REACTIONS OF TRANSITION METAL π-COMPLEXED CATIONS WITH SELECTED NUCLEOPHILES

By

BAIREDDY RAGHAVA REDDY

Bachelor of Science
Osmania University
Hyderabad, India
1973

Master of Science
Osmania University
Hyderabad, India
1975

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
DOCTOR OF PHILOSOPHY
December, 1980

REACTIONS OF TRANSITION METAL π-COMPLEXED CATIONS WITH SELECTED NUCLEOPHILES

Thesis Approved:

Thesis Adviser

E J Eisenbraun

Lionel M. Raff

Margaret K. Essenberg

Norman N Durham
Dean of the Graduate College

ACKNOWLEDGMENTS

I deeply appreciate the constant guidance of Dr. Jeffrey S. McKennis throughout the doctoral program.

I am extremely grateful to my committee members, Dr. Edmund J. Eisenbraun, Dr. Lionel M. Raff and Dr. Roger E. Koeppe for their valuable time and advice in the planning of the program and the evaluation of the thesis work. I am especially grateful to Dr. Margaret K. Essenberg who kindly agreed to be a member of the examining committee with a short notice.

The financial assistance in the form of a teaching assistantship by the Chemistry Department, Oklahoma State University for the period August '75 - May '80 and the summer research fellowships by Gulf Oil Company and Alumni and Friends, Oklahoma State University is sincerely acknowledged with gratitude.

Special thanks to Miss Virginia L. Vaughan for her assistance in the study of some reactions discussed in this thesis; Mr. Stan O. Single and Mr. Norman B. Perriera for their help in obtaining the spectral data and all my past and present lab partners for their understanding, friendship and partnership.

I find the man-made languages to be very inadequate in expressing my appreciation to all my friends who made my stay in Stillwater a memory to be cherished in years to come.

Finally, I would like to express my special thanks to Mr. P. Vijayakumar and Mrs. Janet Sallee for their time and the patience in typing this thesis.

TABLE OF CONTENTS

Chapter Page

LIST OF TABLES

LIST OF FIGURES

Figure Page

CHAPTER I

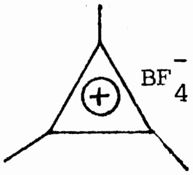
INTRODUCTION

The synthesis and chemistry of carbonium ions (also referred to as carbenium ions or carbocations) has attracted great attention from chemists world-wide since the beginning of the twentieth century. The investigation of the salt-like character of triphenylcarbinol solutions in concentrated sulfuric acid and other ionizing solvents led to the concept of the existence of carbonium ions which was subsequently proved by experimental methods. The existence of carbonium ions was confirmed in 1909 independently by K. A. Hoffman and M. Gomberg who isolated crystalline carbonium ion salts from perchloric acid solutions of triphenylcarbinol[1]. Serious attempts to obtain crystalline solids or solutions of carbonium ions other than those of triarylmethyl carbocations were made only after 1950 in an effort to verify the theories about the involvement of carbonium ion intermediates in solvolysis reactions. The outcome of this exploratory work may be considered among the most remarkable achievements of organic chemistry[2]. A few examples of isolable carbonium ions include triphenylmethyl tetrafluoroborate (1), 1,2,3-triphenylcyclopropenium tetrafluoroborate (2)[3], heptamethyl cyclohexadienylium tetrachloroaluminate (3)[4], tropylium tetrafluroborate (4)[5] and bicyclo[5.1.0]octatrienylium hexachloroantimonate (5)[6] (Figure 1). However, the isolation of several unsubstituted carbonium ions has not been possible. It was recently discovered

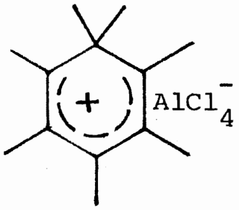
ISOLABLE CARBONIUM IONS:

$(Ph_3C)BF_4$

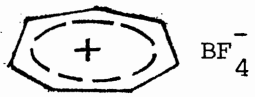
1



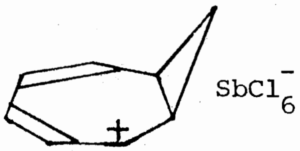
2



3

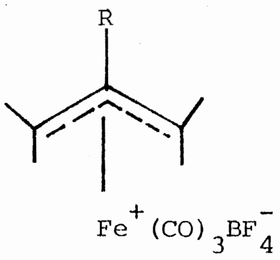


4

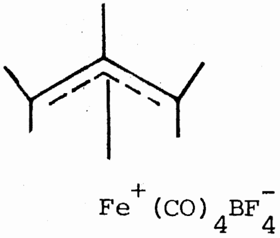


5

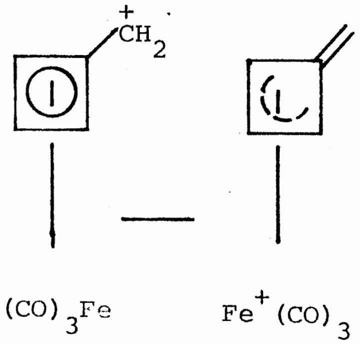
Π-ALLYL COMPLEXES:



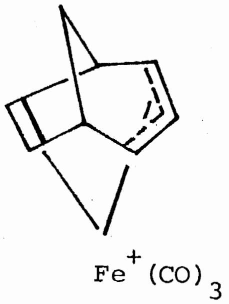
6a: R=H
6b: $R=CH_3$



7



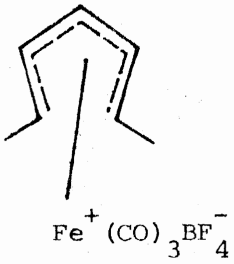
8



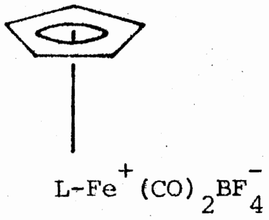
9

Figure 1. Examples of Isolable Organic and π-Complexed Organometallic Cations

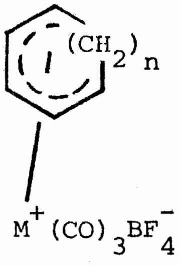
DIENYL COMPLEXES:



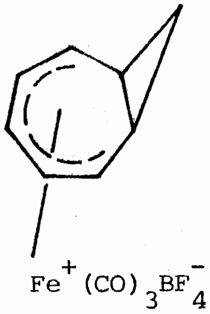
10



11a: L=CO
11b: L=Olefin

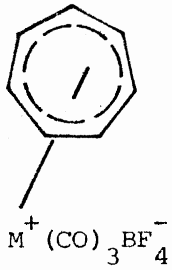


12a: n=1; M=Fe
12b: n=1; M=Ru
12c: n=1; M=Os
13 : n=2; M=Fe
14 : n=3; M=Fe

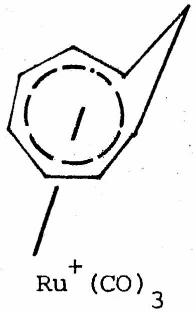


15

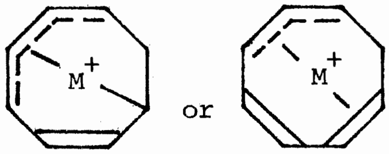
TRIENYL COMPLEXES:



16 : M=Fe
17a: M=Cr
17b: M=Mo
17c: M=W



18



19: M=Fe(CO)$_3$

Figure 1. (Continued)

that several transient carbonium ions when complexed to a transition metal atom, can be isolated as stable crystalline salts of complex anions such as BF_4^-, ClO_4^-, BPh_4^- and Br_3^-.

Cationic transition metal π-complexes can be conveniently classified based on the coordinated organic ligand. Examples of some π-allyl, dienyl and trienyl complexes are given in Figure 1. Several such organometallic cations in which an organic moiety is coordinated to a transition metal carbonyl group and the entire molecule bears at least one unit of positive charge, have been isolated and studied over the past twenty five years. This area of organometallic chemistry has been reviewed recently.[7]

Nature of Bonding

With few exceptions (e.g. 6) (Figure 1), in all the cationic transition metal π-complexes the metal atom has the electronic configuration of the following inert gas as predicted by the EAN (Effective Atomic Number) rule.[8] The nature of bonding in the cationic π-complexes has been interpreted qualitatively in terms of the Dewar-Chatt description of the bonding in olefin-metal complexes which involves two types of orbital interactions.[9] One type consists of the interaction of filled π-orbitals of the unsaturated carbocation system with the vacant orbitals of appropriate symmetry on the metal ("forward coordination"). The second type which is especially prominent in these complexes consists of the interaction between filled atomic orbitals on the metal and the low-lying vacant molecular orbitals of the conjugated organic moiety ("back-donation" or "back-bonding"). Since all conjugated organic cations have relatively low-lying vacant molecular orbitals associated with the π-orbital framework, back-bonding is easily achieved in cationic π-complexes. The back-donation also reduces the build up of excessive electron density on the metal due to forward coordination.

The ability of a metal to share electrons with a coordinated ligand depends not only on the metal but also on the charge on the metal. Decreased positive charge on the metal increases the back-donation phenomenon and conversely. Thus many of the thermodynamically stable cationic π-complexes involve metals in low oxidation states.

Due to the orbital interactions described above, the positive charge in a cationic π-enyl transition metal carbonyl complex is extensively delocalized over the entire molecule, which accounts for the extraordinary stability of such a complex compared to the free carbonium ion. Hence, the actual structure of a π-complexed cationic metal carbonyl is a hybrid of several resonance structures wherein the positive charge is localized on the coordinated organic ligand, the metal or a carbon monoxide moiety. This is illustrated below with (cyclohexadienyl)irontricarbonyl cation <u>12a</u> as the typical example (Figure 2).

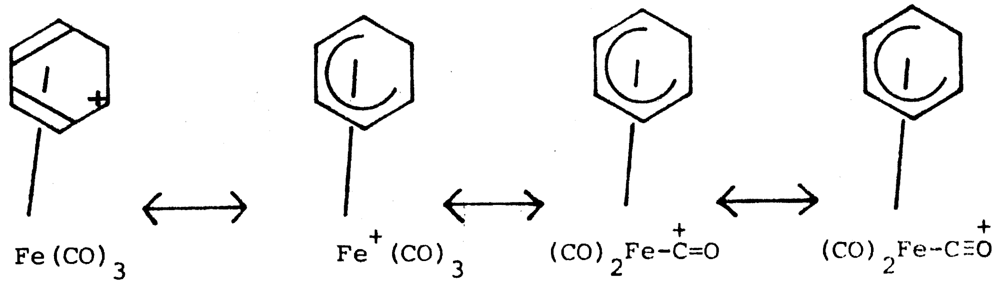


Figure 2. Resonance in <u>12a</u>

Extended Hückel calculations involving 12a indicate that the total charge on the pentadienylcarbon segment of $(C_6H_7)^+$ decreases ten-fold upon complexation to a $Fe(CO)_3$ moiety.[10] INDO calculations involving $[(C_6H_7)Fe(CO)_3]^+$ (12a) and $[(C_7H_7)Cr(CO)_3]^+$ (17a) suggest that complexation of cyclohexadienyl and tropylium carbocations to $M(CO)_3$ (M=Fe and Cr respectively) results in an increase of bond-index values for the ring.[11] As a consequence, the organic cations are less electrophilic in the complexed state than in the free ionic state.

Reactions With Nucleophiles

Although complexation to a metal species modifies the chemical properties of the organic cation, many such complexes, nonetheless, still behave like carbonium ions towards nucleophiles with nucleophilic attack occurring at a carbon of the organic ligand (Figure 3). However, as suggested by the resonance structures 20b and 20c (Figure 3) in which the positive charge is localized on the metal or the carbonyl carbon, nucleophilic attack at these sites can also be observed.

The π-system in cyclic (dienyl)irontricarbonyl complexes is generally less susceptible to nucleophilic addition than in the acyclic analogues.[12-14] For example, cationic irontricarbonyl complexes of cyclopentadienyl, cyclohexadienyl and cycloheptadienyl cations, 11a, 12a and 13, respectively (Figure 1), fail to react with water at pH 7 whereas the acyclic pentadienyl complexes, e.g., 10 (Figure 1) react readily at ca pH 3. These results were viewed as an indication of the greater positive charge on the metal in the cyclic complexes than in the acyclic analogues.

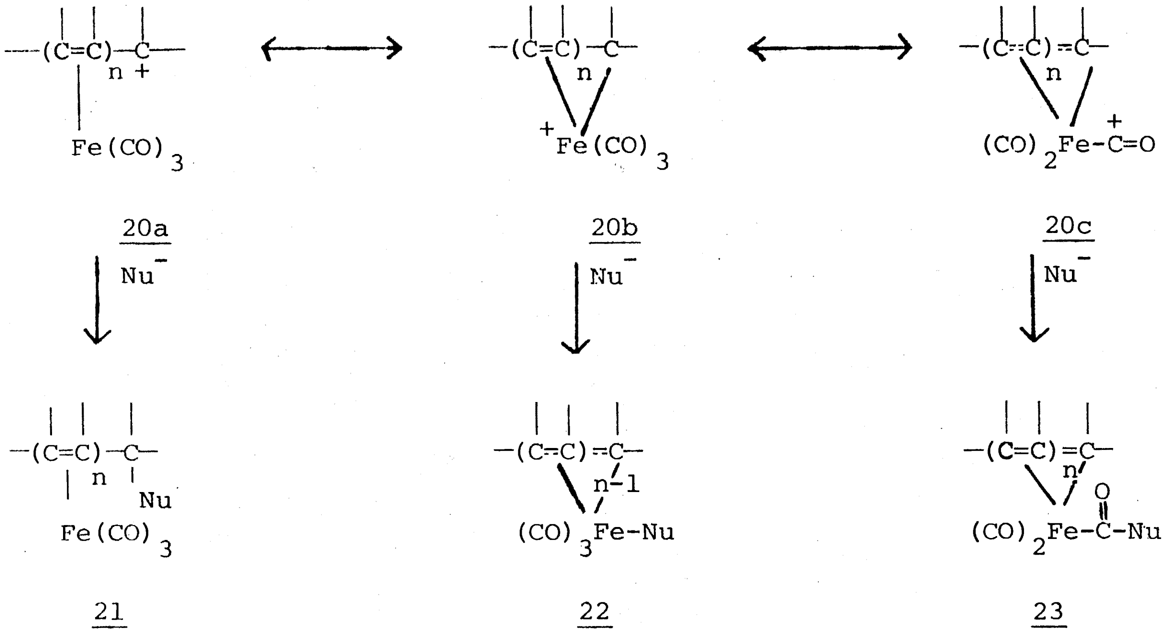
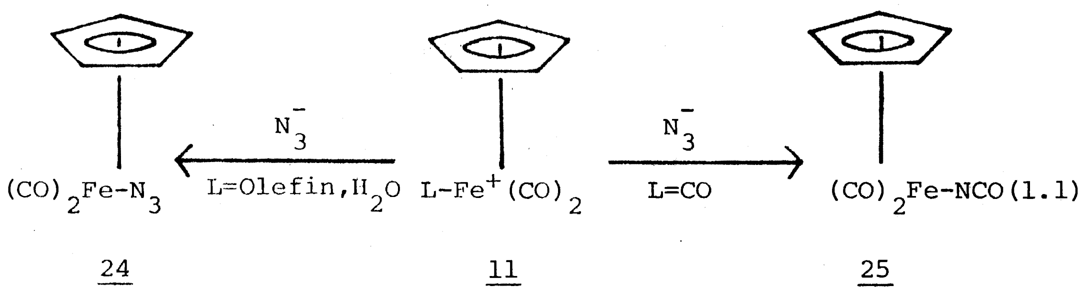
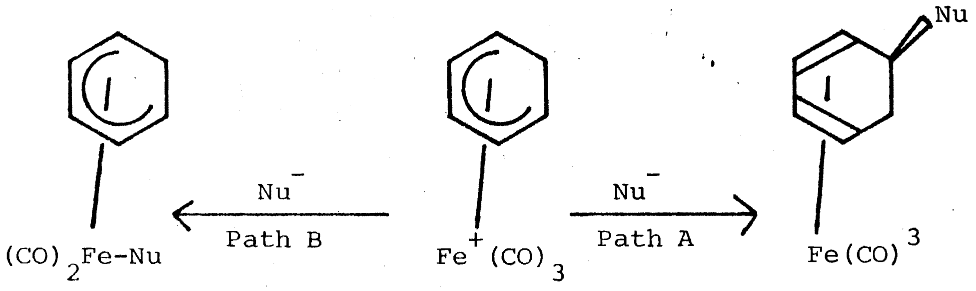


