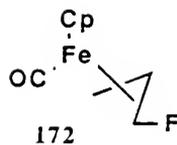


Figure 44 contains a table which shows how the  $^{13}\text{C}$  NMR chemical shifts for corresponding carbon atoms in the pi-allyl species produced in this work match up.

During the course of the reaction two other products were detected in the fluorine spectrum; however, they could



Chemical Shift (ppm)

F            -172.88

$J_{\text{FHgem}} = 71.1 \text{ Hz}$

$J_{\text{FHsyn}} = 12.2 \text{ Hz}$

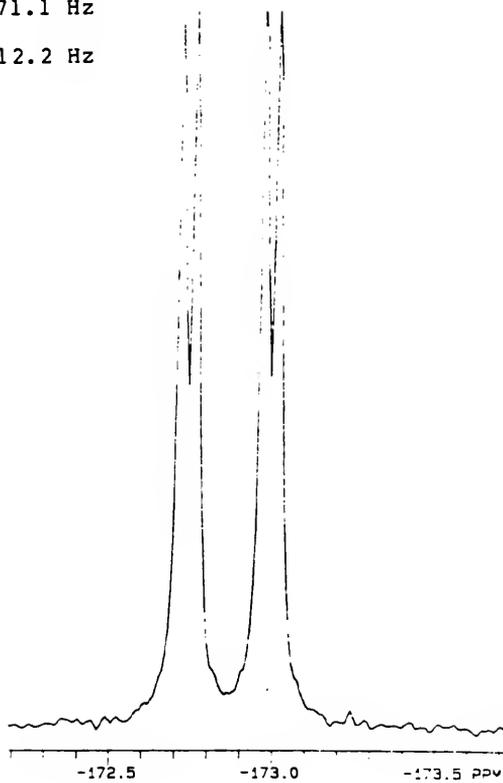
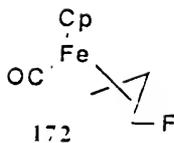


Fig. 41.  $^{19}\text{F}$  NMR spectrum of compound 172 in  $\text{C}_6\text{D}_6$ .



Chemical Shift (ppm)

|                  |       |
|------------------|-------|
| M-CO             | 221.0 |
| -HC-F            | 108.9 |
| Cp               | 80.3  |
| -CH-             | 61.5  |
| -CH <sub>2</sub> | 22.9  |

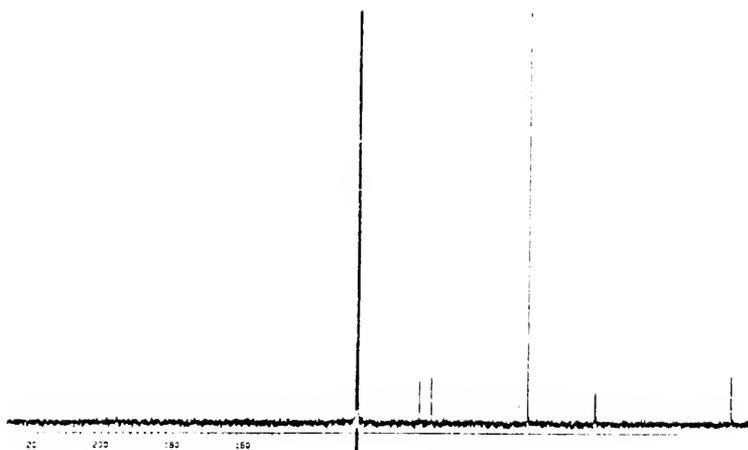


Fig. 42.  $^{13}\text{C}$  NMR spectrum of compound 172 in  $\text{C}_6\text{D}_6$ .

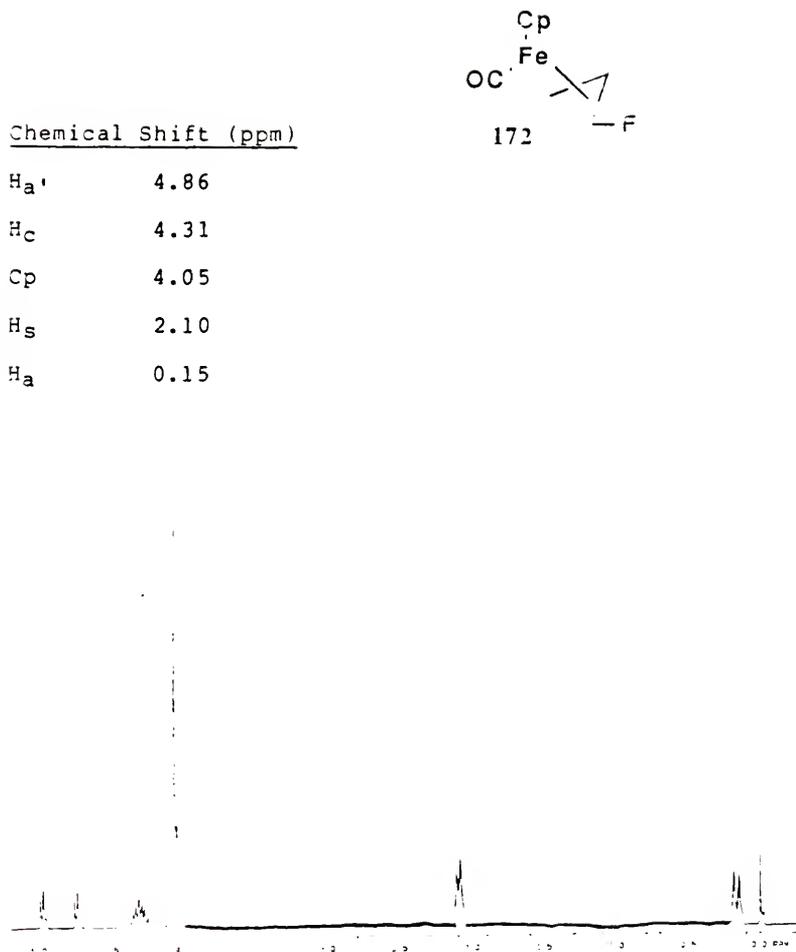
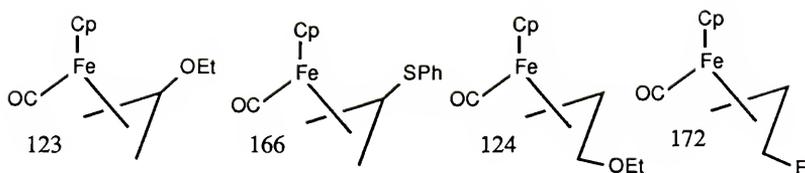


Fig. 43. <sup>1</sup>H NMR spectrum of compound 172 in C<sub>6</sub>D<sub>6</sub>.

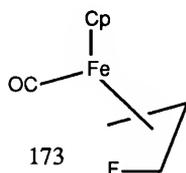


Chemical Shift (ppm)

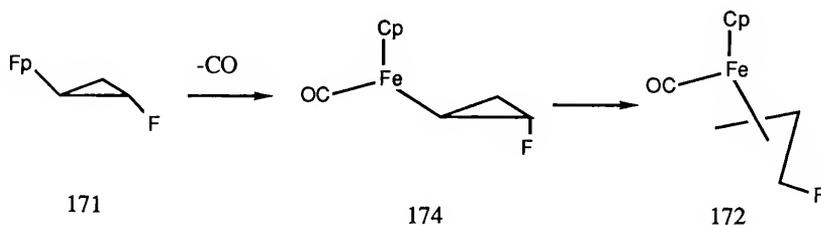
|                    | <u>123</u> | <u>166</u> | <u>124</u>   | <u>172</u>   |
|--------------------|------------|------------|--------------|--------------|
| Fe-CO              | 221.0      | 222.3      | 222.2        | 221.0        |
| C-X                | 134.0      | 142.2      | 99.9         | 108.9        |
| Cp                 | 79.5       | 80.9       | 79.9         | 80.3         |
| -CH <sub>2</sub> - | 23.5       | 42.1       | 22.4<br>61.0 | 22.9<br>61.5 |

Fig. 44. <sup>13</sup>C chemical shifts in C<sub>6</sub>D<sub>6</sub> for the pi-allyl complexes produced in this work.

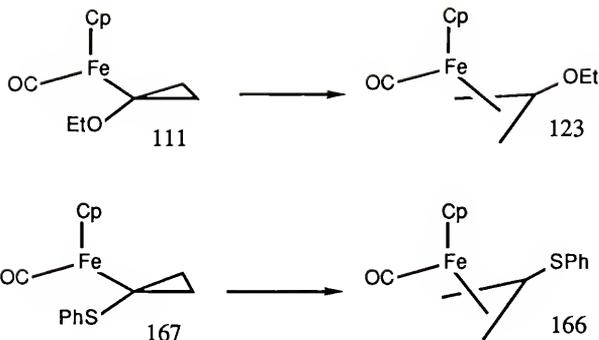
not be isolated. They were formed in minor amounts. Inspection of their coupling constants revealed that even these minor products had no three-bond F-H couplings in the range characteristic of trans-olefinic substitution. In other words it did not appear that any of the minor products of the reaction could have been the anti substituted pi-allyl complex 173.



If the pi-allyl complex 172 (formed from the photolysis of the trans-substituted sigma complex 171) comes about by the rearrangement of the 16e- complex 174 in a fashion

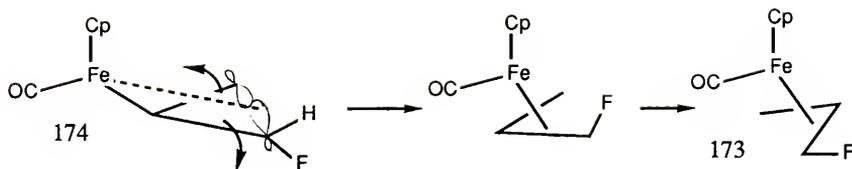


analogous to the rearrangements of 111 and 167, the stereoselectivity of the reaction rules out a direct insertion mechanism. This requires the assumption that 172 is the kinetic product formed from the rearrangement of 174.



Of the isomeric pi-allyls, the syn-fluoro 172 should be the most thermodynamically stable, based on Rosenblum's results for the analogous chloro-substituted system. This chloro system undergoes anti-to-syn isomerization with a half-life of 40 minutes at 62° C. This is considerably faster than the methoxy system whose half-life is 6 hours at 94° C. It is not known how easily the fluoro system isomerizes.

Since the identity of the kinetic product of the rearrangement is not known with certainty, a direct insertion mechanism cannot be excluded. However, if the kinetic product is the syn-fluoro pi-allyl 172 the direct insertion mechanism cannot be correct because it requires that the wrong isomer, 173, be produced from 174 upon endo-exo isomerization (known to be rapid at -10° C. for the chloro system).



The chemistry of the fluorocyclopropyl system is not known in the detail as are the chemistries of the ethoxycyclopropyl and thiophenylcyclopropyl systems. Therefore, one must be cautious when using observations based upon the chemistry of the fluoro system to rationalize the behavior of other systems. Many questions remain unresolved, and the results which have been obtained for fluoro-substituted cyclopropyl systems seem to resist simple explanation. The results of these studies will now be presented.

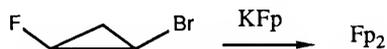
In order to prepare the appropriate fluorine substituted sigma complexes, KFc was reacted separately with cis and trans-1-bromo-2-fluorocyclopropane. The starting materials were not contaminated with their isomers; this was ascertained by gas chromatographic analysis. When the trans isomer was used, a mixture of the cis and trans substituted beta fluoro cyclopropyl sigma complexes were obtained. The complexes were characterized by spectroscopic methods and high resolution mass spectrometry. The cis and trans

isomers could be easily distinguished by their  $^{19}\text{F}$  NMR spectra. The trans isomer gives a multiplet in which there



are three large couplings (70.8, 29.3 and 19.5 Hz) for the geminal and cis F-H interactions and one small coupling of 4.9 Hz for the trans F-H splitting. The multiplet of the cis isomer contains two large (geminal and cis) and two small trans couplings. Integrations performed on the fluorine and proton spectra revealed that the trans isomer 171 was formed in 82.3% whereas the cis isomer 175 accounted for only 17.7% of the product mixture. The results indicate that the reaction proceeded with retention of configuration at the reaction center in a ratio of 4.7 to 1 over inversion.

When K<sub>2</sub>F<sub>6</sub> was reacted with cis-1-bromo-1-fluorocyclopropane quite a different result was obtained. Only a trace of any sigma complex was detected after the reaction mixture had been chromatographed. The main iron



containing product was Fp<sub>2</sub>. This result was unexpected and is difficult to explain. The cause for this difference in

reactivity of the cis and trans isomers is yet to be determined. Such differences in reactivity re-emerged in the photochemistry of the sigma complexes 171 and 175.

As was previously stated, the trans sigma complex 171 yielded the syn substituted pi-allyl 172. When the cis-fluoro sigma complex 175 was irradiated, no net photochemical change was observed: the concentration of 175 (based on NMR integral comparison against the internal standard ferrocene) remained unchanged during 16 hours of irradiation. It is again not known with certainty why this isomer should be photo-inactive while the trans isomer is smoothly converted to the pi-allyl complex.

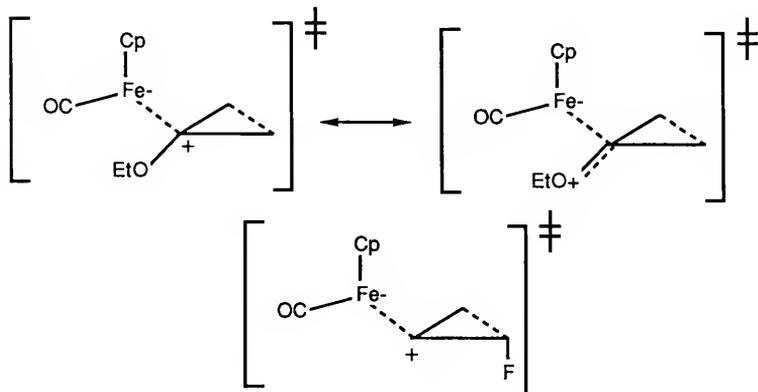
The behavior of the cis and trans 1-bromo-2-fluorocyclopropanes offers some insight into the difference in the reactivities of the cis and trans beta-fluoro sigma complexes upon irradiation. It is known that the rate of the solvolysis of the trans bromide is 19 times faster than



of the cis compound. The explanation for this result is that the disrotatory ring opening of the beta C-C bond requires that the fluorine rotate outwards in the trans compound and inward in the cis. The fluorine atom exerts an electronic effect which favors outward rotation, hence

lowering the energy of the transition state for the solvolysis of the trans compound by about 2.2 kcal/mol. This effect can only be observed for a transition state structure in which cleavage of the C-C bond between the two beta carbon atoms is occurring.<sup>113</sup>

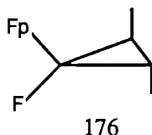
These facts can be used to posit an explanation of the pi-allyl rearrangements. If the transition state leading to the pi-allyl from the unsaturated cyclopropyl complex requires a substantial weakening of the Fe-C sigma bond such that the iron moiety is considered a leaving group, it can be seen that the alpha ethoxy, thiophenyl and trans-fluoro substituents should all exhibit a stabilizing effect. The



first two via delocalization of the partial positive charge which would accrue on the alpha carbon as the iron leaves; the third via an effect analogous to the one found in the cyclopropyl solvolyses previously mentioned. Furthermore,

if there is also a weakening of the C-C bond between the carbon atoms, the preference for outward rotation of fluorine in the trans-fluoro system would explain the stereochemistry of the pi-allyl product.

A most interesting result was obtained during an attempt to prepare the alpha fluoro sigma complex 176.



Under the conditions which usually produce a sigma complex, 1-bromo-1-fluoro-trans-2,3-dimethylcyclopropane was treated with KFp. The reaction mixture was filtered and the solvent was removed. A  $^1\text{H}$  NMR spectrum of the crude product revealed two Cp containing materials. The high-field region of the spectrum possessed resonances appropriate for the desired sigma complex. The crude product was chromatographed on a silica gel column using a solution of 10% ethyl acetate in hexanes (v/v). A yellow oil was obtained. When pure hexanes was added to the oil as a prelude to further purification via chromatography, a yellow solid precipitated from the solution. The solid was filtered off and dried under nitrogen.

The solid melted between 174 and 176° C. It was completely soluble in benzene. The infra red solution

spectrum revealed two stretches at 2010.4 and 1958.9  $\text{cm}^{-1}$  which are characteristic of the terminal dicarbonyl symmetric and asymmetric stretching modes found in  $\text{Fp}$  complexes. Figure 45 depicts the proton NMR spectrum of the compound. Two quartets are found at 3.72 and 6.16 ppm; two doublets are found at 1.48 and 1.05 ppm. The singlet belonging to the Cp ring protons is found at 3.98 ppm. The  $^{13}\text{C}$  NMR spectrum shown in Figure 46 contains two peaks in the terminal carbonyl region at 217.3 and 216.9 ppm. A quaternary carbon appears at 149.9 while two methine carbons (determined by distortionless enhancement by polarization transfer, DEPT) are found at 132.2 and 84.1 ppm. The Cp carbons come in at 85.3 ppm, and two methyl groups have resonances of 23.7 and 20.0 ppm. Figure 47 contains a representation of the  $^{19}\text{F}$  NMR spectrum of the compound. A singlet was found at -213.3 ppm.

Assigning a structure to this compound which is consistent with all of the data presents some difficulties. A structure which is consistent with all of the spectroscopic data is the fluoride salt of the 1,3-dimethylallene complex 177. Lisko and Jones have prepared the triflate salt of this compound.<sup>101</sup> A comparison of the proton and carbon shifts of the two compounds shows the shifts differ quantitatively for some atoms, the spectra of the two compounds are quite similar in all other respects.

Chemical Shift (ppm)

|                  |      |
|------------------|------|
| H                | 6.05 |
| Cp               | 4.25 |
| H                | 4.11 |
| -CH <sub>3</sub> | 1.77 |
| -CH <sub>3</sub> | 1.37 |

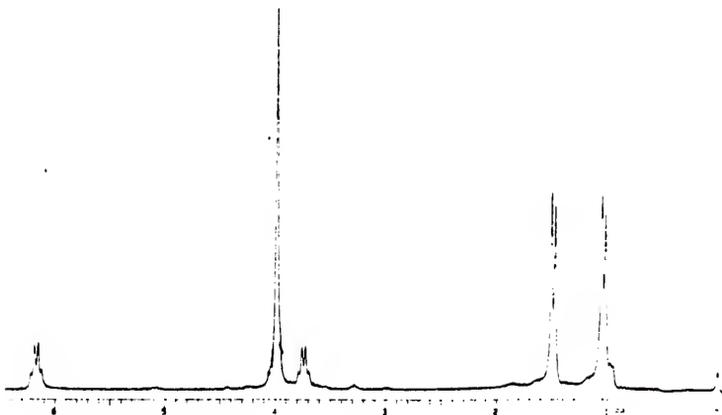
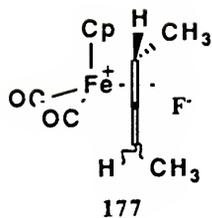


Fig. 45. <sup>1</sup>H NMR spectrum of compound 177 in C<sub>6</sub>D<sub>6</sub>.

Chemical Shift (ppm)

|                  |       |
|------------------|-------|
| M-CO             | 217.3 |
|                  | 216.9 |
| -CH              | 132.2 |
| Cp               | 85.3  |
| -CH              | 84.1  |
| -CH <sub>3</sub> | 23.7  |
| -CH <sub>3</sub> | 20.0  |

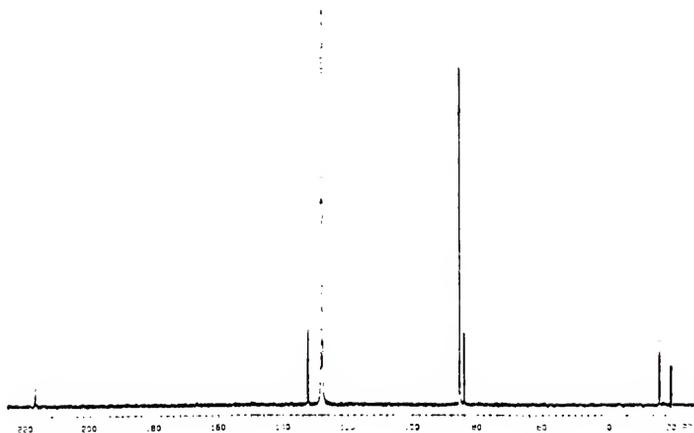
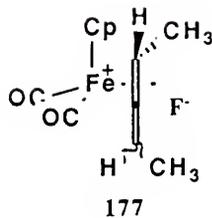


Fig. 46. <sup>13</sup>C NMR spectrum of compound 177 in C<sub>6</sub>D<sub>6</sub>.

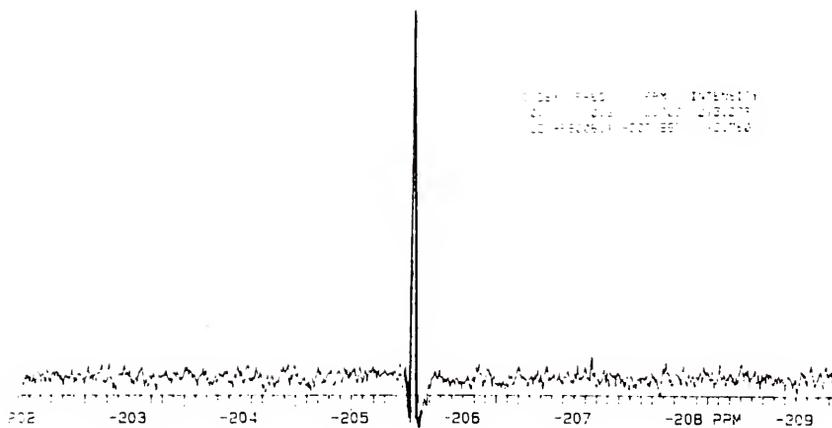
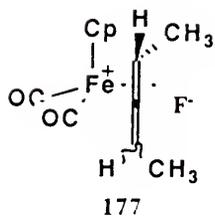
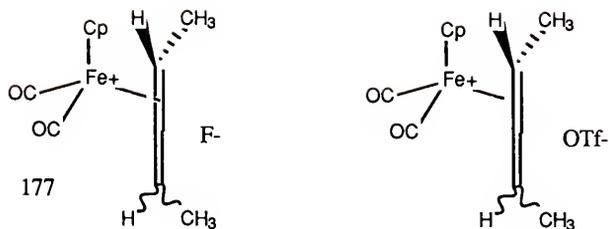
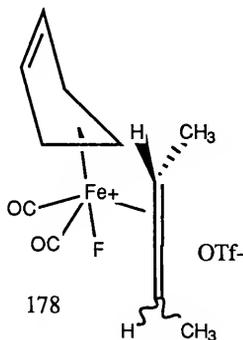


Fig. 47.  $^{19}\text{F}$  NMR spectrum of compound 177 in  $\text{C}_6\text{D}_6$ .



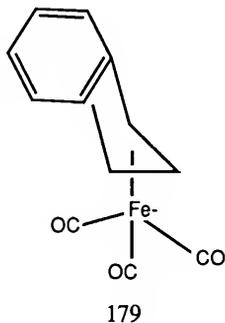
One interesting observation is that the compound is completely soluble in benzene and a solution of 10% ethyl acetate in hexanes (v/v). If 177 corresponds to the actual structure of the compound, the salt is amazingly soluble in the non-polar solvent mentioned above.

Another structure which must be considered is that of 178. This structure is covalent and therefore avoids the



objection raised by the solubility in non-polar solvents. The  $^{19}\text{F}$  shift of  $-213.3$  ppm is a little farther upfield than

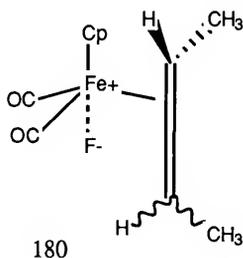
those reported for fluorines in rhodium complexes (-169.6 and -196.6 ppm).<sup>114</sup> The carbonyl groups of this structure would also be chemically non-equivalent (in 177 they are diastereotopic due to the chiral allene ligand), and as such, would be consistent with the <sup>13</sup>C NMR structure of the compound. Since the carbon and proton spectra show singlets for the Cp ring, the h<sup>3</sup>-Cp ligand must be undergoing a fluxional process which equilibrates the ring carbon and hydrogen atoms. An h<sup>3</sup>-Cp, carbonyl iron complex has never been isolated: one group has reported the isolation of such a slipped ring complex at low temperatures,<sup>115</sup> but this has been disputed.<sup>116</sup> The h<sup>3</sup>-indenyl anion 179 has recently



been reported by Cutler.<sup>117</sup> Further evidence against this structure are the results of a low-temperature NMR experiment: no change in the proton resonance of the compound was detected as the temperature of the NMR probe was lowered to -60° C.; however, it could be the case that a

lower temperature than this is needed in order to slow down the fluxional process of compound such as 178.

Another representation of the structure of the compound in light of all of the data is 180. In this species

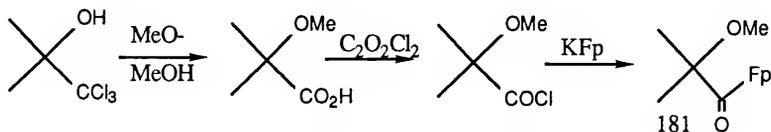


there is considerable ion pairing between the iron and fluorine atoms. Such a pairing would impart considerable covalent character to the compound, alleviate the necessity for ring slippage and allow for non-equivalent carbonyls. It is known that ion pairing can produce additional IR absorptions in the carbonyl region.<sup>118</sup> Depending upon the substitution pattern and the extent of the ion pairing, significant absorptions can appear at lower wave numbers.<sup>119</sup> Such absorptions are not seen in the IR spectrum of the compound. On the other hand, the fact that the chemical shift of the fluorine found in the compound is 17 to 44 ppm upfield of those reported for covalent organometallic compounds is consistent with additional negative charge being present on the fluorine atom in the isolated complex.

It was realized that a crystal structure would greatly aid in elucidating the true structure of this compound. Unfortunately, x-ray quality crystals could not be obtained despite repeated recrystallization attempts.

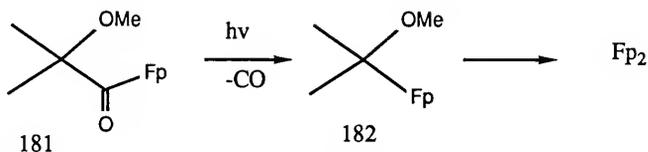
The origin of the allene was not investigated, but it is likely that the allene ligand owes its existence to the opening of a cyclopropylidene ligand. Several mechanisms could be presented to account for the generation of such a species, it is likely that either an alpha-elimination of the fluorine atom to the iron center or an Fp-assisted ionization of the fluorine would give rise to a cyclopropylidene: a covalent structure for the product would favor the alpha-elimination pathway since ring-slippage would be required in order to avoid a 20e- iron center; an ionic structure would favor the ionization pathway.

Finally, the acyclic acyl complex 181 was prepared as shown in the scheme below. The complex was photolyzed in



benzene. The reaction was followed by NMR spectroscopic methods. It was found that the acyl complex rapidly decarbonylated to give the sigma complex 182. Further

irradiation of the sigma complex resulted in the quantitative formation of  $Fp_2$  as the sole CpFe containing

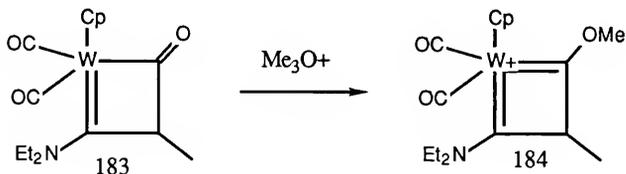


species. This result is in accord with the work of Casey. He found that photolysis of 182 in the presence of triphenylphosphine resulted in the isolation of  $Fp_2$  rather than the phosphine substituted sigma complex.<sup>65</sup>

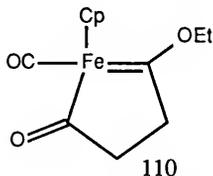
At no time during the course of the photolysis was any evidence obtained of an acyclic carbene complex resulting from the alpha-elimination of a methyl group. If decarbonylation of 182 occurred followed by homolytic Fe-C bond fission, coupling and CO absorption, the result indicates that methoxy stabilization in the absence of strain relief is not sufficient to drive the alpha alkyl elimination competitively with homolytic Fe-C bond cleavage. However, Casey's experimental results imply that a 16e- species is not produced with a sufficiently long lifetime to allow it to be trapped with phosphine. If this is the case, no judgement can be made as to the impact of the components of strain relief and alkoxy carbene stabilization on the alkyl alpha-elimination.