Figure 3. Modes of Addition of Anions to a (π-Enyl)irontricarbonyl Cation (n=2)

With cyclic π-enyl complexes, the ring size of the coordinated organic ligand seems to play an important role in determining the site of nuclophilic attack. For example, the cyclopentadienyl complexes 11a and 11b (Figure 1) react with nuclophiles at the metal and the carbonyl carbon respectively (Equation 1.1); rarely is ring addition observed.[15-18]

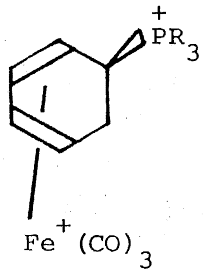


However, with increase in ring size nucleophilic addition to the ring predominates. For instance, (cyclohexadienyl)irontricarbonyl cation 12a upon reaction with neutral or anionic nuclophiles, e.g., alkoxides,[19,20] zinc and cadmium organics[21], ketones,[22,23] amines[22,24] and aromatic[25-27] or heterocyclic compounds,[28,29] gives 5-substituted cyclic 1,3-dienyl irontricarbonyl complexes (e.g., 26) (Path A; Equation 1.2). The substituent is invariably found to be in the *exo*-position on the ring relative to the $Fe(CO)_3$ moiety. Tertiary phosphines add to the ring to give ionic 1:1 phosphonium species (e.g., 27).[30] Interestingly, in contrast to the aforementioned nucleophiles, halide ions give predominantly metal substituted products[19,31] (e.g., 28) (Path B; Equation 1.2).

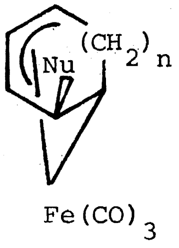


(1.2)

28 12a 26



27



29

Similar chemistry has been observed for the cycloheptadienyl,[19,32] and cyclooctadienyl[33] irontricarbonyl complexes 13 and 14a. A tendency towards the formation of σ, η^3-allyl products (e.g., 29) in addition to the 1,3-diene complexes is observed with increase in ring size.[34,35]

Very little is known about nucleophilic additions to the (tropylium)irontricarbonyl cation 16. However, addition of nucleophiles (e.g., H^-, HS^- and CH_3O^-) to tropylium tricarbonyl complexes of Group VI metals, viz., Cr, Mo and W (17a-c) (Figure 1) yields the ring-substituted complexes[36-42] 33 (Figure 4). On the other hand, reductive dimerization[43] to 30 and 31, ring contraction[44] to the (benzene)tricarbonyl complex 32 or ring displacement[45] can be competing side reactions with certain nucleophiles (Figure 4).

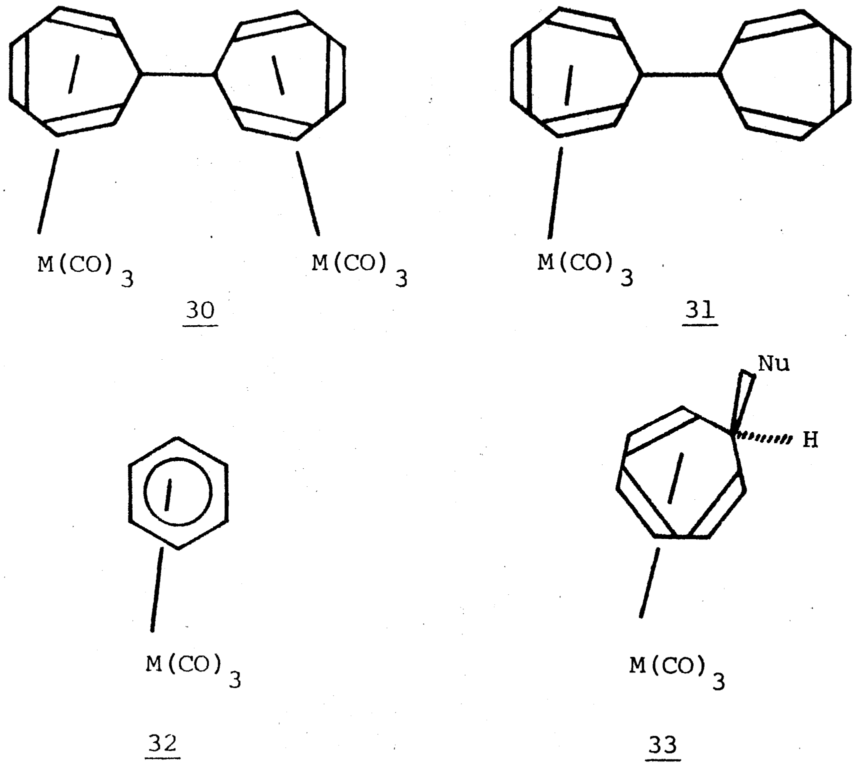
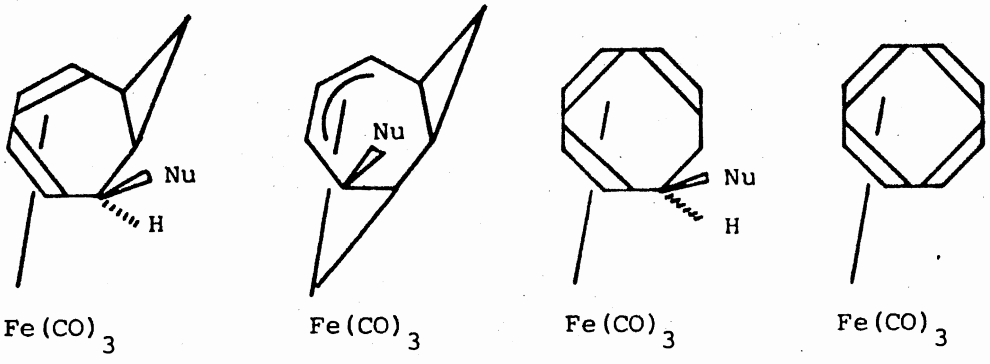


Figure 4. Products From the Nucleophilic Additions to $[(C_7H_7)$-$M(CO)_3]^+$ (M=Cr, Mo, W)

The bicyclo[5.1.0]octatrienyl irontricarbonyl cation 15 reacts with nuclophiles to give the expected *exo*-substituted diene 34 and the σ, η^3-allyl 35 complexes as well as the products with ring opening 36 and 37[46-49] (Figure 5).



34 35 36 37

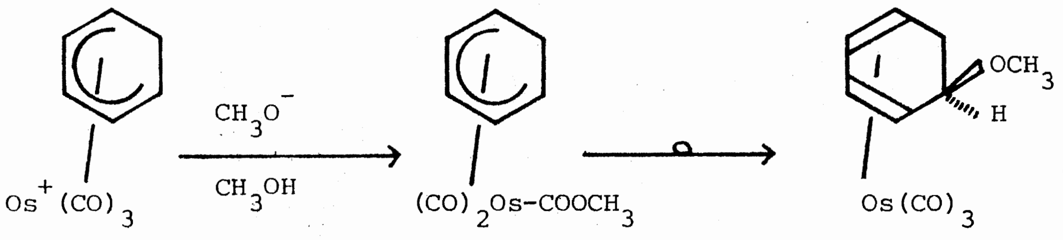
Figure 5. Products From the Nucleophilic Additions to the Bicyclic Cation 15

The Mechanism of Ring-Substitution

With Anionic Nucleophiles

The frequently observed, stereospecific *exo*-addition of both anionic and neutral nucleophiles to cationic π-complexes is generally rationalized in terms of direct attack by the nucleophile on the ring from the *exo*-side, the side remote from the M(CO$_3$) moiety. Recent studies suggest that the nucleophile may initially attack the metal or a carbonyl carbon forming an intermediate which then yields the observed ring-substituted product.

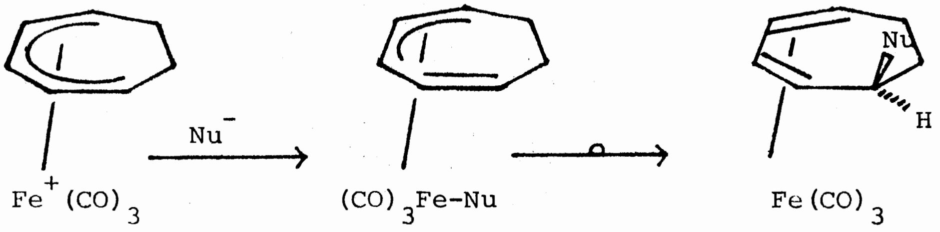
For instance, addition of methoxide ion to the (cyclohexadienyl)-osmiumtricarbonyl cation 12c led to the isolation of the organometallic carbomethoxy ester 38 which in organic solvents or even in the solid state could be transformed into (*exo*-5-methoxy-1,3-cyclohexadiene)-osmiumtricarbonyl (39) exclusively[50] (Equation 1.3).



12c 38 39

(1.3)

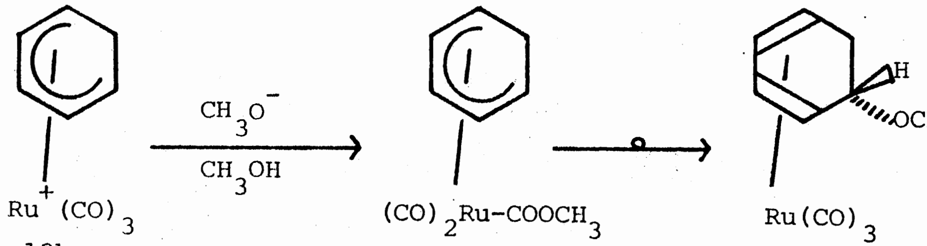
Addition of either N_3^-, $C_2H_5O^-$ or $P(n\text{-}Bu)_3$ to the (cycloheptadienyl)irontricarbonyl cation 13 is claimed to proceed through initial attack at the metal leading to the intermediate complex 40 which then yields the *exo*-substituted cycloheptadiene complex 41[51] (Equation 1.4).



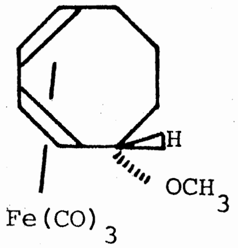
13 40 41

(1.4)

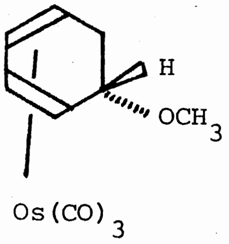
On the other hand, intermediate complexes formed by addition of the nucleophile to the carbonyl carbon or the metal can also yield the *endo*-substituted complexes. For instance, addition of methoxide ion to the (cyclohexadienyl)rutheniumtricarbonyl cation 12b led to the isolation of the carbomethoxy ester complex 42 which purportedly rearranged to the *endo*-substituted complex 43 (Equation 1.5).[52] Similar rationalization has been suggested for the formation of the *endo*-substituted product (44) in the reaction of methoxide ion with the (cyclooctadienyl)-irontricarbonyl cation 14a.[33]



12b 42 43 (1.5)



44



45

Interestingly, formation of (endo-5-methoxy-1,3-cyclohexadiene)osmiumtricarbonyl (45) from the reaction between methanol and (cyclohexadienyl)osmiumtricarbonyl cation was postulated as proceeding through nucleophilic attack at the metal.[50]

With Neutral Molecules

Kinetic study of the reaction of several β-diketones with cyclic dienyl complexes[23] indicates a two-step mechanism as shown below:

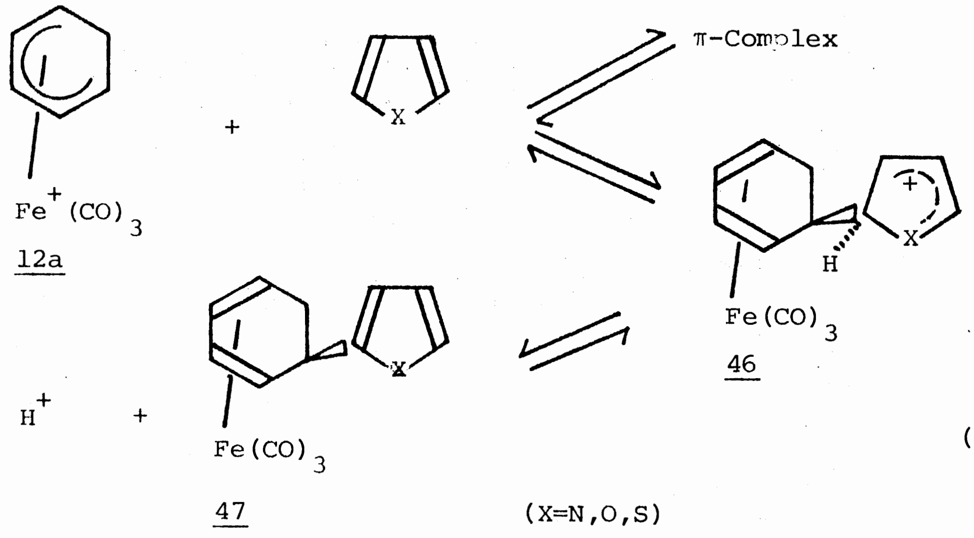
$$HB \rightleftharpoons H^+ + B^-$$

$$B^- + H^+ + RBF_4 \xrightarrow{slow} R\text{-}B + HBF_4 \qquad (1.6)$$

(BH = β-diketone; RBF_4 = Dienyl complex)

The first step involves a pre-equilibrium reaction generating a reactive carbanion B^-, which reacts with the dienyl complex to give the ring-substituted product with exo-stereochemistry. The order of reactivity was found to be: $[(C_6H_7)Os(CO)_3]^+ \sim [(C_6H_7)Fe(CO)_3]^+ > [(C_6H_7)Fe(CO)_2PPh_3]^+ > [(C_7H_9)Fe(CO)_3]^+ > [(C_6H_6(OMe))Fe(CO)_3]^+ >>> (C_7H_9)Fe(CO)_2I$, $(C_7H_9)Fe(CO)_2CN$, $[C_6H_6(OMe)]Fe(CO)_2I$. The similar rate constants for the (cyclohexadienyl)tricarbonyl complexes of iron and osmium 12a and 12c respectively, do not support the involvement of the metal in the rate-determining step; hence, the kinetic results were readily rationalized in terms of direct attack of the intermediate anion upon the organic moiety.

The reactions of the (cyclohexadienyl)irontricarbonyl cation 12a with heterocyclic aromatic molecules such as pyrrole, indole, furan and thiophene and activated aromatic molecules such as 1,3,5-trimethoxybenzene and 1,3-dimethoxybenzene yielded ring substituted complexes and were interpreted as electrophilic aromatic substitution by the cyclohexadienyl ring upon the aromatic molecule[53] (Equation 1.7). The high degree of positional selectivity observed with various aromatic substrates was explained by the reactivity-selectivity principle; since the cationic dienyl complex 12a is a relatively weak nucleophile, it is expected to be more selective.