CHAPTER IV  
SYNTHESIS OF A NOVEL  
IRON DICARBENE COMPLEX

In 1976 Beck and his co-workers took advantage of extant preparative methods for generating carbene complexes and prepared the tungsten dicarbene complex 184 by treating the acyl-carbene complex 183 with trimethyloxonium

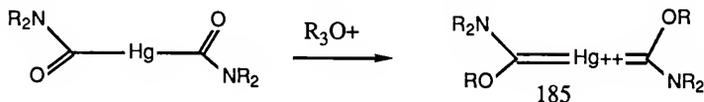


tetrafluoroborate.<sup>120</sup> This result was of interest because of the close relationship of the acyl-carbene 183 with the product of the photo-induced rearrangement of the sigma complex 109, namely 110. An attempt was made to prepare a

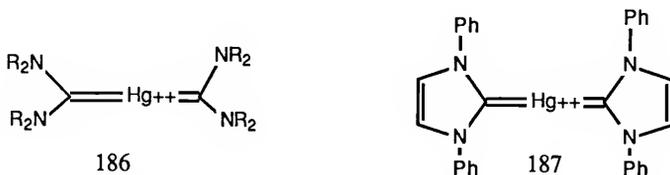


dicarbene complex from 110 by using the same synthetic strategy.

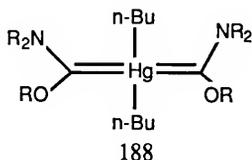
Dicarbene metal complexes have been known for quite a while. Gerhart reported the synthesis of a mercury complexed dicarbene in 1967. Although 185 was prepared by



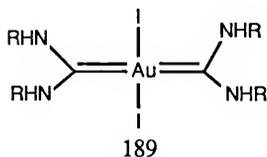
alkylating a diacyl complex,<sup>1,21</sup> other methodologies were developed which allowed the mercury complexes 186 and 187 to



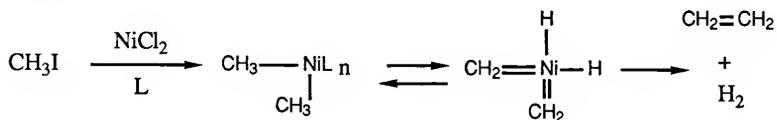
be prepared.<sup>1,22</sup> Although the above complexes are dications, the neutral dicarbene 188 has also been synthesized.<sup>1,23</sup>



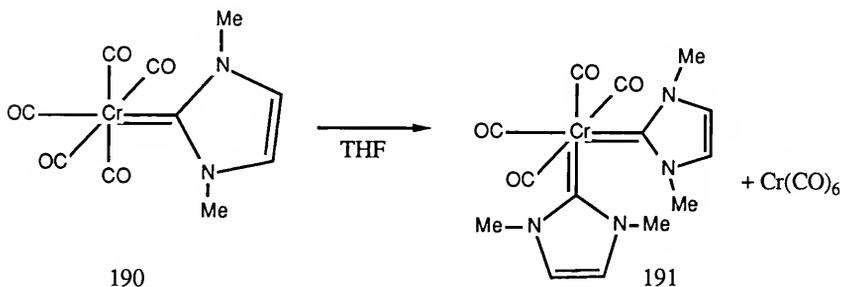
The method for preparing these dicarbene has also been used to prepare the gold complex 189.



Interest in dicarbene complexes was spurred by several groups who postulated their intermediacy in certain chemical processes. The best evidence for their roles as intermediates in the decomposition of metal alkyls comes from the experiments of Faraday.<sup>124</sup> He found evidence for their formation in the isolation of alkenes from nickel alkyls by the reaction of Grignard reagents with nickel halides.



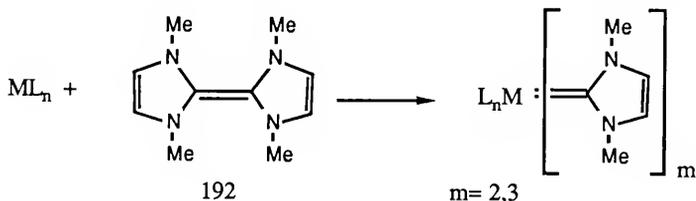
Heberhold was able to isolate chromium dicarbene complexes from the photolysis of carbene complexes such as 190.<sup>125</sup> He called such reactions dismutations. Ofele found



that he could interconvert cis and trans dicarbene complexes via an electrochemical redox process.<sup>126</sup> He also prepared

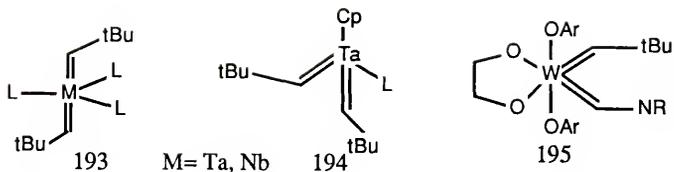
phosphine substituted molybdenum analogs of these dicarbenes.

Perhaps the most prodigious progenitor of dicarbene complexes is Lappert. He discovered that by heating or photolyzing various metal complexes in the presence of the electron rich alkene 192, he could produce di- and even tricarbene complexes of iridium, rhodium, gold, chromium, nickel and platinum.<sup>127</sup> Curiously, only a monocarbene would form when  $\text{Fe}(\text{CO})_5$  was heated in benzene with the alkene.

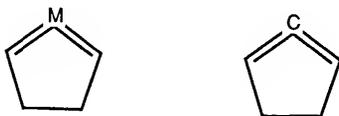


Lappert has extended his list of dicarbenes to include molybdenum.<sup>128</sup> He also has begun the study of the reactions of his dimethylimidazolidin-2-ylidene complexes with various reagents.<sup>129</sup> No explanation was given for the reluctance of iron to form poly-carbene complexes in this reaction.

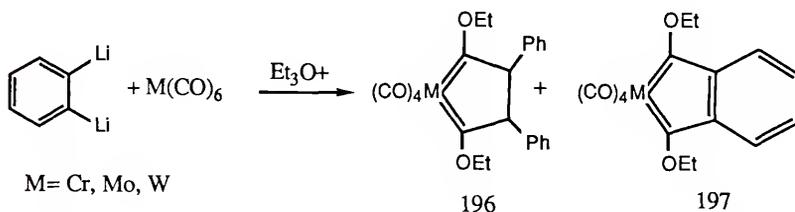
Schrock was able to show that dicarbene complexes could be formed with early transition metals. He was able to synthesize the dicarbene complexes 193 and 194.<sup>130</sup> These complexes do not add nucleophiles to the carbenic carbons. Schrock has also prepared mixed carbene-nitrene complexes of tungsten such as 195.<sup>131</sup>



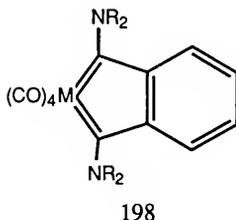
Fischer has prepared metallacyclic dicarbene complexes using various methods for their generation. As was previously mentioned, he has alkylated acyl-carbene complexes to prepare 2-metallacyclobuta-1,2-dienes. These compounds can be thought of as metallocyclic allenes where



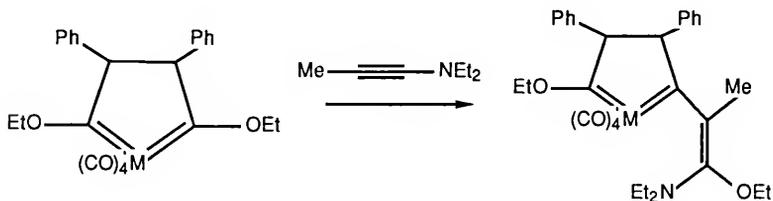
the metal replaces the sp hybridized carbon atom. He has also made the five-membered dicarbene complexes of chromium, molybdenum and tungsten 196 and 197.<sup>132</sup> These complexes



undergo aminolysis reactions with secondary amines to produce the diamine stabilized dicarbenes 198.



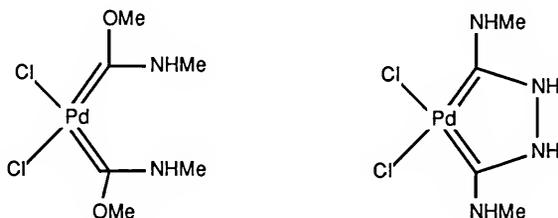
Study of the dicarbene complexes by  $^{13}\text{C}$  NMR reveals that the carbene atoms have chemical shifts of 312 to 337 ppm even though the complexes are uncharged.<sup>133</sup> The terminal carbonyls have resonances of 215-228 ppm and the methylene carbons of the ethoxy groups appear at 77-81 ppm. These dicarbenes react with electron rich alkynes to produce substituted diacarbene complexes as shown below.<sup>134</sup> Schubert



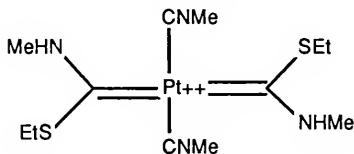
has shown from x-ray structures that the benzenalated dicarbene ligands are planar, whereas the beta phenyl

cyclic dicarbene ligands have a sterically-induced twist of the metallacyclic ring.<sup>135</sup>

Cis dicarbene complexes of palladium have been prepared by Enemark<sup>136</sup> and Nardelli<sup>137</sup>. This method involves treating platinum salts with methyl isocyanide in methanol

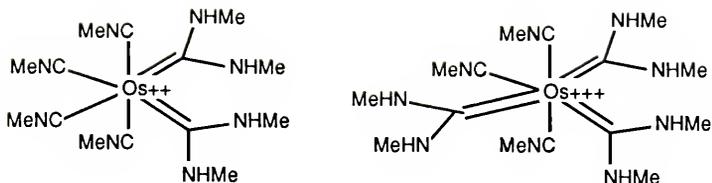


or hydrazine. Enemark has reported that a trans dicarbene dication of platinum 199 can be prepared. Richards has made

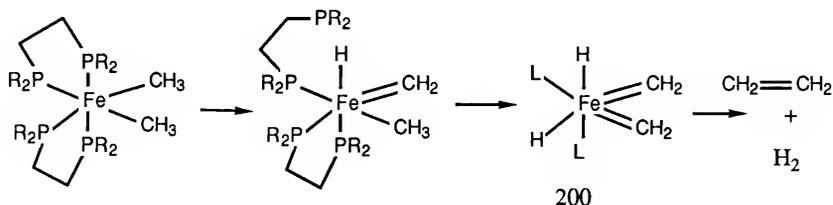


199

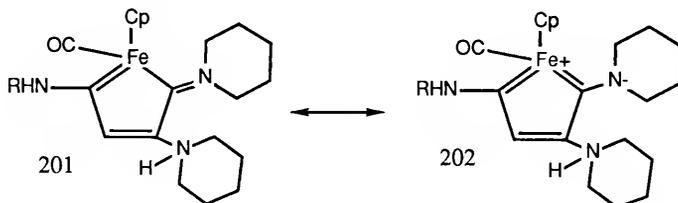
di- and tricarbene complexes of osmium using the above method. Interestingly, the analogs of ruthenium and iron could not be produced, indeed, even mono-carbene complexes were not obtained.



Although it appears that iron has a reluctance to form poly-carbene complexes, iron dicarbenes have been proposed as intermediates in the decomposition iron alkyls. Yamamoto has done work with dimethyl iron complexes which point to the intermediacy of the iron dicarbene complex 200.<sup>138</sup> No

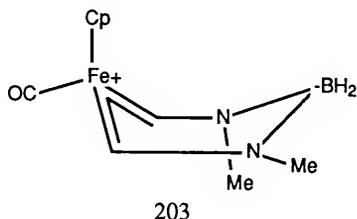


direct detection of the 200 was obtained. Yamamoto did report the synthesis of an iron complex 201 which has a dicarbene resonance form 202; however, the x-ray structure

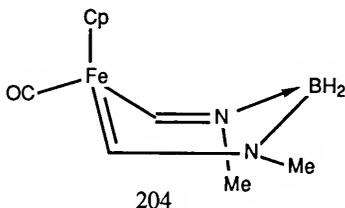


shows a 0.03 angstrom difference between the two Fe-C bonds. The dicarbene form was not preferred by the authors.

Enemark<sup>139</sup> and Treichel<sup>140</sup> have reported the preparation and x-ray structure the iron complex 203. The



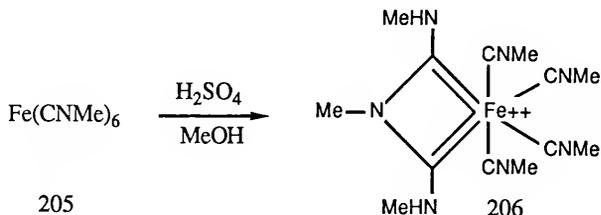
<sup>1</sup>H NMR spectrum of 203 shows that the alpha proton has a resonance of 11.1 ppm: this is characteristic of a proton attached to a carbenic carbon. Some evidence has been presented to show that the structure 204 may be a



better representation of the compound. The x-ray determination supports the contention that this is a true dicarbene complex since the Fe-C bond length of 1.882 angstroms is in the appropriate range for an iron carbon

double bond and significantly shorter than a single bond to an  $sp^2$  hybridized carbon (1.996 angstroms).<sup>141</sup>

A true iron dicarbene has been synthesized by Balch.<sup>142</sup> When the hexaisocyanide iron complex 205 is treated with methanol in sulfuric acid, the cationic dicarbene 206 is

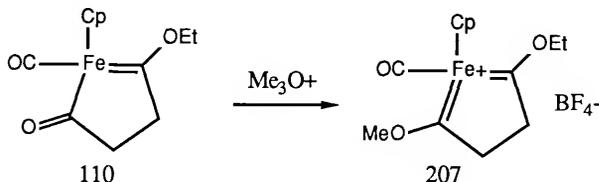


isolated. This procedure will also produce 1,2-metallacyclobutadiene complexes of platinum and palladium.

The generation of a true iron dicarbene complex from the acyl-carbene 110 would be of interest because only one undisputed iron dicarbene exists. It is not known why iron dicarbene complexes are so scarce, but it may be related to the weakness of the Fe-C double bond in such complexes. The evidence for this is that osmium di- and tricarbene complexes are known, but the ruthenium and iron analogs could not be produced by similar methods. Metal-carbon bond strengths decrease as one proceeds up the iron triad (osmium having the strongest, iron the weakest).<sup>5b</sup> It could be that if iron dicarbene complexes form, they may not possess the thermodynamic stability necessary in order to be

isolated. Regardless of the reason, iron dicarbene complexes are quite rare.

When a sample of the acyl-carbene complex 110 was dissolved in methylene chloride, a red solution was obtained. Upon the addition of one equivalent of trimethyloxonium tetrafluoroborate at room temperature, the red color gave way to a bright yellow upon stirring under a nitrogen blanket for 5 minutes. A yellow solid was obtained by precipitation with cold ethyl ether. The structure of the solid was determined to be that of the dicarbene complex 207.



Figures 48 and 49 depict the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 207. In the proton spectrum, it is noteworthy that the  $-\text{OCH}_2$  and  $-\text{OMe}$  peaks occur at 4.8 and 4.6 ppm respectively. This is the range characteristic of protons on carbons adjacent to oxygen atoms which stabilize a carbenic center. In the carbon spectrum, two carbene resonances are seen at 344.5 and 342.5 ppm. This is

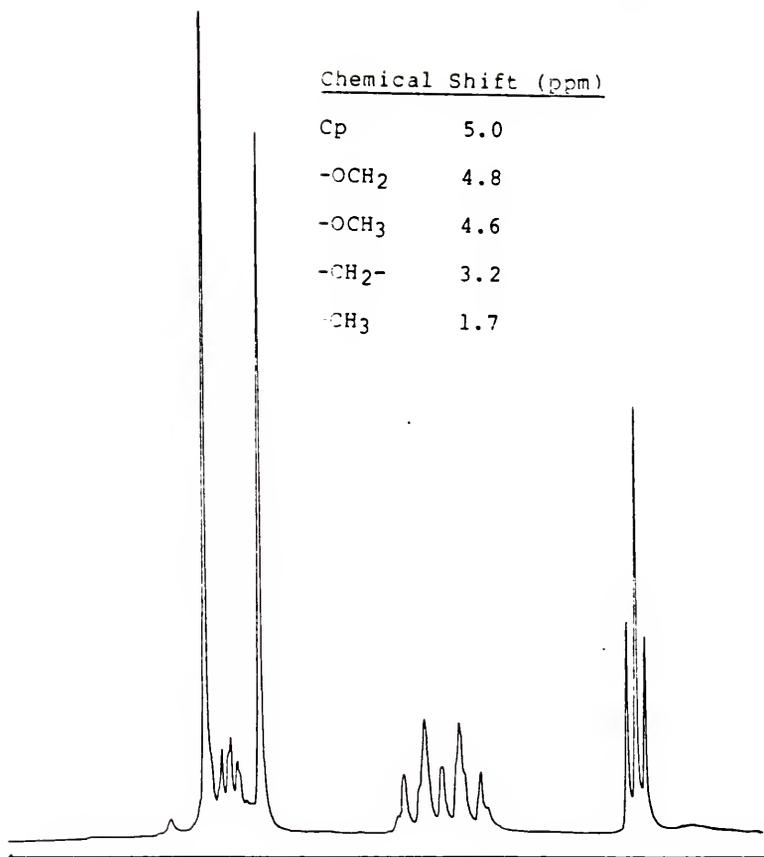
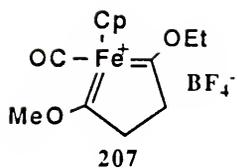
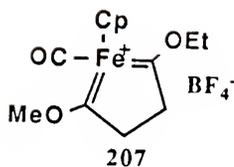


Fig. 48. <sup>1</sup>H NMR spectrum of compound 207 in CD<sub>2</sub>Cl<sub>2</sub>.



Chemical Shift (ppm)

|                    |       |
|--------------------|-------|
| M=C                | 344.5 |
|                    | 342.5 |
| M-CO               | 211.6 |
| Cp                 | 88.7  |
| -OCH <sub>2</sub>  | 77.8  |
| -OCH <sub>3</sub>  | 67.3  |
| -CH <sub>2</sub> - | 51.1  |
|                    | 51.0  |
| -CH <sub>3</sub>   | 14.7  |

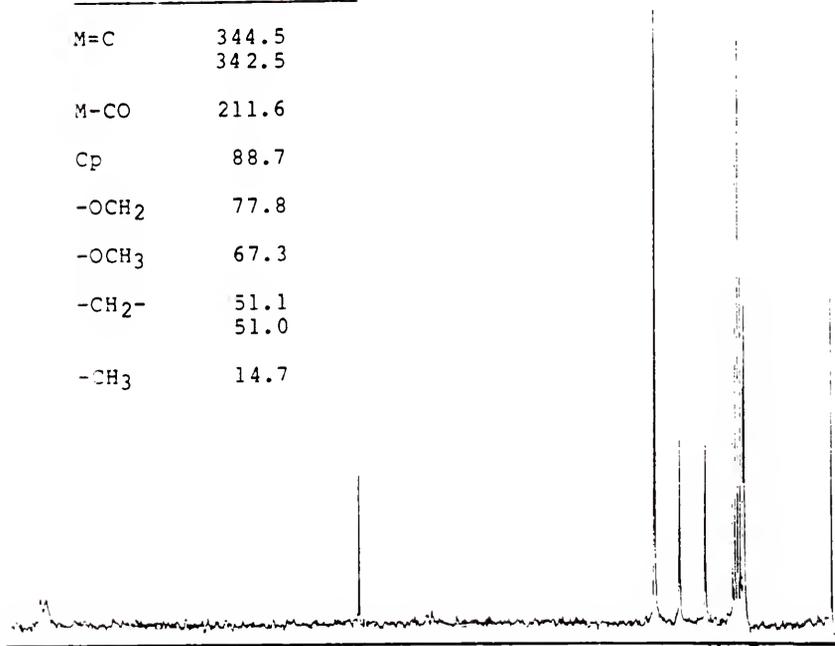


Fig. 49. <sup>13</sup>C NMR spectrum of compound 207 in CD<sub>2</sub>Cl<sub>2</sub>.

slightly downfield of the carbene peaks found by Fischer for his neutral dicarbene of tungsten (312-337 ppm) but well within the region delineated by the various metallacyclic alkyl- and acyl-carbene complexes described in this work (334-348 ppm). Figure 50 shows a table listing the various iron carbenes described in this work and the corresponding  $^{13}\text{C}$  NMR chemical shifts of their carbenic carbon atoms.

Other peaks of interest in the carbon spectrum include the Cp ring carbons at 88.5, the  $-\text{OCH}_2$  group at 78.1 and the  $-\text{OMe}$  group at 67.3 ppm. The assignment of the last two were made with the aid of an attached proton test (APT) pulse sequence. Further evidence of the dicarbene structure was given by the single terminal M-CO stretch in the IR spectrum at  $1995\text{ cm}^{-1}$ . Repeated recrystallizations of 207 at low temperature from methylene chloride and ethyl ether produced an analytical sample which gave a satisfactory elemental analysis for carbon and hydrogen. A molecular ion was detected by mass spectrometry as well as ions corresponding to a fragment of 207 which had lost CO and those characteristic of  $\text{CpFeCO}$  containing species.

Compound 207 is the first reported cationic  $\text{CpFeCO}$  dicarbene. Its isolation from the reaction of 110 with trimethyloxonium tetrafluoroborate extends Fischer's preparative method to the iron group of transition metals. The compound can also be regarded as a metallacyclic allene

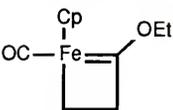
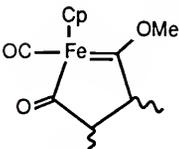
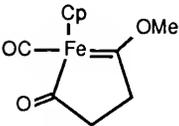
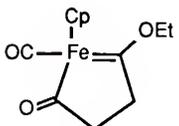
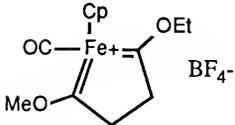
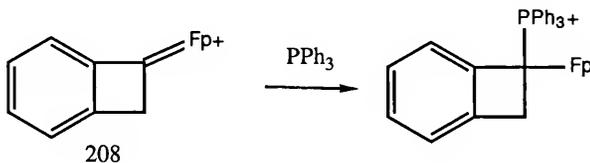
| <u>Compound</u>  | <u>Chemical Shift (ppm)</u> |
|--|-----------------------------|
|  <p>119</p>   | 334.3                       |
|  <p>47</p>    | 348.1                       |
|  <p>105</p>   | 343.4                       |
|  <p>110</p>   | 342.0                       |
|  <p>207</p> | 344.5<br>342.5              |

Fig. 50.  $^{13}\text{C}$  chemical shifts for carbene atoms of compounds produced in this work.

complex in which the metal occupies the central position in the allene moiety.

It is known that reactive cationic Fp carbene complexes will combine with triphenylphosphine to produce phosphine adducts in which the phosphorus atom directly bonds with the carbenic carbon atom. Giering demonstrated this with his benzenalated carbene 208.<sup>143</sup> To see if the reactivity of



the cationic dicarbene complex 207 paralleled this behavior, 207 was treated with triphenylphosphine.

The dicarbene was dissolved in methylene chloride and an excess of triphenylphosphine was added (1.1 equivalents). The reaction was monitored by NMR methods. After 24 hours, the yellow solution had become a dark red. Figure 51 shows the <sup>1</sup>H NMR spectrum of the reaction mixture (the aromatic region was omitted for the sake of clarity). A new Cp peak has appeared upfield of the old one. The resonance envelope due to the -OCH<sub>2</sub> groups is still present as well as the triplet of the -CH<sub>3</sub> of the ethyl group. Most interesting is the two singlets found near 2 ppm. These could be due to new methoxy groups in the product.

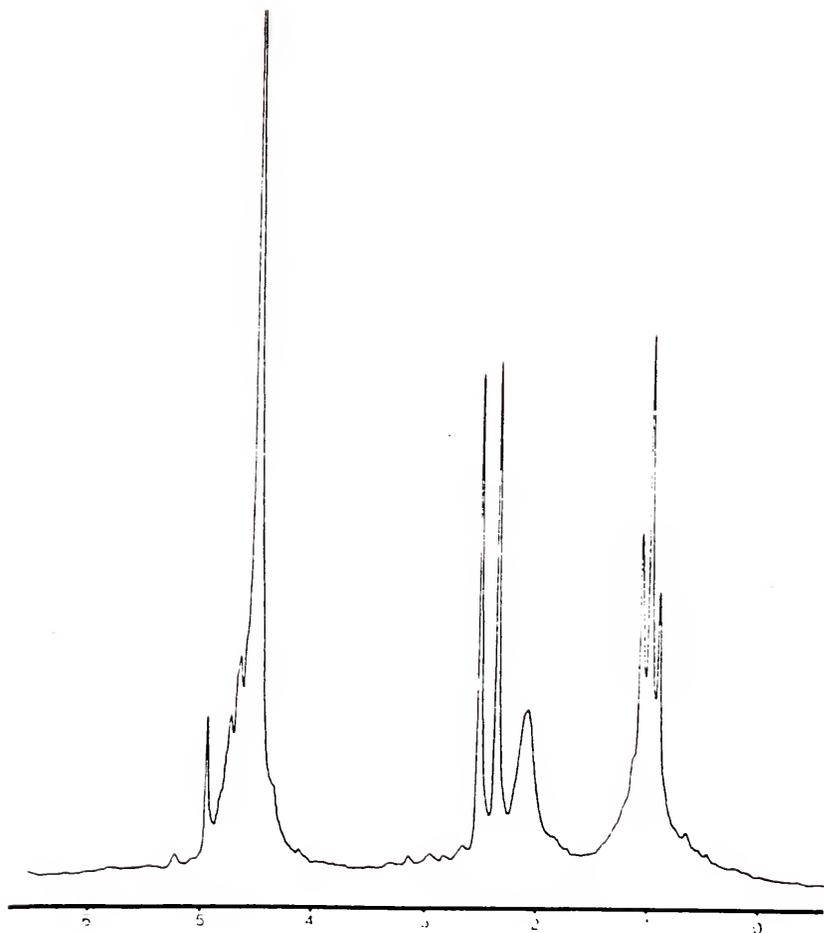


Fig. 51.  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  of the product of the reaction of 207 with triphenylphosphine.

Figure 52 shows the  $^{13}\text{C}$  NMR spectrum of the reaction mixture. Only one carbene resonance remains (339.4 ppm). A terminal carbonyl is present as is evident from the peak at 209.3 ppm, and a new Cp resonance occurs at 87.9 ppm. Peaks at 75.6 and 14.9 may be assigned to the methylene and methyl units of the ethoxy group, but no peak is found in the area indicative of a methoxy group attached to a carbene carbon. Only one peak is found in the area where the ring methylenes occur: 48.5 ppm. Farthest upfield is found a small doublet characteristic of a quaternary carbon atom which is attached to an iron atom. The splitting of the doublet is 58.6 Hz, well within the range of P-C one bond couplings. Two peaks are found at 120.9 and 117.2 ppm.

An IR spectrum of the mixture was taken and it revealed a single terminal carbonyl stretch at  $1990\text{ cm}^{-1}$ . Further characterization of the compound was not possible due to its instability. Cold ethyl ether was added to the reaction mixture resulting in the separation of a yellow oil from the red mother liquor. The yellow oil could not be induced to crystallize. Attempts to obtain crystals from the red mother liquor failed. Removal of the solvent from the red liquid resulted in the deposition of an intractable brown solid.