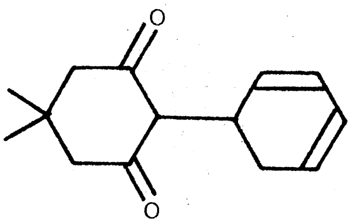


(1.7)

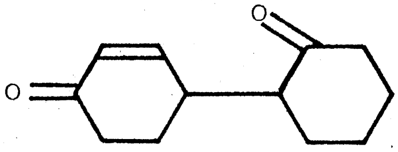
The formation of ring-substituted products in the reactions of cationic π-enyl metal carbonyl complexes through initial nucleophilic attack at either the ring, the metal, or the carbonyl carbon indicate the complexity of the mechanism of the reaction. Interestingly, INDO calculations involving the (cyclohexadienyl)irontricarbonyl cation 12a suggest that no correlation exists between the magnitudes of the positive charges on the dienyl carbon atoms and the site of nucleophilic attack.[11] The charge data would predict the site preference C(2) > C(3) > C(1), whereas the nucleophiles are known to add to 12a exclusively at C-1. The correlation of the site of attack on the ring with bond-index values suggest that the nucleophilic addition reactions involve early transition states. An ion-pair has been suggested as the possible early transition state for the addition of anionic nucleophiles to 12a. Other molecular orbital calculations involving $[(\text{cyclopentadienyl})\text{Fe(CO)}_3]^+$ (11b), $[(\text{cyclohexadienyl})\text{Fe(CO)}_3]^+$ (12a) and $[(\text{cycloheptadienyl})\text{Fe(CO)}_3]^+$ (13) suggest that nuclophilic attack in the series is likely to involve initial attack at the metal.[54]

Synthetic Potential

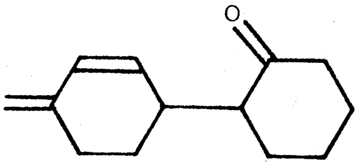
Although the mechanism(s) of the reactions between π-enyl metal carbonyl complexes and nucleophiles are not well understood, the synthetic potential of the reaction has nevertheless been shown to be extremely promising. The predominant ring-addition of nucleophiles to dienyl iron-carbonyl cationic complexes, coupled with the ease of oxidative removal of the metal from the products constitutes a novel, simple synthetic route to substituted dienes. For example, this approach is extremely useful in the preparation of cyclohexadiene and cyclohexene derivatives (e.g., 48-52)[21,22,23,27,55-58], as well as cycloheptadiene derivatives (e.g., 53)[32]. Organic molecules which could not be conveniently prepared through conventional synthetic routes, such as the homotropone 54,[46] and the substituted bicyclic derivatives of cyclooctatriene (e.g., 55)[46,47,59,60] have been made using this method. Recently the synthetic utility of the (cyclohexadienyl)irontricarbonyl cation 12a has also been extended to natural product chemistry.[29]



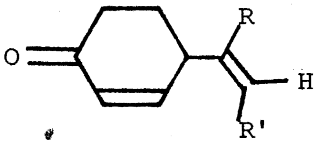
48



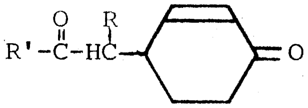
49

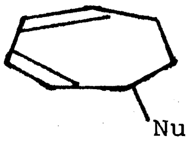


50

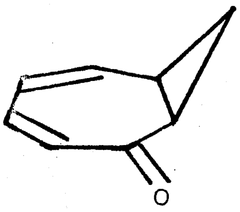


51

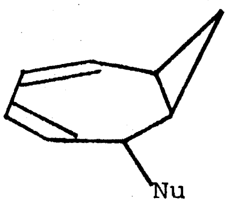




53



54



55

CHAPTER II

STATEMENT OF THE PROBLEM

Cationic transition metal π-complexes constitute a very important class of organometallic compounds of great interest to chemists. Such complexes represent the achievements of the recent exploratory research towards stabilizing highly reactive, and often transient, carbocations which have been either postulated, and/or predicted, to be common reaction intermediates. Very often carbonium ions π-complexed to metal carbonyl moieties retain their characteristic electrophilic properties, a fact which makes organometallic π-complexed cations synthetically, as well as theoretically appealing. Although a wide variety of nucleophiles have been reacted with (π-enyl)irontricarbonyl complexes, relatively few attempts have been made to understand some of the basic features of the reactions, a few of which are listed below:

1. The effect of ring-size.
2. Role of the metal.
3. Fate of nucleophilic additions to the metal, the carbonyl carbon and the organic ligand.
4. Mechanism of ring substitution.
5. The differences in the nucleophilic behavior of anionic versus neutral nucleophiles towards π-enyl cationic complexes.
6. The correlation of inherent, interdependent properties of the nucleophile (e.g., softness or hardness, polarizability,

basicity, nucleophilicity and solubility with the site of nucleophilic attack.

7. The reductive coupling reactions observed with certain nucleophiles and π-enyl complexes.

In view of the preceding, reactions of selected nucleophiles with cationic π-enyl ironcarbonyl complexes were proposed to provide a better insight into some of the above relatively less understood features of the reactions; the investigation of such reactions constitutes the content of this thesis. Additionally, coupled with these studies, the design and exploration of novel nucleophiles, which upon reaction with transition metal π-complexed cations would lead to exclusive addition to the organic moiety, were also to be pursued.

CHAPTER III

RESULTS AND DISCUSSION

Reactions of Azide Ion With Cationic π-Enyl Irontricarbonyl Complexes

The effect of the ring-size upon the electrophilicities of various sites in the cationic complex was to be evaluated by examining the reactions of a series of cyclic π-enyl irontricarbonyl complexes with a chosen common nucleophile under similar experimental conditions. Azide ion was chosen as the common nucleophile to differentiate the relative electrophilicities of various sites in a series of cationic π-enyl irontricarbonyl complexes for the following reasons:

1. The azide ion is classified as a borderline base according to HSAB (Hard-Soft Acid-Base) theory.[61]

2. The reactions of azide ion with (dienyl)irontricarbonyl complexes are known to yield a variety of products, which were rationalized in terms of nucleophilic reactions at the metal, the carbonyl carbon and the organic ligand. It was deemed important to determine whether the suggested mechanism[51] involving initial nucleophilic attack at the metal prior to the formation of ring substituted *exo*-complex is general (Equation 1.4).

3. The ring-substituted azidodiene irontricarbonyl complexes which might be obtained in the proposed reactions are potential precur-

sors to novel, heterocyclic transition metal π-complexes.

The series of the π-complexed irontricarbonyl cations to be reacted with azide ion included the following complexes in which the organic ring was varied but the rest of the molecule kept constant: $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ (<u>12a</u>), $[(\eta^5\text{-}C_7H_9)Fe(CO)_3]BF_4$ (<u>13</u>), $[(\eta^5\text{-}C_7H_7)Fe(CO)_3]BF_4$ (<u>16</u>) and bicyclic $[(\eta^5\text{-}C_8H_9)Fe(CO)_3]BF_4$ (<u>15</u>).

In addition to the aforementioned series of complexes, azide ion was also to be allowed to react with (tropylium)tricarbonyl complex of molybdenum (a second row, group VI transition metal) (<u>17b</u>) in order to evaluate the influence of the metal upon the site of nucleophilic attack in the π-complexed cations.

Choice of Solvent

The choice of the solvent for the reactions between a π-complexed cation and a nucleophile is limited not only by the solubility of both the reactants in the chosen solvent, but also by the stability of the cationic complex in the chosen solvent. In general, cationic complexes are sparingly soluble in alcohols, dichloromethane and tetrahydrofuran, but are highly soluble in acetone, nitromethane, acetonitrile, and water. However, complexes such as $[(C_7H_7)Fe(CO)_3]BF_4$ (<u>16</u>)[62], acyclic (pentadienyl)irontricarbonyl complexes,[12] e.g., <u>10</u>, and (π-allyl)irontricarbonyl complexes,[63] e.g., <u>6</u>, are known to react with water to give alcohols and ketones. Acetonitrile is known to react with $[(C_7H_7)Mo(CO)_3]BF_4$ (<u>17b</u>) at the metal by ring displacement.[45] However, the π-enyl complexes used in this study have not been reported to react with acetone under ambient conditions. Sodium azide is sparingly soluble in dry acetone; however, small amounts of moisture (<u>ca</u>. 0.5%)

present in the commercially available reagent-grade acetone increases its solubility. Thus in the current study acetone was chosen as the solvent for the proposed additions of the azide ion to the cationic π-enyl metal carbonyl complexes.

Reaction With (Cyclohexadienyl)irontricarbonyl Cation 12a

The reaction of the cyclohexadienyl complex 12a with sodium azide in acetone led to an immediate color change from dark yellow to pale yellow and within two hours the reaction mixture turned red. IR spectra taken at regular intervals during the reaction showed the gradual disappearance of the peaks at 2110 and 2060 cm^{-1} with the concomitant appearance of new peaks at 2085 ($C-N_3$ asym. stretch), 2045 and 1985 cm^{-1}. However, no additional changes in the IR spectra were observed either during or after the formation of the red color. With longer reaction times, the red color was replaced by a dark brown color accompanied by the deposition of a rust-brown solid, suggestive of the formation of iron oxides as decomposition products. When the progress of the reaction was monitored by TLC, only one component (R_f 0.63) was observed prior to the formation of the red color, whereas during the red color formation, another component with a R_f value .90 was observed. TLC analysis, of the reaction mixture after the red color has been replaced by extensive decomposition indicated the presence of only the initial component.

Upon work-up and product analysis either before or several hours after the red color formation, two products were isolated. The major product (~ 90%) was identified to be (exo-5-azidocyclohexa-1,3-diene)-

irontricarbonyl (56). The minor product, formed only in trace amounts, was identified as 2-hydroxy-2-methyl-4-pentanone (57). The sterochemistry of the azide moiety on the ring in 56 was assigned by analyzing the ^{1}H-NMR spectrum. Facile abstraction of the azide group from the complex by the trityl cation 1 also confirmed the stereochemistry of the azide group on the ring (Figure 6).

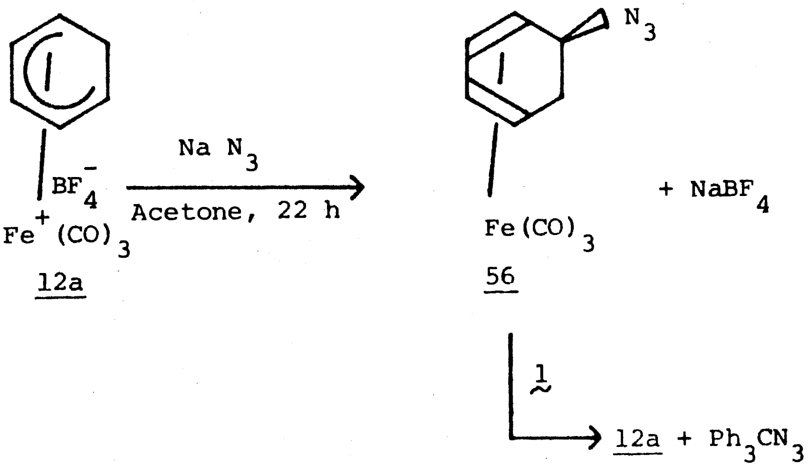
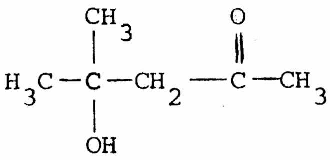


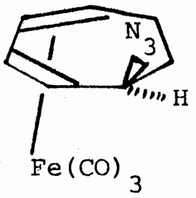
Figure 6. Addition of Azide Ion to 12a and Abstraction of Azide Ion From 56 With $(Ph_3C)BF_4$ (1)

The color changes and the infrared spectral changes observed during the progress of the reaction are in striking contrast to those reported for the reaction between $[(C_7H_9)Fe(CO)_3]BF_4$ (13) and sodium azide in dichloromethane[50] (Equation 1.4). In the latter reaction, upon mixing the reactants a red color formed immediately which was accompanied by the rapid growth of IR absorption at 2033 cm^{-1} followed by the slow appearance of another band at 2085 cm^{-1} at the expense of the band at 2033 cm^{-1}. Upon work-up, only (exo-5-azidocyclohepta-1,3-diene)irontricarbonyl (58) was obtained. The red color was attributed to the formation of metal-substituted azido complex 59 and the IR bands at 2033 and 2085 cm^{-1} were attributed to asymmetric stretching frequencies of an azide group bonded to the iron atom and the ring, respectively. It was concluded that the azide ion initially adds to the metal to give the (π-allyl)azidoirontricarbonyl complex 59 which then rearranges to the observed ring substituted product 58.

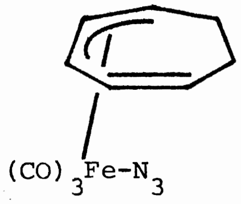


$$H_3C-\underset{OH}{\overset{CH_3}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

57



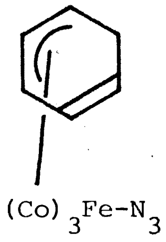
58



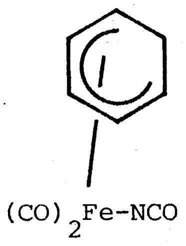
59

Although the immediate appearance of an IR band at 2085 cm^{-1} in the reaction between $[(C_6H_7)Fe(CO)_3]BF_4$ (12a) and sodium azide suggests the formation of a $C-N_3$ bond upon mixing the reactants, the red color formed during the progress of the reaction is puzzling.

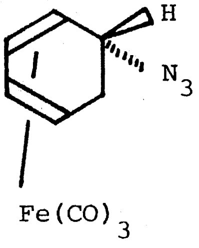
When the reaction between 12a and sodium azide was carried out in acetone which had been dried over anhydrous potassium carbonate for several days, a complicated mixture of products was obtained. Spectral analysis of the product mixture and partially separated fractions suggested that in addition to the exo-azido complex 56 and the ketone 57 at least three more organometallic complexes were present in the product mixture. Attempts to separate the product mixture completely into its components by chromatographic techniques and fractional crystallization techniques were futile. The IR spectra of the unidentified components of the product mixture suggested the structures of the metal-substituted azido complex 60, the isocyanate complex 61 and the ring-substituted endo- complex 62 (see experimental).



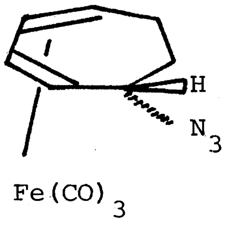
60



61



62



63

The color changes observed when the reaction was carried out in dry acetone were somewhat irreproducible. The red color was invariably observed although sometimes it was replaced by a light yellow color, at other times by a dark brown color indicative of the iron oxides. The red color persisted longer under anhydrous conditions but dissipated quickly upon addition of water to the reaction mixture. The yield of the ring-substituted exo-azido complex 56 was less under anhydrous conditions (ca. 40-60%), with the other complexes being formed in larger amounts. Thus it appears that the reaction is extremely sensitive to the presence of trace amounts water present in the solvent.

Solvent dependence of the reaction between sodium azide and (cyclohexadienyl)irontricarbonyl cation 12a was discovered when the reaction was performed in dichloromethane; the reaction mixture remained yellow throughout the reaction period and (exo-5-azidocyclohexa-1,3-diene)irontricarbonyl (56) was the only observed product.