It is apparent from the spectral data that reaction between 207 and the phosphine has occurred. The shift of

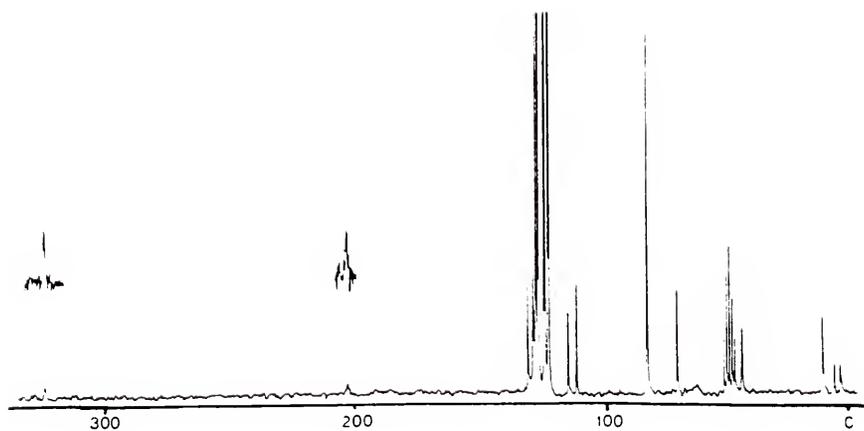
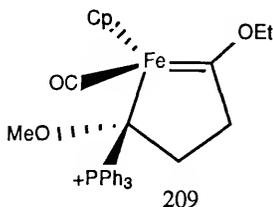
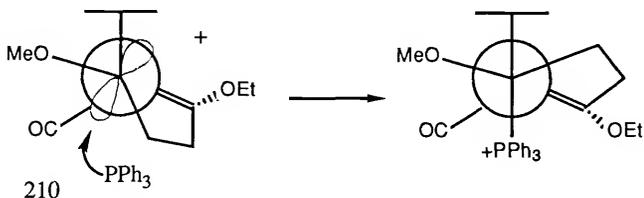


Fig. 52.  $^{13}\text{C}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  of the product of the reaction of 207 with triphenylphosphine.

the methoxy group and relatively unchanged nature of the ethoxy group in the proton and carbon spectra indicate that some sort of attack took place, but only at the carbene center substituted by the methoxy group. The disappearance of one carbene peak in the  $^{13}\text{C}$  spectra and the emergence of the high-field quaternary phosphine-split doublet are in accord with this view. One structure which could be the result of such an attack would be 209.



This adduct is analogous to the one reported by Giering. The bulkiness of the triphenylphosphine could be sufficient to allow for the regiospecific discrimination between the methoxy and ethoxy substituted carbenic centers. As the Newman projection 210 attempts to show, high



stereoselectivity is expected for this reaction as the bulky phosphine should prefer attack away from the Cp ring in order to minimize steric interactions with it. Of course, a smaller nucleophile should show less preference and result in low stereoselectivity and regioselectivity.

All the peaks in the carbon spectrum shown in Figure 52 can be assigned to atoms in structure 209. The peak at 120.9 ppm is assigned to the methoxy group and the one at 117.2 is assigned to the ring methylene adjacent to the phosphonium substituted carbon atom. If attack occurs as in 210, the steric bulk of the phosphine coupled with the preferred orientation of the remaining carbene ligand should result in the phosphonium group maintaining an antiperiplanar orientation with the Cp ring. This orientation would force the methoxy group and the ring methylene adjacent to the center of the attack into the deshielding region of the Cp ring. This coupled with any inductive effect which the phosphonium group would have could explain the downfield shift of these peaks.

The  $^1\text{H}$  NMR spectrum poses some difficulties to such a facile assignment. The most obvious is the two peaks at approximately 2 ppm. If the NMR corresponds to that of a single material, the two methoxy groups are inconsistent with structure 209. Also, if the geometry of 209 is such that the methoxy and adjacent ring methylene groups' carbon

atoms are deshielded by the Cp ring in the  $^{13}\text{C}$  spectrum, why are not similar downfield shifts of the corresponding proton resonances observed.

It does not appear that an adequate structure for the product of the reaction of dicarbene complex 207 with triphenylphosphine can be proposed from the data presented here. It is, however, safe to say that the phosphine did react with the dicarbene. The product, whatever its true structure, possesses a Cp ring, a terminal carbonyl, an ethoxy substituted carbene and a quaternary carbon atom attached to the iron center which is substituted with a phosphorus containing ligand.

In summation, the first  $\text{CpFeCO}$  cationic dicarbene complex has been prepared. The method of Beck for synthesizing dicarbenes from acyl-carbene complexes has been extended to the iron triad. Evidence was presented for the reaction of triphenylphosphine with the dicarbene complex at one of the carbenic centers. The instability of the reaction product precluded unambiguous characterization and determination of its structure.

CHAPTER V  
EXPERIMENTAL

Hexane, diethyl ether and tetrahydrofuran were distilled from benzophenone ketyl. Methylene chloride was distilled from  $P_2O_5$  under nitrogen and was degassed prior to use. Benzene was distilled from SilicaPent under nitrogen. The silica gel use was M.C.B. 230-400 mesh. All chromatographic separations were accomplished by the low-pressure flash column method of Still.<sup>144</sup> Low-temperature columns were run using a triple-jacketed column in which isopropanol (cooled with dry ice) was recirculated through the innermost jacket, the second was a sealed vacuum jacket and a continuous stream of dry nitrogen was flushed through the outermost jacket. The silica gel use was degassed overnight (0.25 mm Hg, 25° C) prior to use. NMR spectra were taken on a Varian EM-360 (60 MHz), JEOL FX-100 (100 MHz), Varian XL-200 (200 MHz), Nicolet NC-300 (300 MHz) or a Varian XL-300 (300 MHz). Infrared data were recored on either a Perkin-Elmer 137 or a Nicolet 5DXB FTIR spectrometer. Atlantic Microlab, Inc. or the University of Florida Chemical Analysis Service performed C, H analyses. Melting points (uncorrected) were

obtained using a Thomas-Hoover apparatus. All solutions containing transition metal complexes, as well as any resulting solids, were manipulated under inert atmosphere (Schlenk line or glove box) conditions.

#### Synthesis of 1-Methoxycyclopropanoyl Chloride 104

The title compound was prepared from cyclopropyl phenyl sulfide in an overall yield of 7.9% following the method of Hanna<sup>64</sup> as adapted from Lisko.<sup>63</sup> <sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>) 3.47 (s, 3H, OCH<sub>3</sub>), 1.57 (m, 4H, CH<sub>2</sub>) lit. 3.51 (s, 3H), 1.66 (m, 4H).

#### Synthesis of Dicarbonyl( $\eta^5$ -cyclopentadienyl)(1-methoxycyclopropanoyl)iron 99

To a stirred suspension of potassium dicarbonyl( $\eta^5$ -cyclopentadienyl)ferrate (KFp)<sup>145</sup> (0.6 g, 2.9 mmol) at -78° C in 25 ml of THF was added under nitrogen via a steel cannula a solution of 1-methoxycyclopropanoyl chloride (0.37 g, 2.7 mmol) in 10 ml of THF. The mixture was allowed to stir at -78° C for 1 hour, warm to room temperature and stir at ambient temperature for 1 hour. A brown solid was filtered from the reaction mixture and the solvent was removed in vacuo. The residual viscous brown material was chromatographed on silica gel using 10% ethyl acetate/hexanes (v/v) as the elutant. A yellow band was collected and concentrated to 0.41 g (65.9%) of an amber

oil. IR (CCl<sub>4</sub>) 2020, 1950, 1620 cm<sup>-1</sup>; <sup>1</sup>H NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) 4.33 (s, 5H, Cp), 3.13 (s, 3H, OCH<sub>3</sub>), 1.2-0.8 ppm (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (25 MHz, C<sub>6</sub>D<sub>6</sub>) 255.7 [M(CO)R], 215.6 (M-CO), 86.5 (Cp), 78.9 (-C-OMe), 56.8 (OCH<sub>3</sub>), 15.5 ppm (CH<sub>2</sub>); mass spectrum, m/e 248 (-CO), 220 (-2CO), 192 (-3CO), 186 (Cp<sub>2</sub>Fe<sup>+</sup>), 177 (FpCO<sup>+</sup>), 149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>). Anal. Calcd. for C<sub>12</sub>H<sub>12</sub>FeO<sub>4</sub>: C, 52.21; H, 4.38. Found: C, 52.34; H, 4.40.

Synthesis of 1-Carbonyl-h<sup>5</sup>-cyclopentadienyl-5-methoxyferracyclopent-5-en-2-one 105

An NMR tube was charged with dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(1-methoxycyclopropanoyl)iron (0.29 g, 1.04 mmol), a few boiling stones and 0.6 ml of C<sub>6</sub>D<sub>6</sub>. The tube was fitted with a rubber septum and irradiated with a 450 W medium pressure Hg lamp in the cell of a sonicator at 25° C. After 6 hours, the solvent was removed in vacuo and the residue was chromatographed on silica gel using 10% ethyl acetate/hexanes (v/v) as the elutant. All colored materials were allowed to elute. A red band remaining atop the column was then brought down with pure ethyl acetate. Upon removal of the solvent 0.05 g of a red crystalline material were obtained. mp 79-81° C; IR (CCl<sub>4</sub>) 1955, 1650 cm<sup>-1</sup>; <sup>1</sup>H NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) 4.41 (s, 5H, Cp), 3.60 (s, 3H, OCH<sub>3</sub>), 2.3-2.1 ppm (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) 343.4 (M=C), 268.8 [M(CO)R], 216.6 (M-CO), 87.5 (Cp), 64.6 (OCH<sub>3</sub>), 53.0,

49.1 ppm (CH<sub>2</sub>); mass spectrum m/e 248 (M<sup>+</sup>), 220 (-CO), 192 (-2CO), 177 (Fp<sup>+</sup>), 149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>); Anal. calcd. for C<sub>11</sub>H<sub>12</sub>FeO<sub>3</sub>: C, 53.26; H, 4.88. Found: C, 53.15; H, 4.91.

Synthesis of 1-Bromo-1-ethoxycyclopropane 108

The title compound was prepared in a 57.6 overall yield by the method of Hanna<sup>64</sup> from ethyl 2-chloropropionate. <sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>) 3.72 (q, 2H, OCH<sub>2</sub>), 1.27 (t, 3H, CH<sub>3</sub>), 1.0-0.3 ppm (m, 4H, CH<sub>2</sub>); lit. 3.69, 1.31, 1.1-0.5 ppm.

Synthesis of Dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(1-ethoxycyclopropane)iron 109

To a stirred suspension of KFP (1.31 g, 6.1 mmol) was added 1-bromo-1-ethoxycyclopropane (1.00 g, 6.1 mmol) at -78° C via cannula under nitrogen. The mixture was allowed to stir at low temperature for 1 hour followed by a warming to room temperature. The mixture was then allowed to stir at ambient temperature for 2 additional hours after which time a brown, pasty solid was filtered from the reaction vessel. The residual brown paste was chromatographed on silica gel using 10% ethyl acetate/hexanes (v/v) as the elutant. A yellow band was collected which yielded 0.74 g (46.6%) of an reddish orange oil. IR (CHCl<sub>3</sub>) 1999, 1943 cm<sup>-1</sup>; <sup>1</sup>H NMR (60 MHz, C<sub>6</sub>D<sub>6</sub>) 4.4 (s, 5H, Cp), 3.4 (q, 2H, OCH<sub>2</sub>), 1.1 (t, 3H, CH<sub>3</sub>), 1.0-0.4 ppm (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) 217.6 (M-CO), 87.1 (Cp), 63.4 (OCH<sub>2</sub>), 60.6 (Fe-C), 19.6 (CH<sub>2</sub>), 15.9 ppm (CH<sub>3</sub>); mass spectrum m/e 262 (M<sup>+</sup>), 234

(-CO), 206 (-2CO), 186 (Cp<sub>2</sub>Fe<sup>+</sup>), 177 (Fp<sup>+</sup>), 149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>), 85 (C<sub>3</sub>H<sub>4</sub>OEt<sup>+</sup>); Anal. calcd. for C<sub>12</sub>H<sub>14</sub>FeO<sub>3</sub>: C, 54.98; H, 5.39. Found: C, 54.84; H, 5.42.

1-Carbonyl-1-h<sup>5</sup>-cyclopentadienyl-5-ethoxyferracyclopent-1-en-2-one 110

The title compound by the same procedure which was used for the generation of 2-(carbonyl-h<sup>5</sup>-cyclopentadienyliron-3-methoxycyclopent-2-en-1-one from dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(1-ethoxycyclopropane)iron (0.55 g, 2.1 mmol). A red solid weighing 0.131 g (23.8%) was obtained. mp 71-72° C; IR (CCl<sub>4</sub>) 1950, 1646 cm<sup>-1</sup>; <sup>1</sup>H NMR (60 MHz, C<sub>6</sub>D<sub>6</sub>) 4.5 (s, 5H, Cp), 4.0 (q, 2H, OCH<sub>2</sub>), 2.3 (m, 3H, CH<sub>2</sub>), 1.1 ppm (t, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) 342.0 (M=C), 270.0 [M(CO)R], 216.9 (M-CO), 87.5 (Cp), 74.8 (OCH<sub>2</sub>), 53.1, 49.3 (CH<sub>2</sub>), 14.8 ppm (CH<sub>3</sub>); mass spectrum m/e 262 (M<sup>+</sup>), 234 (-CO), 206 (-2CO), 186 (Cp<sub>2</sub>Fe<sup>+</sup>), 177 (Fp<sup>+</sup>), 149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>); Anal. calcd. for C<sub>12</sub>H<sub>14</sub>FeO<sub>3</sub>: C, 54.98; H, 5.39. Found: C, 54.96; H, 5.43.