Reaction With (Cycloheptadienyl)irontricarbonyl Cation 13

The reaction between (cycloheptadienyl)irontricarbonyl cation 13 and sodium azide in reagent grade acetone led to the same IR spectral changes and color changes as those observed in the reaction of (cyclohexadienyl)irontricarbonyl cation 12a with sodium azide in acetone. The IR absorption at 2033 cm^{-1}, in coincidence with the red color formation observed for the same reaction in dichloromethane,[51] could not be detected in the present case, as the peaks at 2085, 2040 and 1980 cm^{-1} were very strong and overlapping. Monitoring the progress of the reaction by TLC indicated that a minimum of three products were present at all times, although in varying amounts. Analysis of the product mixture suggested (*exo*-5-azidocyclohepta-1,3-diene)irontricarbonyl (58) to be the major product and one of the possibly three minor components was identified as 2-methyl-2-hydroxy-4-pentanone (57). The other minor components were unstable and decomposed even at 0^oC. ^1H-NMR and ^{13}C-NMR spectra of the minor components suggests the presence of the metal-substituted azido complex 59 and the ring-substituted azido complex 63.

If the reaction between (cycloheptadienyl)irontricarbonyl cation 13 and sodium azide were to proceed through initial nuclophilic addition at the metal prior to the formation of the ring-substituted *exo*-azido complex 58 as reported previously, only one product is expected to be formed in the initial stages of the reaction; two during the progress of the reaction and one at the end of the reaction. Presence of at least three components at all times during the progress of the reaction as seen from TLC analysis suggests competitive nucleophilic addition at more than one site on the cationic complex 13. It was not clear whether the contradiction of our results with those reported[51] for the same reaction in dichloromethane was due to different reaction mechanisms operating in two different solvents or due to the misinterpretation of the data in the literature. Interestingly, reinvestigation of the reaction between (cycloheptadienyl)tricarbonyliron cation 13 and sodium azide in dichloromethane, in our hands, yielded neither the red color formation nor the IR spectral changes as reported. Additionally, workup of the reaction after the specified reaction time (30 min) resulted in the recovery of the unchanged cationic complex 13 in excess of 90% yield.

Reaction With (Tropylium)tricarbonyliron Tetrafluroborate (16)

Tropylium metal carbonyl complexes are of special interest because they involve the complexation of an organic cation, which is extremely stable in the uncomplexed state due to the extra stabilization achieved by the aromatic π-electron system. In the complexed and uncomplexed tropylium ion, the chemical shift equivalence of all the protons in $(C_7H_7)^+$ is observed at room temperature.[62] The single absorption in the ^{1}H-NMR spectra of $(C_7H_7)BF_4$ (4), $(\eta^5\text{-}C_7H_7)Fe(CO)_3\ BF_4$ (16) and $(\eta^7\text{-}C_7H_7)M(CO)_3\ BF_4$ (17a-c) (M=Cr, Mo, W) has been interpreted in terms of resonance for 4 and 17 and in terms of valence-tautomerism and fluxional behavior of the $Fe(CO)_3$ moiety for 16[62] (Figure 7).

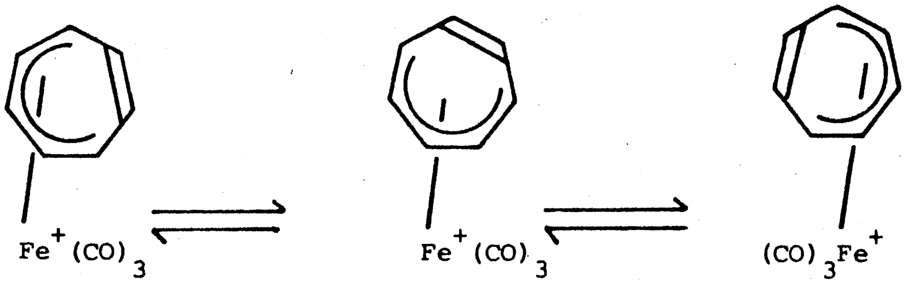


Figure 7. Valence-Tautomerism ("Ring-Whizzing") in 16

Although a great deal of information is available regarding the behavior of tropylium tricarbonyl complexes of Cr, Mo and W, 17a, b and c, respectively, towards nucleophiles, the behavior of $[(\eta^5\text{-}C_7H_7)Fe(CO)_3]BF_4$ (16) towards nucleophiles other than water is unknown. It seems that the difficulties encountered in the preparation of (tropylium)tricarbonyliron tetrafluoroborate (16) are partially responsible for such lack of knowledge. Previous experiments suggest that addition to the ring in the (tropylium)tricarbonyl complexes of group VI transition metals (Cr, Mo, W), 17a-c, is possible only with hard bases whereas soft bases preferentially attack the metal leading to CO substitution.[42]

In view of the classification of azide ion as a borderline base, the addition of azide ion to the (tropylium)tricarbonyl complexes of iron and molybdenum, 16 and 17b, respectively, is of special importance in correlating the effects of complexation of a π-enyl carbonium ion to different transition metals with the properties of the transition metal. The transition metal complexes of 7-azidocycloheptatriene are also of special interest in view of the ionization tendencies of the free ligand 64 in the polar solvents acetone, dimethylcarbonate, dioxane, acetonitrile, methanol and liquid SO_2.[64] (See Figure 8).

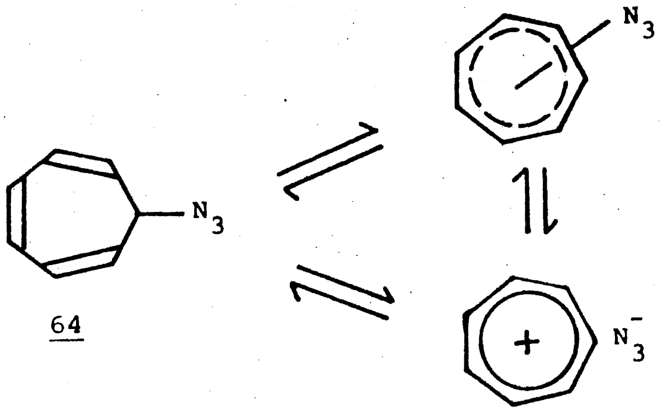
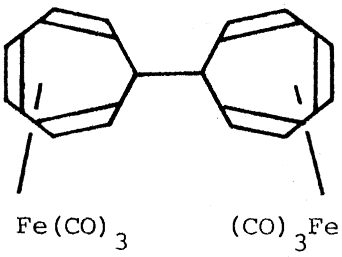
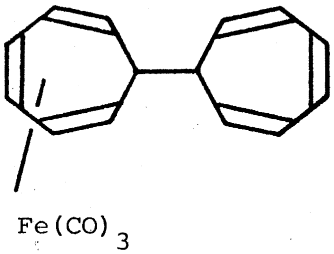


Figure 8. Topomerization and Ionization in Tropylazide

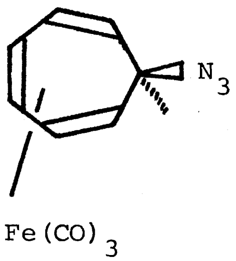
When $(C_7H_7)Fe(CO)_3BF_4$ and NaN_3 were allowed to react in reagent-grade acetone, formation of neutral irontricarbonyl complexes were observed by IR. However, no IR absorption at 2085 cm^{-1} suggestive of the formation of a $C\text{-}N_3$ bond could be detected. Analysis of ^1H-NMR spectrum of the mixture suggested the presence of the dimers 65 and 66 in addition to some unidentified products. When a blank reaction was run with the cationic complex 16 and acetone, similar neutral products were obtained. It was clear that conversion of (tropylium)irontricarbonyl complex 16 to neutral products by dissolution in acetone prohibits the use of acetone as the solvent for nucleophilic additions to 16. When the reaction between 16 and sodium azide was conducted in anhydrous tetrahydrofuran, gradual appearance of IR absorption bands at 2085, 2045 and 1985 cm^{-1} and an accompanying color change from bright yellow to pale yellow were observed. Upon workup (*exo*-7-azidocycloheptatriene)-irontricarbonyl (67) was obtained exclusively. The assigned stereochemistry of the azide moiety at C-7 in 67 was suggested by the ^1H-NMR spectrum of the complex and also by the facile abstraction of the azide ion from 67 by trityl cation 1.



65



66



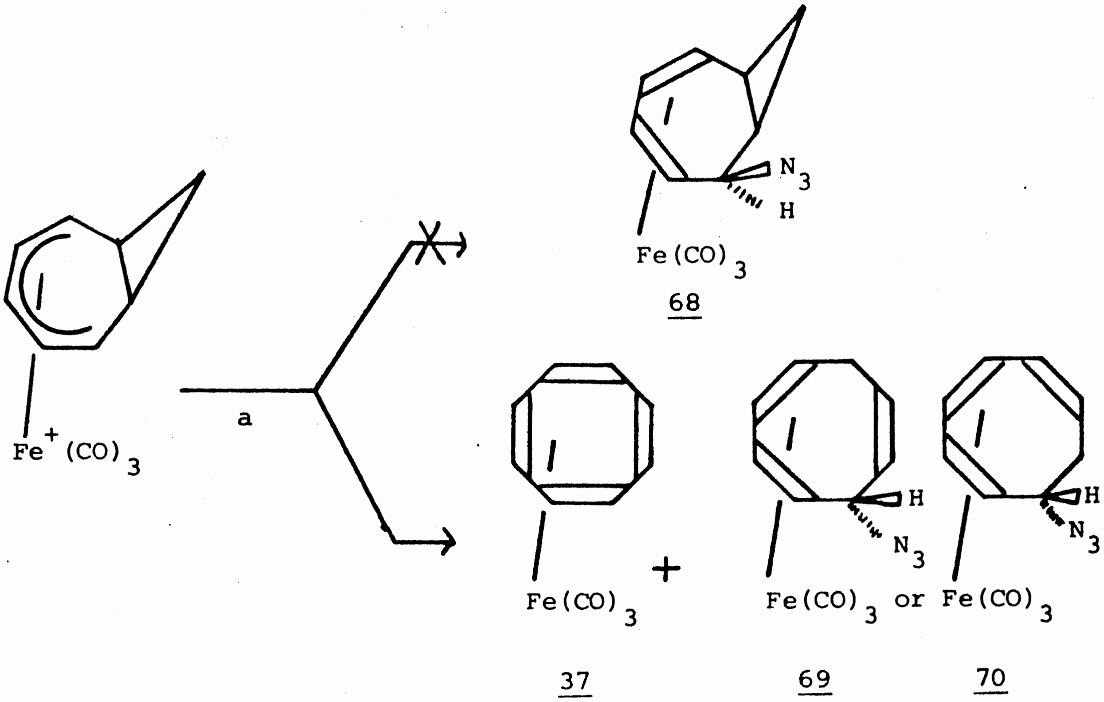
67

Neither color changes nor IR spectral changes during the course of the reaction suggested addition of the azide ion at the metal or the carbonyl carbon. ^1H-NMR spectrum of the crude reaction product indicated the presence of only the ring-substituted complex 67. Thus direct addition of the nucleophile to the ring is favored.

The proton nmr spectrum of the azido complex 67 in $DCCl_3$ is extremely well resolved in contrast to the extensive line broadening observed at room temperature in the same solvent for the free ligand, tropyl azide (64).[64] The ^1H-NMR spectra of the complex 67 in acetone and acetone-D_2O were very similar to that in $DCCl_3$ but for minor solvent shifts. A variable temperature study of the proton nmr spectra in acetone-d_6 at temperatures up to 50°C did not produce line broadening or coalescence of the signals for the ring protons. At ca. 50°C, loss of spectral resolution due to the paramagnetic matter from the decomposition of the complex took place. Interestingly, the ^1H-NMR spectrum of tropyl azide (64) in acetone and acetone-D_2O at 30°C consisted of only a singlet, attributed to the fast topomerization of the azido group causing the chemical equivalence of the ring protons.[64a] In view of the preceeding, clearly, the rate of azide migration leading to the coalescence of ring protons observed for tropyl azide has decreased tremendously upon complexation to the $Fe(CO)_3$ moiety. Such dramatic decrease of the rate of azide migration in (exo-7-azidocycloheptatriene)-irontricarbonyl (67) compared to that in the free ligand 64 may be due to either the non-planarity of the ring in the complexed state or the disruption of the conjugation of the triene system upon complexation.

Reaction With (Bicyclo[5.1.0]octatrienyliron-tricarbonyl Cation 15

Addition of sodium azide to (bicyclo[5.1.0]octatrienyl)irontricarbonyl cation 15 in acetone at room temperature, surprisingly, did not yield the expected bicyclic azido complex 68; instead, (cyclooctatetraene)irontricarbonyl (37) was isolated as the major product. One minor product was detected spectroscopically in the product mixture. Spectral analysis suggested that the minor product is an irontricarbonyl complex of azido-substituted cyclooctatriene; proton and coupled and partially decoupled off-resonance carbon-13 spectra suggested *endo*-substitution on the ring as in 69 and 70. Due to the extremely small amounts of the minor product, coupled with the extreme difficulties encountered in separating it from $(C_8H_8)Fe(CO)_3$ (37) by column chromatography, fractional recrystallization or sublimation, a thorough structural and elemental analysis of the minor product has not been achieved. Formation of only the monocyclic complexes to the exclusion of the ring-substituted bicyclic azido complex 68 was also observed when the reaction was conducted in other solvents such as dichloromethane and THF (Figure 9).



^{a}Sodium azide, acetone, dichloromethane or THF

Figure 9. Reaction of 15 With NaN_3 in Aprotic Solvents at r.t.

In view of the preceding results, determinations of the cause and the manner of ring opening; the pathways leading to the formation of $(C_8H_8)Fe(CO)_3$ (37), and the design of experimental conditions conducive to the exclusive formation of the bicyclic complex 68 were deemed highly important.

Ring-opening could, in principle, have occurred either prior to or following the addition of azide ion to the bicyclic complex 15. If ring-opening occurs prior to nucleophilic addition, the resulting (η^5-cyclooctatrienyl)irontricarbonyl cation 71 could either lose a proton to a solvent molecule or an azide ion yielding $(C_8H_8)Fe(CO)_3$ (37) or react with the azide ion at the metal. If ring-opening occurs after nucleophilic addition to the bicyclic cationic complex 15, such ring-opening is likely to occur in either the metal-substituted on the ring-substituted bicyclic azido complexes, 72 and 68 respectively. Loss of HN_3 from the resulting monocyclic azido complexes 73, 74, 69 or 70 would explain the formation of $(C_8H_8)Fe(CO)_3$ (37). Formation of (*endo*-azidocyclooctatriene)irontricarbonyl complex 69 or 70 could also occur by the intramolecular transfer of the azido group in 74 from the metal to the *endo*-side of the organic ligand. Various possible modes of formation of $(C_8H_8)Fe(CO)_3$ (37) and the ring-substituted monocyclic azido complex 69 or 70 are schematically shown in Figure 10. Reaction of pyridine with the bicyclic cationic complex 15 was shown[49] to proceed by initial nucleophilic attack at the ring to give the bicyclic complex 75, followed by ring-opening and then loss of the pyridinium salt from the monocyclic species 76 yielding $(C_8H_8)Fe(CO)_3$ (37) (Figure 11).

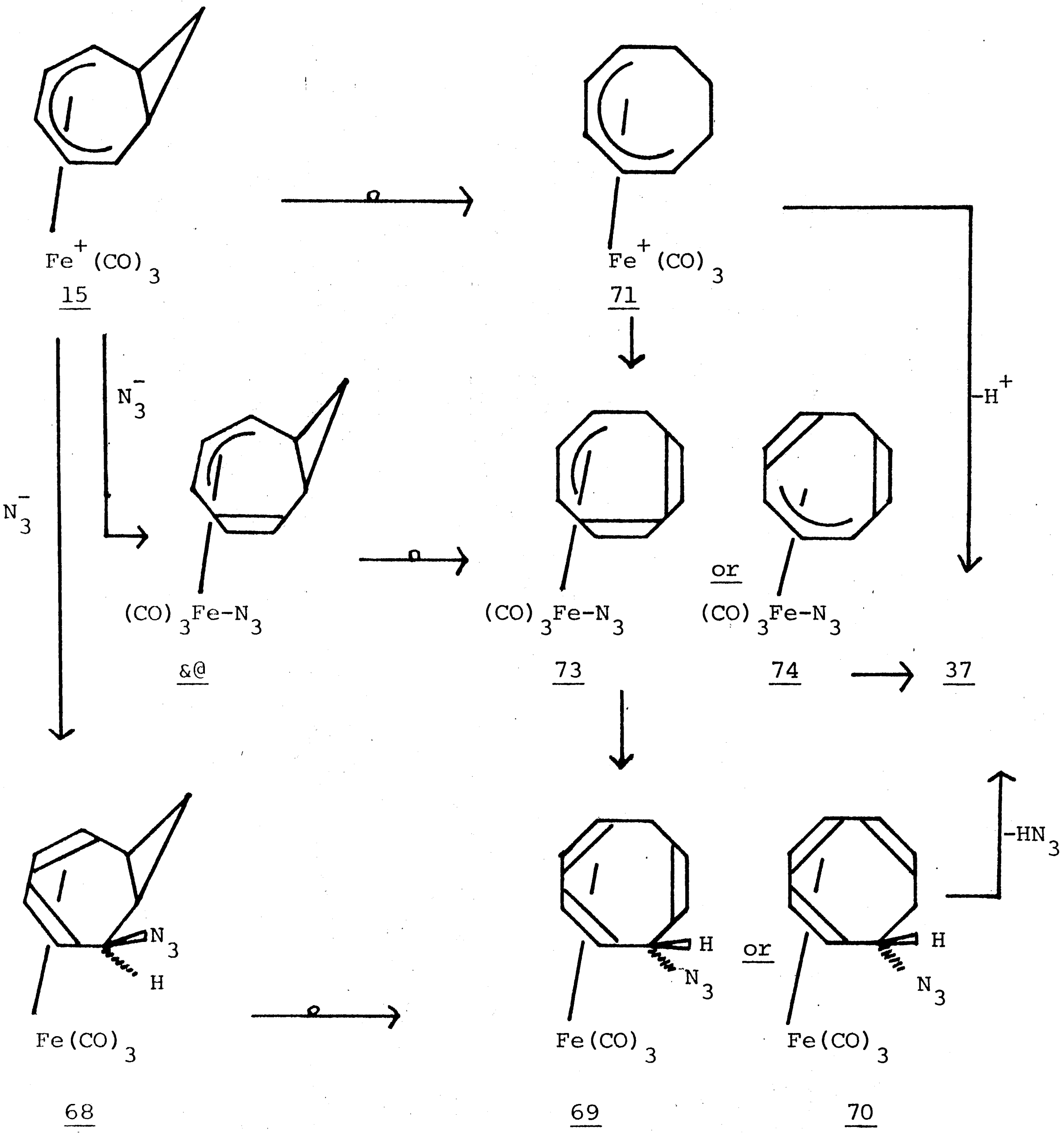
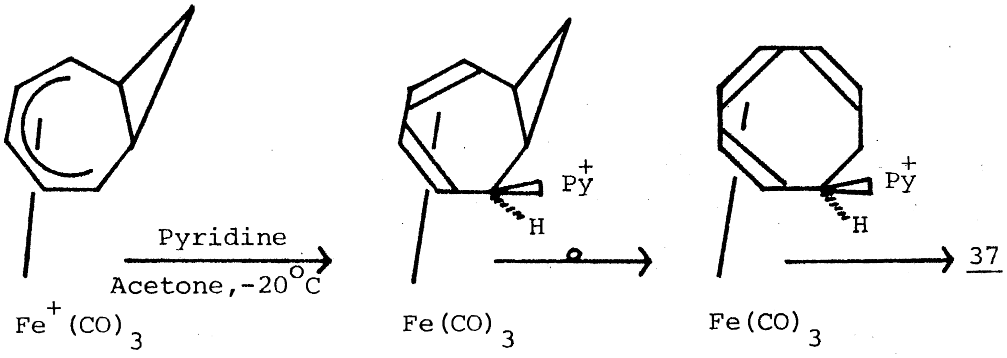


Figure 10. Rationalization of the Formation of $(C_8H_8)Fe(CO)_3$ (37) From the Reaction Between 15 and NaN_3



15 75 76

Figure 11. Addition of Pyridine to 15

In view of the preceeding discussion, $(C_8H_8)Fe(CO)_3$ (37) can be formed from several reaction pathways. In order to determine the role of the solvent in the ring-opening of the bicyclic complex 15 leading to the formation of $(C_8H_8)Fe(CO)_3$ (37), blank reactions were run by dissolution of the cationic complex 15 separately in the solvents acetone, acetonitrile, dichloromethane and THF in the absence of added sodium azide. Surprisingly, $(C_8H_8)Fe(CO)_3$ (37) was formed from the solutions of 15 in various solvents in considerable amounts (Table I). Formation of $(C_8H_8)Fe(CO)_3$ (37) from the bicyclic cationic complex 15 in aprotic solvents in the absence of externally added nucleophiles has not been previously reported. Deprotonation of the cationic complex 15 to yield $(C_8H_8)Fe(CO)_3$ (37) by a base adventiously present in the solvents seems unlikely owing to the diversity of the solvents used and the care exercised in their purification. The most attractive rationalization for the observed deprotonation of bicyclo[5.1.0]octa-

TABLE I

SOLVENT INTERACTIONS OF (BICYCLO[5.1.0]OCTATRIENYL)-TRICARBONYLIRON CATION 15

Reactants	Experimental Conditions	% Yield $[(C_8H_8)Fe(CO)_3]$ (37)
15 + THF	5h/r.t.	Trace (< 1%)
15 + THF	24h/0°C	7%
15 + Acetone	5h/r.t.	39%
15 + CH_2Cl_2	5h/r.t.	24%
15 + CH_3CN	3½h/r.t.	18%
15 (Solid State)	6 mon/0°C	7%

trienyl irontricarbonyl cation 15 to $(C_8H_8)Fe(CO)_3$ (37) in aprotic solvents involves initial coordination of the weakly nucleophilic solvent molecule at iron as in 77 followed by ring-opening in a rate-determining step yielding the monocyclic species 78. The solvent-coordinated monocyclic species 78, owing to its instability, could rapidly lose a proton and the solvent molecule to give the stable end product 37 (Figure 12). The driving force for rapid loss of a proton from the postulated monocyclic species 78 and/or 71 probably comes from the greater stability of $(C_8H_8)Fe(CO)_3$ (37) relative to the monocyclic cationic species in aprotic solvents.

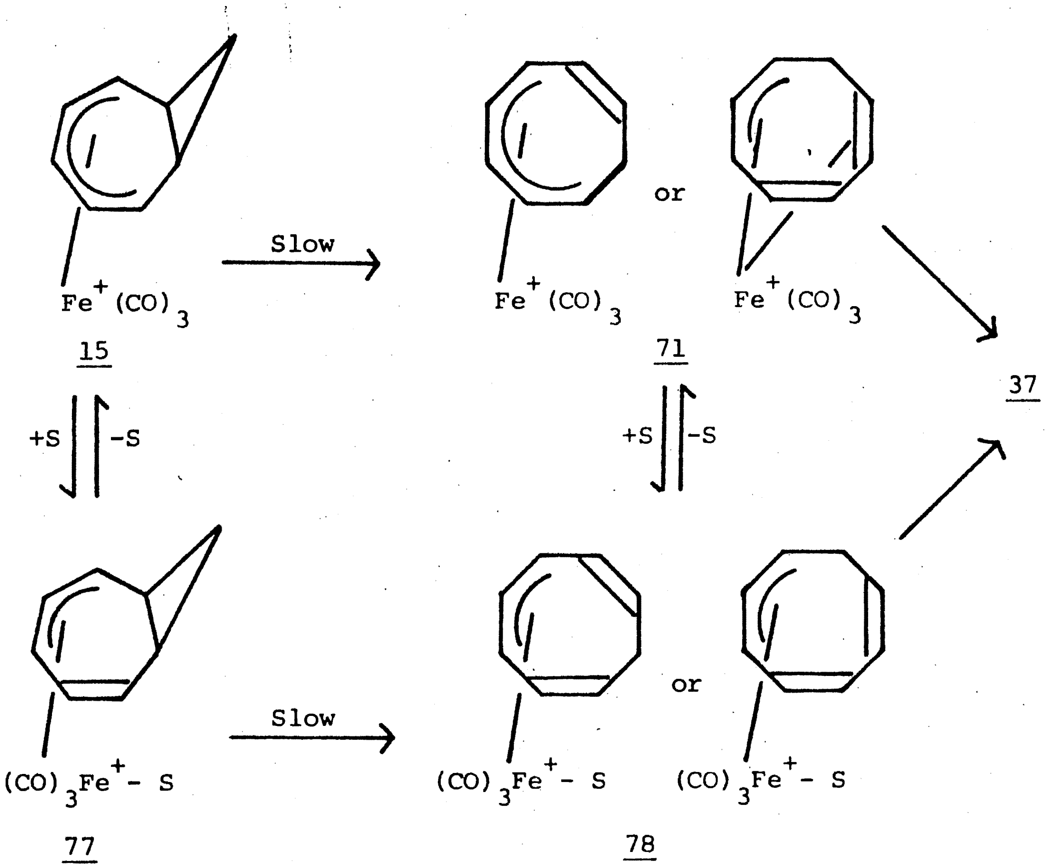


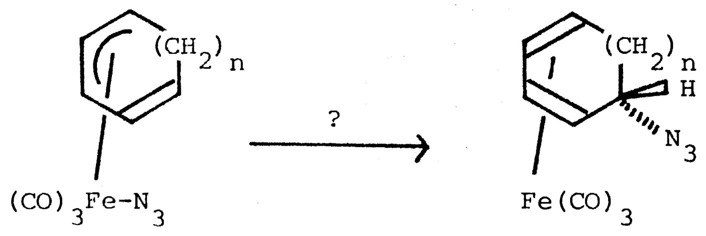
Figure 12. Rationalization of the Deprotonation of 15 in Aprotic Solvents

The postulated rationalization for the formation of $(C_8H_8)Fe(CO)_3$ (37) from the (bicyclo[5.1.0]octatrienyl)irontricarbonyl cation 15 in aprotic solvents (Figure 12) roughly represents the reverse reaction sequence of the protonation of $(C_8H_8)Fe(CO)_3$ (37) in superacid media leading to the irreversible formation of the bicyclic cationic complex 15 through the intermediacy of the monocyclic (η^5-cyclooctatrienyl)irontricarbonyl cation 71.[65] It is possible that the stabilities of the monocyclic and bicyclic isomers of (cyclooctatrienyl)irontricarbonyl cation, 71 or 78 and 15 or 77, respectively, in aprotic solvents are different from those in superacid solvent systems; as a consequence an equilibrium in favor of the monocyclic species 71 and 78, is attained in aprotic solvents.

In view of the observed facile ring-opening of the bicyclic cationic complex 15 leading to the formation of $(C_8H_8)Fe(CO)_3$ in aprotic solvents at room temperature with or without the added nucleophile, investigations to reduce the extent of ring-opening and at the same time increase nucleophilic addition to the bicyclic form became highly desirable. When the reaction between sodium azide and the bicyclic cationic complex 15 was performed in acetone at $0^\circ C$, a bicyclic organometallic product was obtained in addition to the two monocyclic complexes obtained at room temperature viz. 37 and 69 (or 70). The nmr spectral data strongly suggested that the bicyclic product is the expected (exo-2-azidobicyclo[5.1.0]octadiene)irontricarbonyl (68). The bicyclic azido complex 68 was highly unstable and extremely air-sensitive. It decomposed during purification attempts by fractional crystallization and column chromatography. Attempts to obtain exclusively the bicyclic azido complex 68 by further decrease of the reaction temperature, lengthened the reaction times and, unfortunately, increased the amounts of the products due to ring opening. It was clear from the results obtained so far, that the use of aprotic solvents for nucleophilic addition to the bicyclic cationic complex 15 is conducive to ring opening at room temperature and decrease in reaction temperature increased the reaction times leading to the formation of mixture of products. Short reaction times and low reaction temperatures appeared to be necessary in order to maximize the yield of the bicyclic azido complex 68. Thus, when the reaction between sodium azide and the cationic complex 15 was conducted in water at 0°C in a two-phase water-pentane solvent system, the reaction took only 30 min for completion. Proton nmr spectrum of the product mixture suggested bicyclic azido complex 68 to be the major product and the monocyclic complexes 37 and 69 (or 70) to be minor products. When the reaction was conducted at -20°C in an aqueous acetone-pentane solvent system, the bicyclic azido complex 68 was obtained in greater than 95% yield. Formation of the ring-substituted bicyclic azido complex 68 exclusively in aqueous media at sub-zero temperatures suggests that the reaction at room temperature in aprotic solvents might be occurring by ring-opening of the bicyclic cation 15 prior to the nucleophilic addition.

Summary

The results from the current investigations of the reactions between azide ion and (π-enyl)irontricarbonyl cations such as the cyclohexadienyl, cycloheptadienyl, tropylium and bicyclo[5.1.0]octatrienyl irontricarbonyl cations, 12a, 13, 16 and 15, respectively, suggest competitive nucleophilic addition at the ring, the metal and the carbonyl carbon. In all cases, predominant nucleophilic addition to the ring yielding *exo*-substituted complexes was observed. Only in one case nucleophilic attack at the carbonyl carbon resulting in the formation of an isocyanate complex was observed. However, analysis of the minor products from the reactions of sodium azide with $[(C_6H_7)Fe(CO)_3]BF_4$ (12a) and $[(C_7H_9)Fe(CO)_3]BF_4$ (13) suggest the formation of the metal-substituted products. In view of the co-occurrence of the metal-substituted and the ring-substituted *endo*-azido complexes in both the reactions, it seems reasonable to assume that the metal-substituted complexes 59 and 60 might be rearranging to the ring-substituted *endo*-complexes (Equation 3.1), 63 and 62, respectively, rather than the *exo*-complexes as suggested in the literature[51] (Equation 1.4). Such intramolecular transfer of azido group from the metal to the *endo*-side of the organic ligand seems more likely in view of the proximity of the metal-bonded azido group and the *endo*-face of the organic ring.



(3.1)

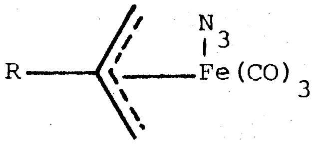
59: n=2
60: n=1

62: n=1
63: n=2

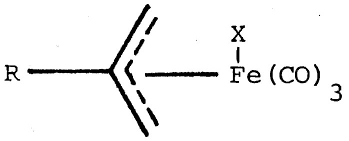
Unfortunately, the intermediate metal-substituted (π-allyl) azidoirontricarbonyl complexes 59 and 60 could not be isolated because they were unstable and formed in extremely small amounts. As a result, the fate of nucleophilic addition of an azide ion to the metal remains relatively less clear. There are no reports of the synthesis or isolation of either cyclic or acyclic (π-allyl)azidoirontricarbonyl complexes; hence, their chemistry is unknown. In view of the preceding, the synthesis and study of (π-allyl)azidoirontricarbonyl complexes in general, was deemed desirable.