Synthesis of Carbonyl(h<sup>5</sup>-cyclopentadienyl)(exo-h<sup>3</sup>-2-ethoxypropenyl)iron 123

An NMR tube was charged with dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(1-ethoxycyclopropyl)iron (0.55 g, 2.1 mmol) along with some boiling chips and 0.6 ml of C<sub>6</sub>D<sub>6</sub>. The tube was fitted with a rubber septum and irradiated in the cell of a sonicator under nitrogen at room temperature. It

was found that the yield of the title compound was dependent upon the time of irradiation, hence yields varied. For maximum yield, the photolysis was continued for 6 hours. The solvent was removed in vacuo, and the residual material was chromatographed on silica gel using 10% ethyl acetate/hexanes (v/v) as the elutant. A yellow band was collected. After solvent removal the yellow material was re-chromatographed on silica using 2% ethyl acetate/hexanes (v/v) as the elutant. The first yellow band was collected. Upon removal of the solvent in vacuo 0.01 g (18.3%) of a yellow solid was obtained. mp 130-132° C; IR (CCl<sub>4</sub>) 1945 cm<sup>-1</sup>; <sup>1</sup>H NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) 4.27 (s, 5H, Cp), 3.37 (q, 2H, J = 6.9 Hz, OCH<sub>2</sub>), 3.12 (d, 2H, J<sub>H<sub>B</sub>H<sub>A</sub></sub> = 1.2 Hz, H<sub>B</sub>), 1.06 (t, 3H, J = 6.9 Hz, CH<sub>3</sub>), 0.69 ppm (d, 2H, J<sub>H<sub>B</sub>H<sub>A</sub></sub> = 1.2 Hz, H<sub>A</sub>); <sup>13</sup>C NMR (25 MHz, C<sub>6</sub>D<sub>6</sub>) 221.3 (M-CO), 133.8 (C-OEt), 79.8 (Cp), 62.7 (OCH<sub>2</sub>), 14.7 ppm (CH<sub>3</sub>); mass spectrum m/e 234 (M<sup>+</sup>), 206 (-CO), 186 (Cp<sub>2</sub>Fe<sup>+</sup>), 121 (CpFe<sup>+</sup>), high resol. Calcd. for C<sub>11</sub>H<sub>14</sub>FeO<sub>2</sub>: 234.03428. Found: 234.036114. Dev. +7.8 ppm.

Synthesis of Carbonyl(h<sup>5</sup>-cyclopentadienyl)(exo-h<sup>3</sup>-syn-1-ethoxypropenyl)iron 124

The title compound was prepared by the same method as was carbonyl(h<sup>5</sup>-cyclopentadienyl)(h<sup>3</sup>-2-ethoxypropenyl)iron with the following modification: the second yellow band of the ultimate chromatographic column was collected. Upon

removal of the solvent in vacuo 0.01 g (11.9%) of a yellow solid was recovered. mp 128-129° C; IR (CCl<sub>4</sub>) 1940 cm<sup>-1</sup>; <sup>1</sup>H NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) 4.49 (m, 1H, H<sub>c</sub>), 4.26 (s, 5H, Cp), 3.83 (d, 1H, J<sub>H<sub>c</sub>H<sub>a</sub>'</sub> = 7.8 Hz, H<sub>a</sub>'), 3.48 (q, 2H, J = 7.2 Hz, OCH<sub>2</sub>), 2.41 (dd, 1H, J<sub>H<sub>b</sub>H<sub>c</sub></sub> = 7.5 Hz, J<sub>H<sub>a</sub>H<sub>a</sub></sub> = 2.1 Hz, H<sub>s</sub>), 1.16 (t, 3H, J = 7.1 Hz, CH<sub>3</sub>), 0.33 ppm (dd, 1H, J<sub>H<sub>a</sub>H<sub>c</sub></sub> = 10.9 Hz, J<sub>H<sub>b</sub>H<sub>a</sub></sub> = 2.1 Hz, H<sub>a</sub>); <sup>13</sup>C NMR (25 MHz, C<sub>6</sub>D<sub>6</sub>) 222.2 (M-CO), 99.9 (C-OEt), 79.8 (Cp), 67.8 (OCH<sub>2</sub>), 61.0 (CH), 22.4 (CH<sub>2</sub>), 15.1 (CH<sub>3</sub>); mass spectrum m/e 234 (M<sup>+</sup>), 206 (-CO), 186 (Cp<sub>2</sub>Fe<sup>+</sup>), 177 (Fp<sup>+</sup>), 149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>), high resl. Calcd. for C<sub>11</sub>H<sub>14</sub>FeO<sub>2</sub>: 234.03428. Found: 234.03428. Dev. +2.9 ppm.

#### Determination of T<sub>1</sub> Relaxation Times

The T<sub>1</sub> relaxation times for the compounds studied in this work were obtained on highly concentrated samples (3.5 M) of the appropriate compound from a Varian XL-200 spectrometer at 50MHz. The automated T<sub>1</sub> inversion-recovery pulse program supplied by Varian was employed using an initial T<sub>1</sub> range of 0-50 seconds.

#### Determination of Concentration Profiles During Photolyses

The relative concentrations of CpFe containing species were determined from <sup>13</sup>C NMR integrations of the Cp peak in comparison to the integral value of an internal standard, ferrocene. A pulse delay of 35 seconds was used to insure

that the integral values would accurately reflect the actual concentrations of the species in question. A typical spectrum required 2000 pulses in order to obtain reasonable resolution. The integral values of the reactive species were compared to the value of the internal standard in each experiment. These values were then scaled by an appropriate factor and referenced to the original concentration of the starting material for each experiment. This concentration was assigned the arbitrary value of 1.00; all other concentrations were therefore fractions of this value. When the effect of solvent was evaluated, the photolysis was carried out with samples of equal concentration (typically 1.3 M) placed in a container surrounding the light source so that each tube was equidistant from the source. The apparatus was manually rotated every 10 minutes to provide for a more equal irradiation of the samples.

Synthesis of Carbonyl( $h^5$ -cyclopentadienyl)(1-ethoxycyclopropyl)(triphenylphosphine)iron 118

An NMR tube was charged with dicarbonyl( $h^5$ -cyclopentadienyl)(1-ethoxycyclopropyl)iron (0.255 g, 0.97 mmol), triphenylphosphine (0.255 g, 0.98 mmol), some boiling chips and 1.5 ml of  $C_6D_6$ . The photolysis was carried out in the apparatus and manner previously described. The sample was irradiated for 2 hours at which time the red solution was poured into 10 ml of hexanes. The solution was cooled

to  $-35^{\circ}$  C. After several hours a 0.45 g (68.8%) red powder had precipitated from the solution. This was recrystallized from cold hexanes to produce analytical samples. mp  $97-99^{\circ}$  C; IR ( $C_6D_6$ )  $1911.8\text{ cm}^{-1}$ ;  $^1H$  NMR (200 MHz,  $C_6D_6$ ) 7.6-6.9 (m, 15H,  $PPh_3$ ), 4.36 (d, 5H,  $J^4_{PH} = 1.5\text{ Hz}$ , Cp), 3.20 (m, 2H,  $OCH_2$ ), 1.00 (t, 3H,  $CH_3$ ), 0.54-0.21 ppm (m, 4H,  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $C_6D_6$ ) 222.4 (d,  $J^2_{PC} = 34.2\text{ Hz}$ , M-CO), 137.6 (d,  $J^1_{PC} = 39.1\text{ Hz}$ ,  $C_1$ ), 133.4 (d,  $J^3_{PC} = 9.8\text{ Hz}$ ,  $C_m$ ), 131.4 (d,  $J^4_{PC} = 7.4\text{ Hz}$ ,  $C_p$ ), 127.6 (d,  $J^2_{PC} = 17.1\text{ Hz}$ ,  $C_o$ ), 85.4 (Cp), 60.9 ( $OCH_2$ ), 53.7 (d,  $J^1_{PC} = 29.3\text{ Hz}$ , C-OEt), 20.1, 17.9 9 ( $CH_2$ ), 16.2 ppm ( $CH_3$ ); mass spectrum chem. ion. m/e 497 ( $MH^+$ ), 468 (-CO), 383 ( $CpFePPh_3^+$ ), 234 (- $PPh_3$ ), 206 (- $PPh_3$ , -CO), 186 ( $Cp_2Fe^+$ ); Anal. calcd. for  $C_{29}H_{29}FeO_2P$ : C, 70.17; H, 5.89. Found: C, 69.34; H, 5.73.

Synthesis of 1- $h^5$ -Cyclopentadienyl-1-triphenylphosphine-5-ethoxyferracyclopent-5-en-2-one 122

An NMR tube was charged with 1-carbonyl-1- $h^5$ -cyclopentadienyl-5-ethoxyferracyclopent-5-en-2-one (0.07 g, 0.27 mmol), triphenylphosphine (0.08 g, 0.28 mmol), some boiling chips and 1.5 ml of  $C_6D_6$ . The photolysis was carried in the apparatus and manner previously described. After 2 hours of irradiation the red solution was chromatographed on silica gel using a low-temperature column. The elutant was 50% ethyl acetate/hexanes (v/v). A red band was collected which yielded 0.11 g (82.1%) of a red solid. mp  $148-149^{\circ}$  C; IR

(C<sub>6</sub>D<sub>6</sub>) 1615 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>) 7.6-6.9 (m, 15H, PPh<sub>3</sub>), 4.48 (d, 5H, J<sup>4</sup><sub>PH</sub> = 1.35 Hz, Cp), 4.10 (m, 2H, OCH<sub>2</sub>), 2.10 (m, 4H, CH<sub>2</sub>), 1.06 (t, 3H, CH<sub>3</sub>); mass spectrum m/e 262 (PPh<sub>3</sub><sup>+</sup>), 234 (-PPh<sub>3</sub>), 186 (Cp<sub>2</sub>Fe), 121 (CpFe<sup>+</sup>); Anal. calcd. for C<sub>29</sub>H<sub>29</sub>FeO<sub>2</sub>P: C, 70.17; H, 5.89. Found: C, 69.98; H, 5.91.

Thermolysis of Carbonyl(h<sup>5</sup>-cyclopentadienyl)(1-ethoxycyclopropyl)(triphenylphosphine)iron

The title compound (0.255 g, 0.97 mmol) was placed in an NMR tube along with some boiling stones and 1.6 ml of C<sub>6</sub>D<sub>6</sub>. The tube was fitted with a rubber septum and was placed in an oil bath maintained at 75° C. The contents of the tube were kept under a blanket of nitrogen with an oil bubbler serving as a pressure release. The tube was heated for 47 hours after which time the contents were emptied into hexanes. Upon chilling the solution to -35° C, 0.189 g (78.9%) of a red solid precipitated from the solution. The identity of the compound was determined to be that of 1-h<sup>5</sup>-cyclopentadienyl(triphenylphosphine)-5-ethoxyferracyclopent-5-en-2-one by virtue of the identical nature of the compounds mp, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass spectrum and elemental analysis with the aforementioned carbene complex obtained from the previous experiment.

Synthesis of Dicarbonyl(h<sup>5</sup>-  
cyclopentadienyl)(cyclopropanoyl)iron 152

The title compound was prepared by the method of Stone<sup>107</sup> in a 53.9% yield from cyclopropanoyl chloride. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>) 4.60 (s, 5H, Cp), 2.48 (m, 1H, CH), 1.20-0.25 ppm (m, 4H, CH<sub>2</sub>).

Synthesis of Dicarbonyl(h<sup>5</sup>-  
cyclopentadienyl)(cyclopropyl)iron 151

A sample of the acyl complex dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(cyclopropanoyl)iron (0.685 g, 2.80 mmol) was placed in an NMR tube along with some boiling chips and 0.6 ml of C<sub>6</sub>D<sub>6</sub>. The sample was irradiated in an apparatus and manner previously described. After 2 hours of irradiation, the solvent was removed from the sample in vacuo and the residual material was chromatographed on silica gel using 10% ethyl acetate/hexanes (v/v) as the elutant. A yellow band was collected which upon removal of the solvent in vacuo yielded 0.186 g (30.7%) of an amber oil. Its spectral properties were identical with those reported for the title compound by Rosenblum.<sup>89b</sup> IR (C<sub>6</sub>D<sub>6</sub>) 2013.8, 1960.6 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>) 4.33 (s, 5H, Cp), 0.80-0.00 ppm (m, 5H, CH, CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>) 217.3 (M-CO), 85.7 (Cp), 8.8 (CH<sub>2</sub>), -9.7 ppm (CH); lit. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) 4.31 (s, 5H), 0.9- -0.1 ppm (m, 5H).

Synthesis of Carbonyl( $h^5$ -  
cyclopentadienyl)(cyclopropyl)(triphenylphosphine)iron 153

A sample of the sigma complex dicarbonyl( $h^5$ -cyclopentadienyl)(cyclopropyl)iron (0.12 g, 0.58 mmol) was placed in an NMR tube along with some boiling chips and 1.5 ml of  $C_6D_6$ . The sample was photolyzed in an apparatus and manner previously described. After 2 hours of irradiation, the contents of the tube were subjected to low-temperature chromatography on silica gel using 10% ethyl acetate/hexanes (v/v) as the elutant. A red band was collected which yielded 0.25g (92.0%) of a red solid. The spectral properties of the compound were identical to those reported in the literature for the title compound.<sup>8,9b</sup> mp 101° C;  $^{13}C$  NMR (50 MHz,  $C_6D_6$ ) 222.5 (d,  $J^2_{PC} = 31.4$  Hz, M-CO), 137.6 (d,  $J_{PC} = 20.1$  Hz), 133.7 ( $J_{PC} = 9.7$  Hz), 128.2 (d,  $J_{PC} = 9.5$  Hz) [ $PPh_3$ ], 85.5 (Cp), 11.7, 9.9 ( $CH_2$ ); -11.0 ppm (d,  $J^2_{PC} = 28.0$  Hz, CH); lit.  $^{13}C$  NMR ( $C_6D_6$ ) 220.1, 138-127, 86.0, 12.1, 10.3, -10.1 ppm.