Synthesis of a Metal-Substituted (π-Allyl)azidoirontricarbonyl Complex

Since cyclic dienylirontricarbonyl cations react with azide ion by substitution predominantly at the ring or the carbonyl carbon, an acyclic (π-allyl)irontricarbonyl cation was chosen to be reacted with azide ion with the hope that the metal could attain an inert gas configuration upon formation of a σ-bond to an azido group.



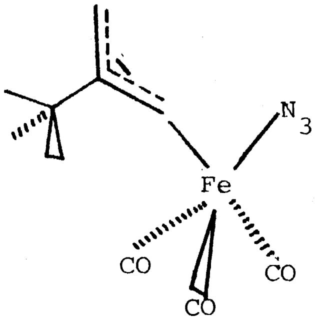
<u>79</u>: R=H
<u>80</u>: R=CH_3



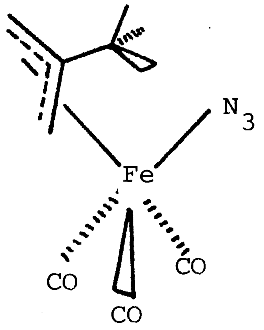
<u>81</u>

Addition of sodium azide to the unsubstituted (π-allyl)irontricarbonyl cation <u>6a</u> in reagent grade acetone led to an extremely unstable product which could not be characterized. Addition of NaN_3 to (2-methyl-π-allyl)irontricarbonyl cation <u>6b</u> in acetone at room temperature led to decomposition of the complex. However, when the same reaction was conducted at $0^{o}C$ in dry acetone (2-methyl-π-allyl)azidoirontricarbonyl (<u>80</u>) was isolated in low yield. The IR absorption band at 2030 cm^{-1} was assigned to the asymmetric stretching frequency of the azide moiety σ-bonded to iron. The value 2030 cm^{-1} is in excellent agreement with that suggested for η^3-$C_7H_9Fe(CO)_3N_3$ (<u>59</u>)[51] (ν 2030 cm^{-1}) and close to that observed for (η^5-C_5H_5)$Fe(CO)_2N_3$ (<u>24</u>) [ν_{asym} M-N_3: 2000 cm^{-1} (KBr); 2010 cm^{-1} (CS_2 and $CHCl_3$)].[17] The carbonyl absorption at

2100 cm^{-1} observed for *80* represents the highest value observed for (π-allyl)Fe(CO)$_3$X (X=Cl, Br, I, NCO) type of complexes. Carbonyl absorptions in the range 2000-2100 cm^{-1} are also characteristic of the cationic π-enyl irontricarbonyl complexes (e.g., *12a*, *13*, *15* and *16*). Thus a tight ion-pair for the M-N$_3$ ($M^+N_3^-$) bond in (2-methyl-π-allyl)-azidoirontricarbonyl may not be an unreasonable assumption. Comparison of the ^{1}H-NMR spectrum of the complex *80* with those of the closely related complexes[66,67] suggested the presence of only the *endo*-isomer although both the stereo-chemical isomers, *exo*- and *endo*- are possible. The prefixes *exo*- and *endo*- are used in the nomenclature of the (π-allyl) Fe(CO)$_3$X type of complexes, e.g., *81*, to designate the orientation of the substituent on the central carbon with respect to the substituent on the metal. ^{1}H-NMR spin-saturation transfer experiments



80: *endo*-

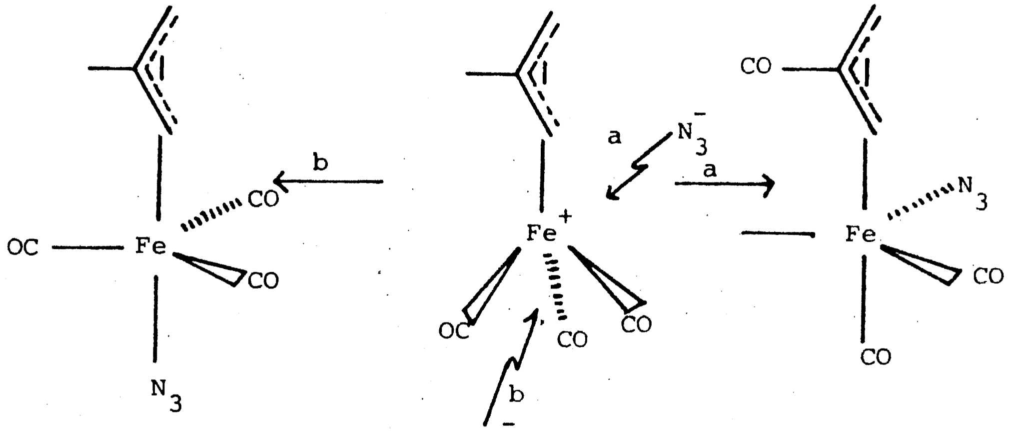


80: *exo*-

with the unsubstituted (π-allyl)Fe(CO)$_3$X complexes (*81*; R=H) suggest that the *endo*- isomer is more stable than the *exo*-isomer, and the equilibrium for the isomer interconversion is in favor of the *endo*-confirmation.[67] When X in (η^3-C_3H_5)Fe(CO)$_3$X (*81*; R=H) is changed from iodide to chloride or when the polarity of the solvent is increased, the equilibrium is shifted more in favor of the *endo*-conformation. The isolation of only the *endo*-isomer in the present case, suggests that the methyl group on the central carbon in 80 probably increases destabilizing spacial interactions with the azido group on the metal in the exo-isomer whereas in the endo-isomer the methyl group and the azide group are far apart from each other.

The ^{13}C-NMR spectrum of the complex 80 in $DCCl_3$ was exactly the same as that of the corresponding chlorocomplex (81; R=CH_3, X=Cl). The chemical shifts of the carbons of the π-allyl system in 80 are shifted downfield compared to those reported for the carbons of the π-allyl system in η^3-$C_3H_7Fe(CO)_3I$ (81; R=H, X=I).[68] This can be accounted for in terms of electronegativity differences of the substituents σ-bonded to iron.

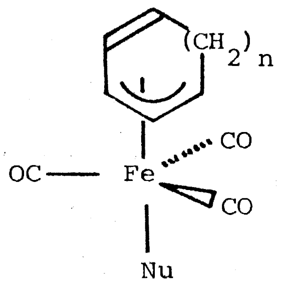
The mechanism of nucleophilic addition at the metal center in cationic (π-allyl)tricarbonyliron complexes is interesting. For instance, the azide ion could, in principle, attack the iron atom in 6b from the sides trans- (or axial) and cis- (or equatorial) to the π-allyl ligand giving rise to two geometrical isomers, as shown in Figure 13.



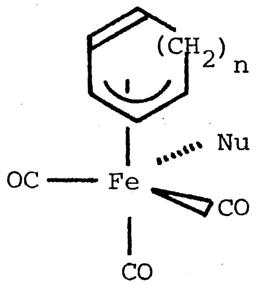
80: trans- 6b 80: cis-

Figure 13. Possible Modes of Nucleophilic Addition to the Metal in 6b

Similar argument can be put forth for the addition of a nucleophile at the metal center of a cationic (dienyl)tricarbonyliron complex such as 12a or 13 leading to *cis*- and *trans*-geometrical isomers of the metal substituted products.



82: *trans*-



82: *cis*-

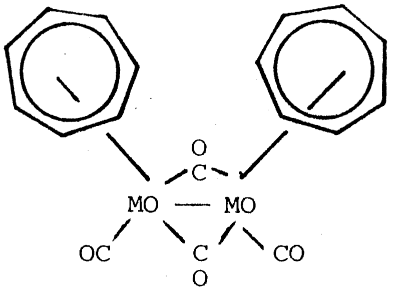
The reactivities and stabilities of such geometrical isomers may be quite different from each other and may give different products upon further reactions. For instance, the *cis*-isomer of the metal-substituted complex 82 is more likely to give the ring-substituted products whereas the *trans*-isomer of 82 is likely to ionize. Frontier molecular orbital calculations for the dissociative carbonyl substitution of $M(CO)_5X$ (M=Mn, Re; X=Cl, Br, I) through the intermediacy of $M(CO)_4X$ suggest that the transition state for the equatorial (*cis*-) approach to the metal by the incoming nucleophile is more favored energetically than when the ligand approaches the metal from the axial (*trans*-) side.[69]

Although x-ray structure analysis was not obtained for (2-methyl-π-allyl)azidoirontricarbonyl (80), the geometry of the complex appears to be *cis*- in view of the close similarities in the spectra of 80 and the chloro complex 81 (R=CH_3, X=Cl), which must possess *cis*-geometry owing to the method of its preparation (see experimental) and confirmation by x-ray studies for similar complexes[70] prepared by the same method.

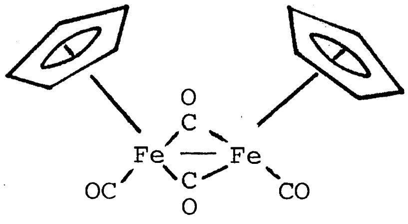
Role of the Metal

The reaction of sodium azide with $[(C_7H_7)Mo(CO)_3]BF_4$ (17b) in acetone, dichloromethane, water or THF yielded dark green solutions. Changes in the metal-carbonyl region of the IR spectrum during the progress of the reaction were very complicated suggesting the formation of different types of molybdenum carbonyl complexes. Infrared and proton nmr spectral analysis of the partially purified fractions of the product mixture suggested the presence of a minimum of three components. The major product, a dark green crystalline solid (hereafter referred to as "green complex 83") was extremely unstable in solution decomposing to a green amorphous solid. It is sparingly soluble in hydrocarbon and ethereal solvents and highly soluble in more polar solvents such as dichloromethane and acetone. The IR spectrum of the "green complex 83" in CH_2Cl_2 suggested the presence of both bridging and terminal carbonyls. Attempts to obtain the ^{1}H-NMR spectrum of the "green complex 83" failed due to either the paramagnetic nature of the complex or its decomposition in solution to paramagnetic materials. One possible structure for the "green complex 83" is bis- (η^7-cycloheptatrienyl)-dimolybdenumtetracarbonyl. Although a dimeric M-M bonded heptahapto molybdenum complex such as 83 is unknown, its formation would not be unreasonable in view of the formation of the closely related dimeric pentahepto iron complex 84 from the decomposition of $(C_5H_5)Fe(CO)_2$-NCO (25). However, the exact structure of the "green complex 83" remains unclear.

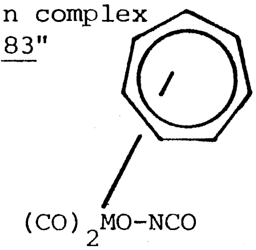
Analysis of the minor products suggested the presence of (η^7-cycloheptatrienyl)dicarbonylmolybdenum isocyanate (85) and (exo-7-azidocycloheptatriene)molybdenumtricarbonyl (86).



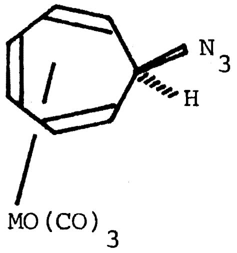
"green complex 83"



84



85



86

The IR spectrum of the isocyanate complex 85 possessed an absorption band at 2220 cm^{-1} characteristic of an isocyanate group attached to a transition metal; the proton nmr spectrum in $DCCl_3$ or acetone-d_6 possessed a single absorption. The proton nmr spectrum of the azido complex 86 suggested that the stereochemistry of the azide moiety on the ring is probably *exo*. When the impure azido complex 86 was reacted with $(Ph_3C)BF_4$ (1), the formation of Ph_3N_3 and $[(C_7H_7)Mo(CO)_3]^+$ cation 17b could be observed by IR spectroscopy during the progress of the reaction. Although evidence for the structural assignment of the minor products is overwhelming, no thorough characterization of the minor products could be carried out because of the extremely small amounts formed and the difficulties encountered in separating them from the "green complex 83".

Comparison of the Reactivities of (Tropylium)-tricarbinyl Complexes of Iron and Molybdenum

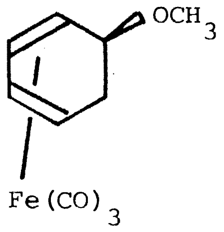
Neither color changes nor IR spectral changes during the progress of the reaction between $[(C_7H_7)Fe(CO)_3]BF_4$ (16) and NaN_3 in THF suggested nucleophilic attack at the metal or the carbonyl carbon; thus direct and exclusive addition at the tropylium ring 16 is favored. On the other hand, the color changes and IR spectral changes during the course of the reaction between $[(C_7H_7)Mo(CO)_3]BF_4$ (17b) coupled with the product analysis strongly suggested nucleophilic attack predominantly at the metal. Isolation of extremely small amounts of the isocyanate complex 85 and the ring-substituted complex 86 suggest negligible nucleophilic attack by the azide ion at the carbonyl carbon and the tropylium ring respectively of the molybdenum complex 17b. It is very likely that the "green complex 83" is formed as a result of initial nucleophilic attack at molybdenum.

The reduced electrophilicity of the tropylium ring in $[(C_7H_7)Mo(CO)_3]BF_4$ (17b) compared to that in $[(C_7H_7)Fe(CO)_3]BF_4$ (16) or the free ligand 4 is consistent with the higher pK_{R+} value (6.2) obtained for the molybdenum complex 17b as compared to that for the iron complex 16 or that (4.8) for the free ligand 4. The reduced electrophilicity of the ring in (tropylium)tricarbonyl complexes of Group VI metals (Cr, Mo, W) were theoretically rationalized[11] in terms of general increase in the π-electron-density and bond-index values for the ring carbons due to complexation. High bond-index values imply low "free-valence" for the formation of a bond with an incoming nucleophile. Kinetic data for the nucleophilic attack by CH_3CN at the metal in $[(C_7H_7)M(CO)_3]BF_4$ (17a-c; M=Cr, Mo, W) suggest the order of the susceptibility of the metal to nucleophilic attack to be Mo >> W > Cr.[45]

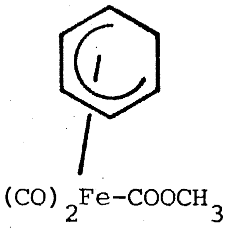
For the first time, in the present investigations a comparison of the reactivity of (tropylium)tricarbonyl complex of a Group VIII metal (iron) has been made with that of a Group VI metal (molybdenum) with respect to a common nucleophile. The electrophilicity of the tropylium ring clearly varies upon complexation to $Fe(CO)_3$ and $Mo(CO)_3$ moieties, and the present data suggest the electrophilicity order of the tropylium ring to be $(C_7H_7)^+ \geq [(C_7H_7)Fe(CO)_3]^+ > [(C_7H_7)Mo(CO)_3]^+$.

Reactions of Selected Oxyanions With (Cyclohexadienyl)irontricarbonyl Cation 12a

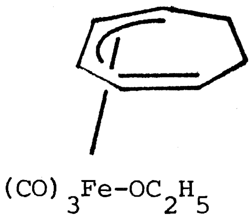
In the literature, several mechanisms, based on very little definitive evidence, have been proposed for the formation of ring-substituted products in the reactions between cyclic (dienyl)irontricarbonyl cations and alkoxide ions in alcoholic solvents. Until recently, the formation of exo-5-methoxy-1,3-cyclohexadiene)irontricarbonyl (87) from the reaction between methoxide ion and (cyclohexadienyl)irontricarbonyl cation 12a in methanol, was believed to be due to the direct attack of the methoxide ion on the ring.[19] It has now been claimed that such addition proceeds through initial nucleophilic attack at the carbonyl carbon to give the carbomethoxy ester complex 88 which finally yields the observed ring-substituted product.[71] Surprisingly, no confirmatory report in support of such a claim has been published. Another report



87



88



40 (Nu=OC$_2$H$_5$)

suggests that the formation of (exo-5-ethoxycyclohepta-1,3-diene)irontricarbonyl (41; Nu-OC$_2$H$_5$) in the reaction of ethoxide ion with (cycloheptadienyl)irontricarbonyl cation 13 in ethanol proceeds through initial nucleophilic attack at the metal followed by the formation of observed ring-substituted product from the metal-substituted intermediate 40 (Nu-OC_2H_5)[51] (Equation 1.4).

In the belief in possible importance of solvent effects upon the reaction mechanism, it was proposed to investigate the reaction of methoxide ion with (cyclohexadienyl)irontricarbonyl cation 12a in an aprotic solvent, such as acetonitrile, rather than in a protic solvent. The reaction of 12a with sodium methoxide in CH_3CN led to a color change from yellow to dark red accompanied by IR spectral changes which included evidence of the formation of neutral diene irontricarbonyl complexes and the development of a bridging carbonyl absorption at 1755 cm^{-1} coincident with the formation of the red product. After workup and chromatographic separation the expected product (*exo*-5-methoxycyclohexa-1,3-diene)irontricarbonyl (87), was obtained in less than one percent yield; the major products were (di-η^5-cyclohexadienyl)tetracarbonyldiiron ("M-M dimer" 89), 5,5'-bis(cyclohexa-1,3-diene)hexacarbonyldiiron ("C-C dimer" 90), *exo*- and *endo*- isomers of (5-hydroxycyclohexa-1,3-diene)irontricarbonyl (91) and [5,5'-oxydi(cyclohexa-1,3-diene)]hexacarbonyldiiron (92) were obtained (Figure 14). These results were unexpected and suggested pronounced solvent effects upon the course of the reaction. Some of the puzzling results from the reaction of the methoxide ion with 12a in CH_3CN include; i) Formation of negligible amounts of (*exo*-5-methoxycyclohexadiene)irontricarbonyl (87); ii) Formation of the dimeric complexes 89 and 90; iii) Formation of the ring-substituted hydroxy and ether complexes, 91 and 92, respectively. In view of the formation of dramatically different products in

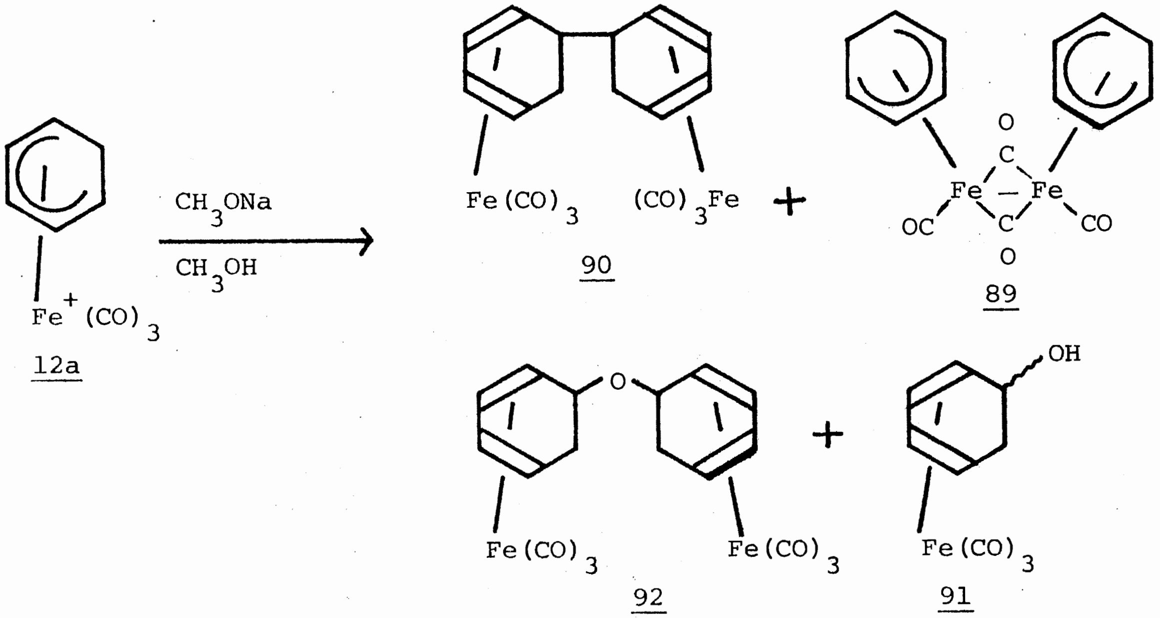
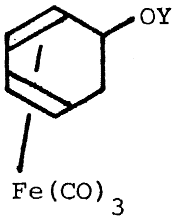


Figure 14. Reaction of $NaOCH_3$ With 12a in CH_3CN

protic and aprotic solvents, the reaction between sodium methoxide and 12a was reinvestigated in methanol. The reaction mixture stayed yellow and the formation of only (*exo*-5-methoxycyclohexa-1,3-diene)irontricarbonyl (87) was observed. Obviously, the reaction between methoxide ion and 12a was taking place by different mechanism(s) in acetonitrile than in methanol. Recall that formation of the red color in the reaction of ethoxide ion with (cycloheptadienyl)irontricarbonyl cation 13 in ethanol was attributed to initial nucleophilic attack at the metal.[51] In our case the red color was due to the gradual buildup of the M-M dimer 89. The formation of M-M dimer 89 has not been reported in the reactions of 12a with nucleophiles. However, formation of the C-C dimer 90 has been reported in the reactions of 12a with alkyl Grignard[20] and alkyllithium reagents.[21] Most puzzling in the acetonitrile reaction was the formation of the 5-hydroxy complex 91 and the ether complex 92. Both 91 and 92 can be prepared from 12a and hydroxide ion in water.[20] Although, acetonitrile has been rigorously dried prior to use, the possibility of trace amounts of water present in the solvent reacting with the methoxide ion to generate hydroxide ion *in situ* which in turn reacts with 12a leading to the formation of the hydroxy and the ether complexes, 91 and 92, respectively, could not be ruled out. It was deemed important to study the reaction of hydroxide ion itself with 12a in acetonitrile. Surprisingly, such reaction again resulted in the formation of the two dimeric complexes 89 and 90, as well as the hydroxy and the ether complexes 91 and 92, respectively. The co-occurrence of the same dimeric complexes and the same ring-substituted complexes in both the reactions was very puzzling. It was desired to determine whether the effects of change in the solvent from alcohols to acetonitrile are the same for the reactions of other oxyanions with 12a. Addition of the bulky oxy-anion, $(CH_3)_3CO^-$, to (cyclohexadienyl)irontricarbonyl cation 12a in acetonitrile at room temperature, again led to the isolation of both the dimeric complexes 89 and 90 and also the ether complex 92. There was no evidence for the presence of *tert*-butoxy substituted organometallic products. When the same reaction was carried out in *tert*-butanol, the ring-substituted *tert*-butoxy complex 93 was obtained in considerable amounts in addition to the dimeric complexes 89 and 90 and the ether complex 92.



93: Y = $C(CH_3)_3$; 94: Y = C_6H_5; 95: Y = $Si(CH_3)_3$

With a reduction in the nucleophilicity or the basicity of the oxyanion, YO^-, by replacement of the electron donating groups, (Y=alkyl) with groups capable of electron withdrawal ($Y=Si(CH_3)_3$, C_6H_5), C-5 substitution became competitive with the formation of the dimers. Addition of phenoxide to 12a in CH_3CN at room temperature yielded (5-phenoxycyclohexa-1,3-diene)irontricarbonyl (94) as the major product. With regard to the effect of temperature upon the reaction products, the limited data in Table II indicate a decrease in dimer formation accompanied by a concomitant increase in substitution at C-5 at low reaction temperatures. Methoxide and tert-butoxide ions did not lead to the ring-substituted 5-methoxy and 5-t-butoxy cyclohexadiene irontricarbonyl complexes, 87 and 93, respectively, even at low temperatures. Strikingly, addition of $(CH_3)_3SiONa$ to 12a in acetonitrile at -45°C gave (exo-5-trimethylsiloxycyclohexadiene)irontricarbonyl (95) quantitatively. The stereochemistry at C-5 in the trimethylsiloxy complex 95 was confirmed by the facile abstraction of the trimethylsiloxy group with $(Ph_3C)BF_4$ (1).

The operation of a free-radical pathway or electron-transfer mechanism(s) in the formation of the dimers 89 and 90, the hydroxy and the ether complexes 91 and 92, respectively, was suggested by the ability to arrest their formation by bubbling oxygen through the reaction mixture. Thus, when oxygen was bubbled through a solution of sodium methoxide and 12a in acetonitrile at room temperature, (exo-5-methoxycyclohexadiene)irontricarbonyl (87) was obtained as the predominant product (47%), as compared to one percent yield in the absence of oxygen and 52% for the same reaction in methanol.

An attractive rationalization (Figure 15) involves the addition of

TABLE II

REACTIONS OF $[(C_6H_7)Fe(CO)_3]BF_4$ (12a) WITH OXY-ANIONS[a]

$^-$O-Y	Solvent	Temp/rxn·time	"M-M" (%) Dimer (89)	"C-C" (%) Dimer (90)	C_5-OY (%)	Total Yield of 91 and 92 (%)
OH[6]	CH_3CN	r·t/5h	9	8	8	27
OCH_3[c]	CH_3CN	r·t/45 min	25	19	<1	26
OCH_3[c]	CH_3CN	-25^oC/4h	9	7	--	42
OCH_3[c]	CH_3CN/O_2	r·t/4h	--	--	48	--
OCH_3[c]	CH_3OH	r·t/24h	--	--	52	--
$OC(CH_3)_3$	CH_3CN	r.t/30 min	45	6	<1	<1
$OC(CH_3)_3$	CH_3CN	-45^oC/60 min	16	10	--	27
$OC(CH_3)_3$	$(CH_3)_3COH$	r.t/4h	16	6	8	5
$OSi(CH_3)_3$	CH_3CN	r.t/10 min	26	11	42	11
$OSi(CH_3)_3$	CH_3CN	-45^oC/15 min	5	--	95	--
OC_6H_5[d]	CH_3CN	r.t/8h	--	--	64	22

[a] [12a] = [$^-$OY] = 50-55 mM.

[b] Reaction 77% complete; yields based on the amount of cation consumed.

[c] Sod. methoxide prepared from Na+CH_3OH

[d] KOC_6H_5 prepared from K + C_6H_5OH; xn 36% complete; yield based on the amount of the cation consumed.

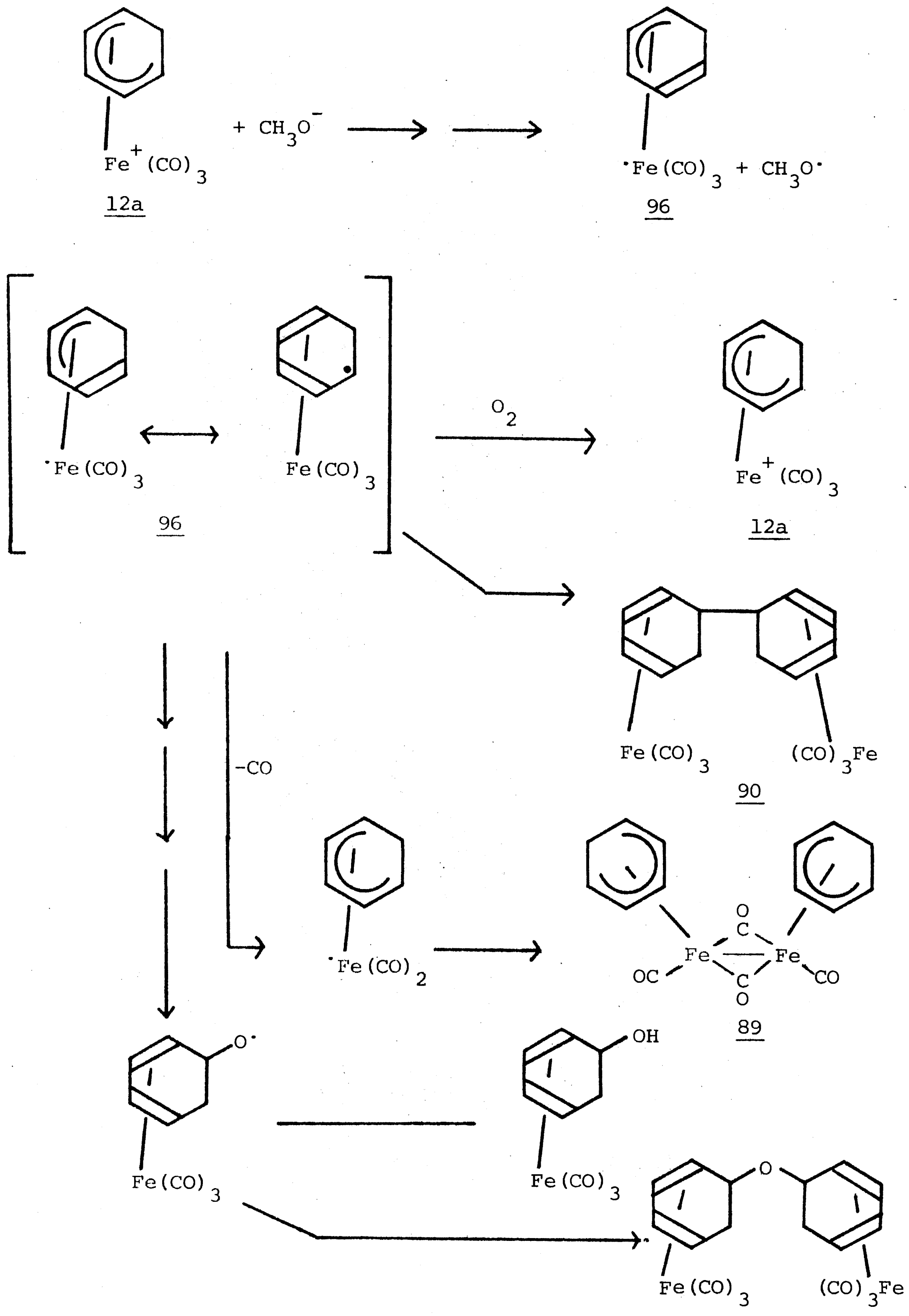


Figure 15. Rationalization of the Products From the rxn Between 12aand CH_3O^-

the methoxide ion to the cationic complex 12a in acetonitrile by both ionic and electron-transfer mechanisms. In the absence of oxygen, the addition by electron transfer supercedes the addition by an ion-pairing mechanism. The organometallic and the organic radicals generated from the electron-transfer reactions, upon random coupling could lead to the formation of the observed products. However, in the presence of O_2 all electron transfer reactions at the metal are totally inhibited whereas the relatively slower nucleophilic addition by ion-pairing continues uninhibited leading ultimately to the exo-methoxy complex 87. In methanol, the methoxide ion seems to react with 12a exclusively by an ion-pairing mechanism.