Thermolysis of Carbonyl( $h^5$ -  
cyclopentadienyl)(cyclopropyl)(triphenylphosphine)iron

The title compound (0.05 g, 0.9 mmol) was placed in an NMR tube along with some boiling stones and 1.6 ml of  $C_6D_6$ . The tube was placed in an oil bath at 75° C and was maintained under a nitrogen blanket vented to an oil bubbler. After 16.5 days, an  $^{13}C$  NMR spectrum of the tube was recorded. The spectrum revealed that the starting

material was still present. Two other compounds were identified on the basis of the resonances present:  $\text{Fp}_2$  from the 88.7 ppm peak (Cp), and carbonyl( $\eta^5$ -cyclopentadienyl)(cyclopropanoyl)(triphenylphosphine)iron from 270.4 [d,  $J^2_{\text{Pc}} = 41.0$  Hz,  $\text{M}(\text{CO})\text{R}$ ], 221.5 (d,  $J^2_{\text{Pc}} = 32.1$  Hz), 85.3 (Cp), 39.4, 36.3 ( $\text{CH}_2$ ), 10.3 ppm (d,  $J^2_{\text{Pc}} = 29.1$  Hz). The mp and IR spectrum of the material was identical to that obtained by Stone.<sup>107</sup> mp 129-131° C; IR ( $\text{C}_6\text{D}_6$ ) 1921.4, 1603.8 lit. mp 131° C; IR ( $\text{CCl}_4$ ) 1922, 1601.

Synthesis of Dicarbonyl( $\eta^5$ -cyclopentadienyl)(1-thiophenylcyclopropanoyl)iron 160

To a stirred suspension of  $\text{KFp}$  (1.02 g, 4.72 mmol) in 10 ml of THF at -78°C was added via cannula under nitrogen 1-thiophenylcyclopropanoyl chloride (0.88g, 4.16 mmol) in 20 ml of THF. The mixture was allowed to stir for 1 hour. It then warmed to room temperature and was allowed to stir at ambient temperature for 2 hours. A muddy, brown solid was filtered from the mixture, and the solvent was removed in vacuo. The remaining material was chromatographed on silica gel using 10% ethyl acetate/hexanes (v/v) as the elutant. The second yellow band was collected which, upon removal of the solvent, yielded 0.418 g (25.0%) of a yellow solid. mp 63.5-65.0° C; IR ( $\text{CCl}_4$ ) 2040, 1980, 1650  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (60 MHz,  $\text{C}_6\text{D}_6$ ) 7.4-6.8 (m, 5H, SPh), 4.23 (s, 5H, Cp), 1.7.0.96 ppm (m, 4H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR (50 MHz,  $\text{C}_6\text{D}_6$ ) 230.3 [ $\text{M}(\text{CO})\text{R}$ ],

215.2 (M-CO), 139.4, 129.1, 127.1, 125.0 (SPh), 86.4 (Cp), 50.1 (C-SPh), 17.8 ppm (CH<sub>2</sub>); mass spectrum m/e 326 (-CO), 298 (-2CO), 270 (-3CO), 186 (Cp<sub>2</sub>Fe<sup>+</sup>), 177 (Fp<sup>+</sup>), 149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>); Anal. calcd for C<sub>17</sub>H<sub>14</sub>FeO<sub>3</sub>S: C, 57.65; H, 3.98. Found: C, 57.74; H, 4.02.

Synthesis of Dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(1-thiophenylcyclopropyl)iron 159

To a stirred suspension of KFP (1.56 g, 7.2 mmol) in 10 ml of THF at -78° C was added 1-iodo-1-thiophenylcyclopropane (2.0 g, 7.2 mmol) via a steel cannula under nitrogen. The mixture was allowed to stir at low temperature for 1 hour followed by warming to room temperature. The material was allowed to stir at ambient temperature for 2 additional hours. A brown solid was filtered from the mixture and the remaining material was chromatographed on silica gel using 10% ethyl acetate/hexanes (v/v) as the elutant. A yellow band was collected which yielded 1.09 g (46.4%) of an amber oil upon in vacuo removal of the solvent. IR (C<sub>6</sub>D<sub>6</sub>) 2010.3, 1955.0 cm<sup>-1</sup>; <sup>1</sup>H NMR (60 MHz, C<sub>6</sub>D<sub>6</sub>) 7.5-6.8 (m, 5H, SPh), 4.0 (s, 5H, Cp), 0.7 ppm (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>) 216.4 (M-CO) 139.6, 131.6, 128.7, 126.4 (SPh), 87.8 (Cp), 20.6 (CH<sub>2</sub>), 10.7 (C-SPh); mass spectrum chem. ion. 327 (MH<sup>+</sup>), 298 (-CO), 271 (-2CO), 217 (FpC<sub>3</sub>H<sub>4</sub><sup>+</sup>), 189 [CpFe(CO)C<sub>3</sub>H<sub>4</sub><sup>+</sup>], 177

(Fp<sup>+</sup>), 149 (CpFeCO<sup>+</sup>); Anal. calcd. for C<sub>16</sub>H<sub>14</sub>FeO<sub>2</sub>S: C, 58.91; H, 4.33. Found: C, 58.51; H, 4.55.

Synthesis of Carbonyl(h<sup>5</sup>-cyclopentadienyl)(h-1-thiophenylcyclopropyl)iron 162

An NMR tube was charged with dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(1-thiophenylcyclopropyl)iron (0.276 g, 0.662 mmol) along with some boiling chips and 0.6 ml of C<sub>6</sub>D<sub>6</sub>. The sample was photolyzed in the apparatus and manner previously described. After 2 hours of irradiation the contents of the tube were poured into 5 ml of hexanes. The liquid was allowed to evaporate to dryness at -35° C over the course of several days. A dirty yellow solid was obtained which could be further purified by low-temperature recrystallization from hexanes. A yellow solid weighing 0.052 g (19.8%) was obtained. Alternatively, the reaction mixture was stripped of its solvent in vacuo and chromatographed on silica gel using 5% ethyl acetate/hexanes (v/v) as the elutant. A yellow band was collected which yielded trace amounts of the title compound as determined from its spectral characteristics. mp 110° C (decomp); IR (C<sub>6</sub>D<sub>6</sub>) 1921.6 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>) 7.7-6.8 (m, 5H, SPh), 3.98 (s, 5H, Cp), 1.2-0.8 ppm (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>) 218.7 (M-CO), 133.2, 129.1, 128.3 127.2 (SPh), 79.8 (Cp) 49.6 (C-SPh), 14.7, 10.9 ppm (CH<sub>2</sub>); mass spectrum chem. ion. m/e 299 (MH<sup>+</sup>), 270 (-CO), 186 (Cp<sub>2</sub>Fe<sup>+</sup>),

149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>); Anal. calcd. for C<sub>15</sub>H<sub>14</sub>FeOS: C, 60.42; H, 4.73. Found: C, 60.19; H, 4.12.

Synthesis of Carbonyl(h<sup>5</sup>-cyclopentadienyl)(h<sup>3</sup>-2-thiophenylpropenyl)iron 166

An NMR tube was charged with dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(1-thiophenylcyclopropyl)iron (0.216 g, 0.662 mmol) along with some boiling chips and 1.5 ml of C<sub>6</sub>D<sub>6</sub>. The sample was photolyzed in the apparatus and manner previously described. After 4 hours of irradiation the tube was immersed in an oil bath which was maintained at 75° C. The contents were kept under a nitrogen blanket with an oil bubbler serving as a pressure release. The tube was heated for 21 hours at which time the solvent was removed in vacuo and the residual material was chromatographed on silica gel using 2% ethyl acetate/hexanes (v/v) as the elutant. The second yellow band was collected, and it was stripped of its solvent. The light yellow oil was re-chromatographed on silica gel using pure hexanes and the elutant. A yellow band was collected which yielded 0.04 g (19.4%) of a yellow solid. mp 133-134° C; IR (C<sub>6</sub>D<sub>6</sub>) 1945.9 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) 7.3-6.8 (m, 5H, SPh), 3.97 (s, 5H, Cp), 2.77 (d, 2H, J<sub>HH</sub> = 1.7 Hz, Hs), 0.78 ppm (d, 2H, J<sub>HH</sub> = 1.7 Hz, Ha); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) 222.3 (M-CO), 142.2 (C-SPh) 129.1, 128.4, 127.7, 125.8 (SPh), 80.9 (Cp) 42.1 (CH<sub>2</sub>); mass spectrum m/e 298 (M<sup>+</sup>), 270 (-CO), 186 (Cp<sub>2</sub>Fe<sup>+</sup>), 149 (CpFeCO<sup>+</sup>), 121

(CpFe<sup>+</sup>); Anal. calcd. for C<sub>13</sub>H<sub>14</sub>FeOS: C, 60.42; H, 4.73.

Found: C, 60.22; H, 4.02.

Synthesis of Carbonyl(h<sup>5</sup>-cyclopentadienyl)(1-thiophenylcyclopropyl)(triphenylphosphine)iron 161

An NMR tube was charged with dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(1-thiophenylcyclopropyl)iron (0.216 g, 0.622 mmol) along with triphenylphosphine (0.17 g, 0.65 mmol), some boiling chips and 1.5 ml of C<sub>6</sub>D<sub>6</sub>. The sample was irradiated in the apparatus and manner previously described. After 1 hour of irradiation, a red solid began precipitating from the solution. The contents were dumped into cold hexanes to suspend the solid. After filtering and three washings with cold hexanes 0.154 g (42.4%) of a red powder was obtained. The material was further purified by low-temperature recrystallization from a benzene/hexanes solvent system. mp 99-101° C; IR (C<sub>6</sub>D<sub>6</sub>) 1921.5 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>) 7.75-6.90 (m, 15H, PPh<sub>3</sub>), 4.499 (s, 5H, Cp), 1.21-0.88 ppm (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>) 222.7 (d, J<sub>PC</sub> = 32.1 Hz, M-CO), 137.4 (J<sub>PC</sub> = 4.2 Hz), 136.7, 135.7, 134.5 (d, J<sub>PC</sub> = 9.8 Hz) [PPh<sub>3</sub>], 129.6, 128.3, 127.9, 126.9 (SPh), 86.3 (Cp) 17.1, 15.5 (CH<sub>2</sub>), 7.7 ppm (d, J<sub>PC</sub> = 21.5 Hz); mass spectrum chem. ion. m/e 532 (-CO), 298 (-PPh<sub>3</sub>), 270 (-PPh<sub>3</sub>, -CO), 263 (PPh<sub>3</sub>H<sup>+</sup>), 186 (Cp<sub>2</sub>Fe<sup>+</sup>), 177 (Fp<sup>+</sup>), 149 (CpFeCO<sup>+</sup>); Anal. calcd. for C<sub>33</sub>H<sub>29</sub>FeOPS: C, 70.72; H, 5.22. Found: C, 70.41; H, 4.90.

Synthesis of Dicarbonyl( $\eta^5$ -cyclopentadienyl)(trans-1-fluorocyclopropyl)iron 171

To a stirred suspension of KFP (1.09 g, 5.04 mmol) at -78° C in 10 ml of THF was added trans-1-bromo-2-fluorocyclopropane<sup>146</sup> via a steel cannula under nitrogen. The material was allowed to stir for 1 hour at low temperature. It then was warmed to room temperature and allowed to stir for an additional 2 hours. A brown solid was filtered from the mixture, and the filtrate was stripped of its solvent in vacuo. The residue was chromatographed on silica gel using 10% ethyl acetate/hexanes as the elutant. A yellow band was collected, concentrated and re-chromatographed on silica gel using pure hexanes. The first yellow band was collected. Upon removal of its solvent in vacuo, 0.143 g (16.8%) of an amber oil was obtained. IR ( $C_6D_6$ ) 2016.3, 1962.1  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $C_6D_6$ ) 4.32 (m, 1H,  $J_{HF} = 70.8$  Hz, CHF), 3.97 (s, 5H, Cp), 1.1 (m, 2H,  $CH_2$ ), 0.21 ppm (m, 1H, Fe-CH);  $^{13}C$  NMR (75 MHz,  $C_6D_6$ ) 216.4 (M-CO), 85.5 (Cp), 80.1 (d,  $J_{CF} = 225.1$  Hz, CF), 15.4 (d,  $J^2_{CF} = 12.7$  Hz,  $CH_2$ ), -5.8 ppm (Fe-C);  $^{19}F$  NMR (282 MHz,  $C_6D_6$ ) -191.21 ppm (m,  $J^2_{HFgem} = 70.8$  Hz,  $J_{HFcis} = 29.3$  Hz,  $J_{HFcis} = 19.5$  Hz,  $J_{HFtrans} = 4.9$  Hz); mass spectrum m/e 236 ( $M^+$ ), 208 (-CO), 149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>) high resl. calcd. for  $C_{10}H_9FFeO_2$ : 235.99359. Found: 235.99274; dev. -3.64 ppm.

Synthesis of dicarbonyl( $h^5$ -cyclopentadienyl)(cis-1-fluorocyclopropyl)iron 175

To a stirred suspension of KFp (1.09 g, 5.14 mmol) in 10 ml of THf at  $-78^\circ$  C was added trans-1-bromo-2-fluorocyclopropane in 20 ml of THF. The mixture was allowed to stir for 1 hour at low temperature. It was then allowed to warm to room temperature and stir for an additional 2 hours. A brown solid was filtered from the reaction mixture and the filtrate was then concentrated. The brown residue was then chromatographed on silica gel using 10% ethyl acetate/hexanes (v/v). A yellow band was collected which was concentrated and re-chromatographed on silica gel using pure hexanes as the elutant. The second yellow band was collected. Removal of the solvent from this fraction in vacuo afforded 0.031 g (3.6%) of an amber oil. IR ( $C_6D_6$ ) 2010.3, 1953.8  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $C_6D_6$ ) 4.31 (m, 1H,  $J_{HF} = 71.4$  Hz, CHF), 4.21 (s, 5H, Cp), 1.10 (m, 2H,  $CH_2$ ), 0.25 ppm (m, 1H, FeCH);  $^{13}C$  NMR (75 MHz,  $C_6D_6$ ) 216.7 (M-CO), 85.3 (Cp), 78.3 (d,  $J_{CF} = 311.8$  Hz, CF), 14.3 (d,  $J^2_{CF} = 10.0$  Hz,  $CH_2$ ), -5.1 ppm (FeC);  $^{19}F$  NMR (282 MHz,  $C_6D_6$ ) -199.2 ppm (m,  $J_{HFgem} = 71.4$  Hz,  $J_{HFcis} = 25.0$  Hz,  $J_{HFtrans} = 6.0$  Hz,  $J_{HFtrans} = 5.2$  Hz); mass spectrum m/e 236 ( $M^+$ ), 208 (-CO), 149 (CpFeCO $^+$ ), 121 (CpFe $^+$ ). high resl. calcd. for  $C_{10}H_9FFeO_2$ : 235.99359. Found: 235.99291; dev. -2.88 ppm.

Synthesis of carbonyl(h<sup>5</sup>-cyclopentadienyl)(exo-h<sup>3</sup>-syn-1-fluoropropenyl)iron 172

A mixture of the trans- (82.3%) and cis- (17.7%) dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(2-fluorocyclopropyl)iron complexes (0.167g, 7.31 mmol) was placed in an NMR tube along with some boiling chips and ferrocene (0.05 g, 3.1 mmol) as an internal standard. The sample was photolyzed in the apparatus and manner previously described. The reaction was monitored over a 16 hour period by <sup>13</sup>C NMR. During this period the trans sigma complex decreased to a negligible concentration; the concentration of the cis sigma complex did not change with time. At the end of 16 hours of irradiation, the solvent was removed from the sample in vacuo and the residue was chromatographed on silica gel using 5% ethyl acetate/hexanes as the elutant. The second yellow band was collected. Upon removal of the solvent in vacuo, .081 g (48.8%) of a yellow solid was recovered. mp 128° C; IR (C<sub>6</sub>D<sub>6</sub>) 1949.7 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) 4.86 (dd, 1H, J<sub>Ha'F</sub> = 71.1 Hz, J<sub>Ha'HC</sub> = 6.4 Hz, Ha'), 4.31 (m, 1H, Hc), 4.05 (s, 5H, Cp), 2.10 (m, 1H, J<sub>HsHC</sub> = 7.7 Hz, Hs), 0.15 ppm (m, 1H, J<sub>HaHC</sub> = 11.3 Hz, Ha); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) 221.0 (M-CO), 108.9 (d, J<sub>CFgem</sub> = 249.6 Hz, CF), 80.3 (Cp), 61.5 (d, J<sub>CFsyn</sub> = 13.9 Hz, CH), 22.9 ppm (d, J<sup>3</sup><sub>CF</sub> = 7.2 Hz, CH<sub>2</sub>); <sup>19</sup>F NMR (282 MHz, C<sub>6</sub>D<sub>6</sub>) -172.88 ppm (dd, J<sub>HFgem</sub> = 71.1 Hz, J<sub>HFsyn</sub> = 12.2 Hz); mass spectrum m/e 208 (M<sup>+</sup>), 180 (-CO),

149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>); Anal. calcd. for C<sub>9</sub>H<sub>9</sub>FFeO: C, 51.96; H, 4.36. Found: C, 52.30; H, 4.30.

Synthesis of dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(h<sup>2</sup>-1,3-dimethylallene)iron fluoride 177

To a stirred suspension of KFP (1.23 g, 5.69 mmol) in 10 ml of THF at -78° C was added 1-bromo-1-fluoro-trans-2,3-dimethylcyclopropane<sup>146</sup> (0.86 g, 5.15 mmol) via a steel cannula under nitrogen. The mixture was allowed to stir at low-temperature for 1 hour. It was then allowed to warm to room temperature and stir for an addition 3 hours. A brown solid was filtered from the reaction mixture, and the residue was chromatographed on silica gel using 10% ethyl acetate/hexanes as the elutant. A yellow band was collected and an amber oil was obtained upon in vacuo removal of the solvent. The oil was dissolved in 1 ml of benzene and 5 ml of hexanes were added to it. This was followed by the precipitation of a yellow solid which was collected by filtration after several washing with cold hexanes. mp 174-176° C; IR (C<sub>6</sub>D<sub>6</sub>) 2010.4, 1958.9 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, toluene-d<sub>8</sub>) 6.05 [q, 1H, J<sub>H-H</sub> = 6.5 Hz, H(free)], 4.25 (s, 5H, Cp), 4.11 [q, 1H, J<sub>H-H</sub> = 6.2 Hz, H(complexed)], 1.77 [d, 3H, J<sub>H-H</sub> = 6.5 Hz, CH<sub>3</sub>(free)], 1.37 ppm [d, 3H, J<sub>H-H</sub> = 6.2 Hz, CH<sub>3</sub>(complexed)]; <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) 217.3, 216.9 (M-CO), 132.2 [CH(free)], 85.3 (Cp), 84.1 [CH(complexed)], 23.7 [CH<sub>3</sub>(free)], 20.0 ppm [CH<sub>3</sub>(complexed)]; <sup>19</sup>F NMR (282 MHz,

C<sub>6</sub>D<sub>6</sub>) -205.557 ppm (s); mass spectrum chem. ion. m/e 265 (MH<sup>+</sup>), 245 (-F), 217 (-CO, -F), 189 (-2CO, -F), 177 (Fp<sup>+</sup>). elec. imp. 245 (-F), 217, (-CO, -F), 189 (-2CO, -F), 177 (Fp<sup>+</sup>), 149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>); Anal. calcd. for C<sub>12</sub>H<sub>13</sub>FFeO<sub>2</sub>: C, 54.56; H, 4.96. Found: C, 54.93; H, 5.03.

#### Synthesis of 2-Methoxy-2-methylpropionic Acid

The title compound was prepared in a yield of 57.6% by the method of Weizmann.<sup>147</sup> mp 163-164° C; <sup>1</sup>H NMR (60 MHz, CHCl<sub>3</sub>) 8.07 (s, 1H, CO<sub>2</sub>H), 3.35 (s, 3H, OCH<sub>3</sub>), 1.43 ppm (s, 6H, CH<sub>3</sub>). lit. mp 160° C.

#### Synthesis of 2-Methoxy-2-methylpropionyl chloride

The title compound was prepared in a 14.7% yield by the method of Richardson.<sup>148</sup> <sup>1</sup>H NMR (60 MHz, CHCl<sub>3</sub>) 3.35 (s, 3H, OCH<sub>3</sub>), 1.53 ppm (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (25 MHz, CHCl<sub>3</sub>) 178.1 (COCl), 84.1 (C-OCH<sub>3</sub>), 52.3 (OCH<sub>3</sub>), 23.4 ppm (CH<sub>3</sub>). lit. <sup>1</sup>H NMR (CHCl<sub>3</sub>) 3.30, 1.48 ppm.

#### Synthesis of Dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(1-methoxy-1-methylpropanoyl)iron 181

To a stirred suspension of KfP (5.2 g, 24.2 mmol) at -78° C in 20 ml of THF was added 2-methoxy-2-methylpropionyl chloride (3.2 g, 23.9 mmol) in 20 ml of THF via steel cannula under nitrogen. The mixture was allowed to stir at low-temperature for 1 hour and then allowed to warm to room temperature. After stirring at ambient temperature for 2

hours, a brown solid was filtered from the mixture. The filtrate was concentrated in vacuo and chromatographed on silica gel using 10% ethyl acetate/hexane (v/v) as the elutant. A yellow band was collected. Evaporation of the solvent in vacuo yielded 0.805 g (12.1%) of a yellow solid. mp 37-39° C; UV (pentane)  $\lambda_{\text{max}}$  = 330 nm (extinction coefficient = 16,578); IR (CCl<sub>4</sub>) 2010, 1965, 1630 cm<sup>-1</sup>; <sup>1</sup>H NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) 4.25 (s, 5H, Cp), 3.03 (s, 3H, OCH<sub>3</sub>), 1.07 ppm (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (25 MHz, C<sub>6</sub>D<sub>6</sub>) 262.3 [M(CO)R], 216.4 (M-CO), 86.8 (Cp), 50.1 (OCH<sub>3</sub>), 39.1 (C-OCH<sub>3</sub>), 21.8 ppm (CH<sub>3</sub>); mass spectrum m/e 278 (M<sup>+</sup>), 205 (FpCO<sup>+</sup>), 177 (Fp<sup>+</sup>), 149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>), 73 (Me<sub>2</sub>COMe<sup>+</sup>); Anal. calcd. for C<sub>12</sub>H<sub>14</sub>FeO<sub>4</sub>: C, 51.83; H, 5.07. Found: C, 51.66; H, 5.13.

Synthesis of Dicarbonyl(h<sup>5</sup>-cyclopentadienyl)[2-(2-methoxypropyl)]iron 182

An NMR tube was charged with dicarbonyl(h<sup>5</sup>-cyclopentadienyl)(2-methoxy-2-methylpropionoyl)iron (0.330 g, 1.12 mmol) along with some boiling chips and 0.6 ml of C<sub>6</sub>D<sub>6</sub>. The sample was photolyzed in the apparatus and manner previously described for 10 minutes. The solvent was stripped from the sample in vacuo, and the remaining material was chromatographed on silica gel using 10% ethyl acetate as the elutant. The first yellow band was collected. Upon removal of the solvent in vacuo, 0.083 g

(32.5%) of an amber oil was obtained. The spectral data agreed with the results of Casey who prepared the title compound via an alternate route.<sup>149</sup> IR (CCl<sub>4</sub>) 2000, 1944 cm<sup>-1</sup>; <sup>1</sup>H NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) 4.09 (s, 5H, Cp), 3.22 (s, 3H, OCH<sub>3</sub>), 1.50 ppm (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) 218.7 (M-CO), 87.1 (Cp), 53.6 (OCH<sub>3</sub>), 39.1 ppm (CH<sub>3</sub>). lit. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) 4.18, 3.10, 1.64 ppm; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) 219, 87.2, 52.1, 39.1 ppm.

Synthesis of 1-Carbonyl-h<sup>5</sup>-cyclopentadienyl-2-ethoxy-5-methoxyferracyclopenta-1,5-diene Tetrafluoroborate 207

A Schlenk tube was charged with 1-carbonyl-h<sup>5</sup>-cyclopentadienyl-5-ethoxyferracyclopent-5-en-2-one (0.087 g, 0.33 mmol), trimethyloxonium tetrafluoroborate (0.05 g, 0.35 mmol) and 10 ml of methylene chloride. The red solution turned bright yellow after stirring at room temperature under nitrogen for 2 hours. Cold ether was added to the tube via steel cannula which caused a fluffy yellow precipitate to form. When the solution warmed from -78° C to room temperature the solid melted to a reddish oil. Upon standing overnight in ether at ambient temperature, the oil solidified and an orange-yellow solid was filtered from the tube. The material was recrystallized from a methylene chloride/diethyl ether solvent system at low temperature. 0.062 g (51.3%) of a yellow solid was recovered. mp 79-80° C; IR (CH<sub>2</sub>Cl<sub>2</sub>) 1995 cm<sup>-1</sup>; <sup>1</sup>H NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 4.03 (s,

5H, Cp), 4.85 (q, 2H, OCH<sub>2</sub>), 4.60 (s, 3H, OCH<sub>3</sub>), 3.2 (m, 4H, CH<sub>2</sub>), 1.68 ppm (t, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (25 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 344.5, 342.4 (M=C), 211.6 (M-CO), 88.7 (Cp), 77.8 (OCH<sub>2</sub>), 67.3 (OCH<sub>3</sub>), 51.1, 51.0 (CH<sub>2</sub>), 14.7 ppm (CH<sub>3</sub>); mass spectrum m/e 368 (M<sup>+</sup>), 268 (-3F, -CO), 186 (Cp<sub>2</sub>Fe<sup>+</sup>), 177 (Fp<sup>+</sup>), 149 (CpFeCO<sup>+</sup>), 121 (CpFe<sup>+</sup>); Anal. calcd. for C<sub>13</sub>H<sub>21</sub>BF<sub>4</sub>FeO<sub>3</sub>: C, 42.43; H, 5.75. Found: C, 42.46; H, 5.78.

Reaction of 1-h<sup>5</sup>-cyclopentadienyl-1-carbonyl-2-ethoxy-5-methoxyferracyclopenta-1,5-diene with triphenylphosphine

A Schlenk tube was charged with the titled dicarbene complex (0.100 g, 3.14 mmol), triphenylphosphine (0.86 g, 3.2 mmol) and 10 ml of methylene chloride. The yellow solution was allowed to stir at room temperature overnight (15 hours) resulting in the formation of a red solution. Cold ether (-78° C) was added to the solution which caused a yellow oily solid to precipitate. The red mother liquor was carefully decanted off and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the solid were recorded. Attempts to recrystallize the solid led to decomposition. <sup>13</sup>C NMR (25 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 339.4, 209.3, 137.5-128.6 (region unresolvable, at least 11 peaks), 120.9, 117.2, 87.9, 75.6, 48.5, 12.9, 9.9, 7.6 ppm.

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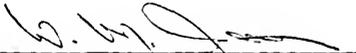
## BIOGRAPHICAL SKETCH

The author was born in Brooklyn, New York, on February 21, 1959. In 1970, he moved with his family to Merritt Island, Florida: a wildlife refuge and the island upon which Kennedy Space Center is built. Early schooling was received in the public systems of New York and Florida; however, in 1977 he entered the University of Notre Dame. After receiving a B.S. in chemistry, with honors, he entered the University of Florida in 1981. Study under Dr. W.M. Jones afforded the opportunity to work in the field of organometallic chemistry.

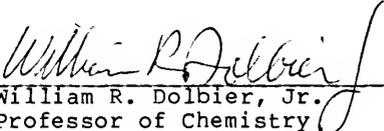
Among the interests of the author are literature, sports and music. He is an incurable browser in book stores; he is an avid participant in football, basketball and soccer; it has been said that he can make an accordion cry or sing.

The author married Miss Amy Fox Rankin shortly after finishing at Florida. They now reside in Westfield, New Jersey where he is employed as a senior chemist in the catalysis section of the polyolefins division of Union Carbide Corporation.

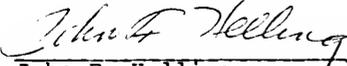
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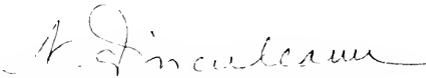
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Assistant Professor of  
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1987

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