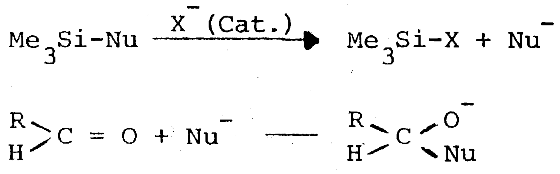
The exact manner in which protic and aprotic solvents, such as alcohols and acetonitrile, affect the course of the reactions between oxyanions and 12a is not clear. Generally aprotic solvents such as CH_3CN and DMF solvate cationic species by coordination much more effectively than anionic species. Protic solvents such as alcohols solvate anionic species by H-bonding much more effectively than cationic species. Thus alkoxide ions in alcohols exist in a highly solvated form due to H-bonding with solvent molecules often resulting in the formation of molecular aggregates. This would decrease the reactivity or enhance the selectivity of the alkoxide ion. In contrast, alkoxide ions in CH_3CN are comparatively less solvated; consequently, they are more reactive and less descriminate in reactions with 12a. It appears as if the ability of the oxyanions to react with 12a by electron-transfer mechanisms parallels the basicity order: $^{-}OH > CH_3O^{-} > (CH_3)_3CO^{-} > (CH_3)_3SiO^{-} > C_6H_5O^{-}$.

The Need for Anion Synthons

The current results as well as those of others,[20,21] suggest that strong anionic nucleophiles react with π-complexed irontricarbonyl cations by electron-transfer leading to the formation of undesirable dimers, at the expense of products due to ring-addition; although manipulation of experimental parameters seems to minimize such deleterious side reactions, such manipulations may not be applicable for all cases. One such example was the reaction of Ph_3Si^- with 12a. Addition of triphenylsilylanion, prepared by the cleavage of $Ph_3SiSiPh_3$ with lithium, to 12a in either THF or acetone at room temperature led predominantly to the formation of both the dimeric complexes 89 and 90. At low temperatures, the reaction was extremely slow. Triphenylsilyl anion can only be made in solution and it disintegrates quickly with time and upon exposure to air. Hence, longer reaction times or bubbling oxygen through the reaction mixture would cause destruction of the anion. Similarly several highly reactive carbanionic species, such as alkyl, allyl and vinyl lithiums and the corresponding Grignard reagents which are extremely air-sensitive, are likely to react with 12a by electron transfer to give dimers. Reductive coupling reactions of (π-enyl)irontricarbonyl cations with anionic nucleophiles constitute an extremely important limitation to the synthetic utility of the reactions.

In order to achieve ring-substitution of (π-enyl)irontricarbonyl cations with strong anion nucleophiles (e.g., Nu^-), use of anion synthons (M-Nu) which could selectively transfer the nucleophilic fragment of the molecule (Nu) to the organic ligand was envisaged. An anion synthon (M-Nu) is a substituted anion (Nu^-) which acts as an anion carrier. Anion synthons can be anionic or neutral and are generally less reactive than the constituting anions. Examples of some carbanion synthons include R_2M (R=Ph, Me_2CH, $CH_2CH{=}CH_2$, $CH{=}CH_2$; M=Cd, Zn) and R_2CuLi; which effectively transfer R^- to an electron-deficient site. Very few attempts[27,57] have been made in the use of anion synthons to accomplish selected nucleophilic transfers to π-enyl irontricarbonyl cations such as 12a. Such approaches need to be further explored and implemented to the extent of routine use.

In recent years several organosilicon compounds and tetra-coordinated organoboron compounds have been finding increasing use as anion synthons in organic synthesis.[72-78] However, their use in organometallic chemistry as anion synthons is very rare.[27,57] Generally, nucleophilic transfers from organosilicon and tetra-coordinated organoboron compounds to an electrophilic site can be best achieved by the use of anion catalysts. An example of such an anion-catalyzed nucleophilic transfer from organosilicon compounds is given below (Equation 3.2).



$$Me_3Si\text{-}Nu \xrightarrow{X^-\,(\text{Cat.})} Me_3Si\text{-}X + Nu^-$$

$$\begin{matrix}R\\H\end{matrix}{>}C=O + Nu^- \longrightarrow \begin{matrix}R\\H\end{matrix}{>}C{<}\begin{matrix}O^-\\Nu\end{matrix}$$

$$(Nu = N_3,\ CN;\ X^- = CN^-,\ N_3^-,\ NC\bar{O},\ CH_3O^-)$$

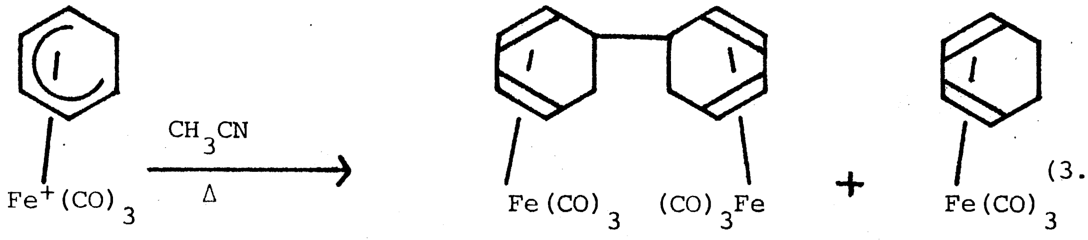
The anion-catalyzed nucleophilic transfers from organosilicon and tetra-coordinated organoboron compounds to cationic π-complexes such as $[(C_6H_7)Fe(CO)_3]BF_4$ can potentially be achieved by small amounts of the fluoride ion liberated from BF_4^-.

The following potential anion synthons (M-Nu) were proposed to be reacted with 12a, in an attempt to achieve exclusive nucleophilic addition to the ring.

M	Nu
Ph_3Si-	-$SiPh_3$
Me_3Si-	-$OSiMe_3$
Me_3Si-	-CH=CH_2
Me_3Si-	-CH_2-CH=CH_2
Me_3Si-	-N_3
$(C_6H_5)B$-	-$C_6H_5^-$

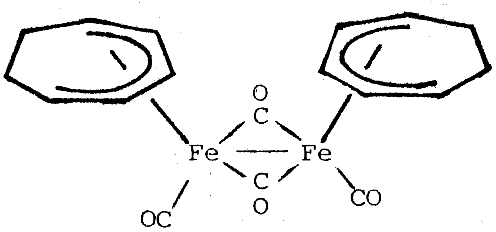
Discovery of Solvent Interaction of $[(C_6H_7)Fe(CO)_3]BF_4$ (12a) With CH_3CN

When hexaphenyldisilane was allowed to react with $[(C_6H_7)Fe(CO)_3]$-BF_4 in acetonitrile at reflux, formation of neutral diene irontricarbonyl species was complete in one hour, but upon workup hexaphenyldisilane was recovered unchanged. Heating 12a in the absence of the disilane in acetonitrile at 90°C also resulted in the formation of neutral products in one hour. Workup of the reaction afforded a mixture of (cyclohexa-1,3-diene)irontricarbonyl (98) and (5,5'-di-cyclohexa-1,3-diene)hexacarbonyldiiron ("C-C dimer 90") in ca. 45% total yield (Equation 3.3). The ratio (98)/(90) was concentration-dependent ranging from a value of ca. 5.8 to 2.6 over the concentration range 33-66 mM. Facile reduction of (cycloheptadienyl)tricarbonyliron tetrafluoroborate (13) also occurred in refluxing acetonitrile, but in contrast to the reaction of 12a, yielded the M-M dimer 99 in 32% yield and also traces of what appeared to be the C-C dimer 100. Suggestive evidence for the existence of a free-radical mechanism stems from the dramatic suppres-

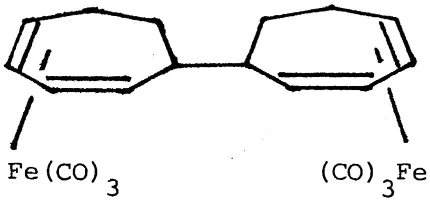


(3.3)

12a 90 98



99



100

sion of the reduction of the cationic complexes 12a and 13 in the presence of oxygen. Continuous slow bubbling of oxygen through a solution of $[(C_6H_7)Fe(CO)_3]BF_4$ (12a) in CH_3CN at reflux gave an 80% recovery of 12a after five hours. No neutral π-complexes were detected, although it is possible any such neutral complexes could have been destroyed under the reaction conditions. Similarly, bubbling oxygen through acetonitrile solution of $[(C_7H_9)Fe(CO)_3]BF_4$ (13) at reflux, yielded a 46% recovery of the cationic complex 13 after five hours and only very small amount of an unidentified neutral π-complex was observed.

Although a weak nucleophile, CH_3CN is known to attack the metal center in the (tropylium)tricarbonyl complexes of Group VI metals (Cr, Mo and W), 17a-c, leading to ring displacement.[45] Similar attack by CH_3CN at the iron atom of the cationic π-complexes 12a and 13 could either liberate the corresponding organic cations and an Fe(O) species, e.g., 101; or alternatively, liberate the organic radicals and a transient Fe(I) species e.g., 102. By analogy to the disporportionation of the iron carbonyls, $Fe_n(CO)_n$, in the presence of nitrogeneous or oxygeneous bases,[79] either or both of the generated iron species could perhaps undergo similar oxidation-reduction processes resulting ultimately in electron-transfer to the cations 12a and 13. The resulting π-allyl irontricarbonyl radicals 96 and 103 undergo further reactions to yield the observed products. The preceding rationalization is schematically represented in Figure 16. Consistent with the importance of nucleophilic attack of CH_3CN at iron, the rate of reduction of the complex 12a in the relatively weaker nucleophilic solvent, benzonitrile, is much slower than that in CH_3CN. Similar reduction in rate of nucleophilic attack by C_6H_5CN at the metal compared to that by CH_3CN has been observed in the reaction of these nitriles with the Group VI metal carbonyls.[80]

Reactions of Selected Organosilicon Compounds With 12a

In view of the reduction of 12a in refluxing acetonitrile in the absence of added nucleophiles, the later reactions of organosilicon compounds with 12a in acetonitrile were conducted at 45°C. No appreciable reduction of the cation 12a was observed in acetonitrile at 45°C. Reactions of hexamethyldisiloxane and vinyltrimethylsilane with 12a in acetonitrile at 45°C for 24 h led to greater than 90% recovery of the unchanged cationic complex. Reaction of allyltrimethylsilane to 12a under the same conditions led to the isolation of, exclusively, the ring-substituted product, (*exo*-5-allylcyclohexa-1,3-diene)irontricarbonyl (105) in 62% yield.

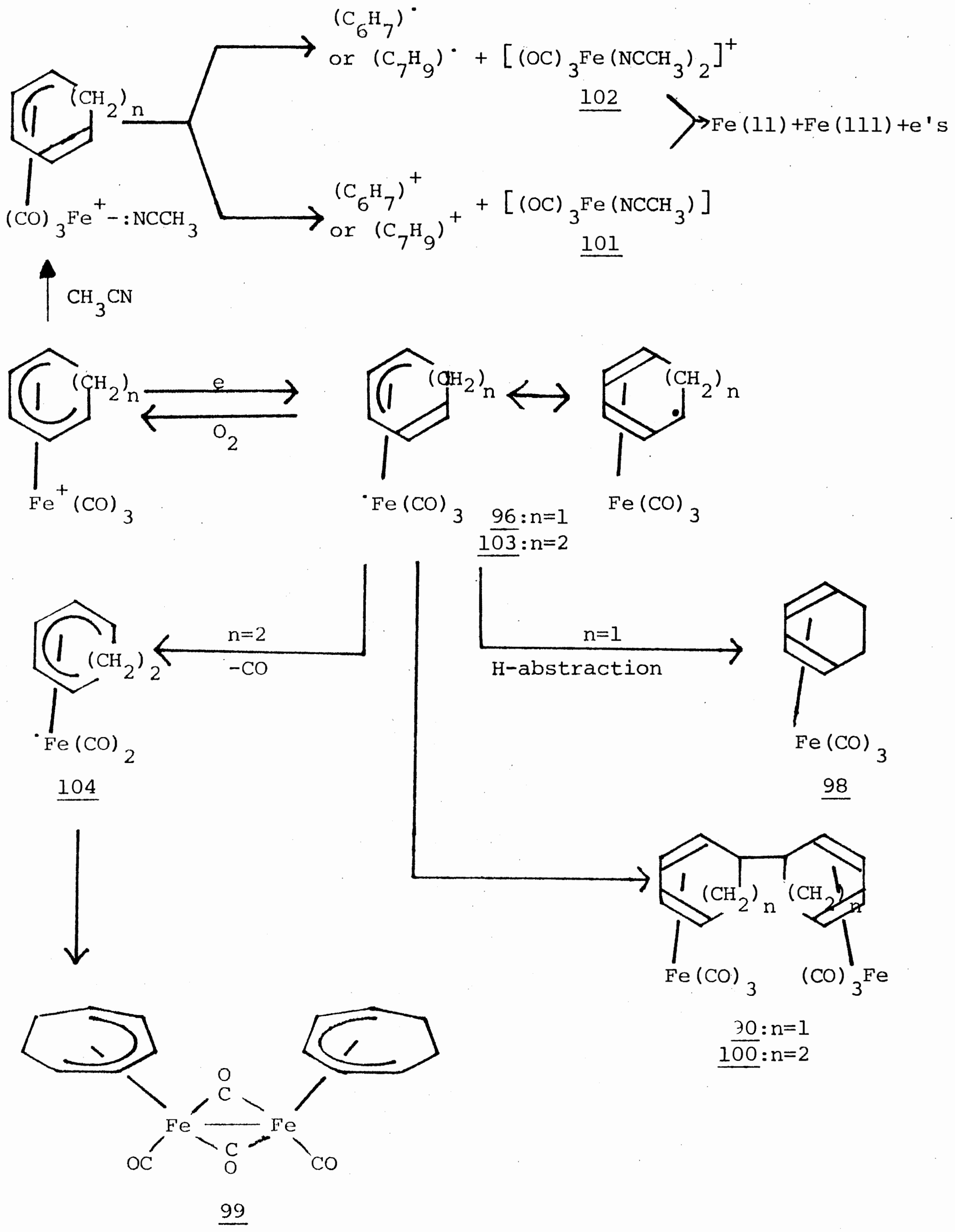
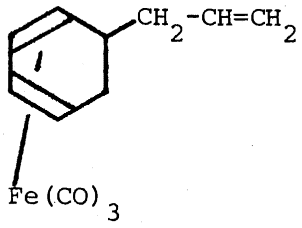


Figure 16. Rationalization of the Reduction of 12a and 13 in CH_3CN



105

Addition of azidotrimethylsilane to 12a in acetone at elevated temperatures led to a mixture of products, the major product being (exo-5-azidocyclohexa-1,3-diene)irontricarbonyl (56). However, when the same reaction was carried out at room temperature for one hour the exo-azido complex 56 was isolated exclusively in 50% yield. Interestingly, longer reaction times did not lead to increased yields of 56, but when the recovered cation 12a was stirred with additional amount of Me_3SiN_3, the ring-substituted azido complex 56 was again obtained in 50% yield. Thus the azido complex 56 could be obtained in total yields up to 95%. Addition of trimethylsilylazide to (cycloheptadienyl)irontricarbonyl cation 13 under the same conditions yielded a mixture of predominantly the exo-substituted complex 58 together with what appeared to be either ring-substituted endo-azido complex, 63. Reaction of Me_3SiN_3 with $[(C_7H_7)Fe(CO)_3]BF_4$ in THF at room temperature yielded exclusively (exo-7-azidocycloheptatriene)irontricarbonyl in 50% yield. The reaction of Me_3SiN_3 with $[(C_7H_7)Mo(CO)_3]BF_4$ (17b) in acetone, THF or dichloromethane again led to the formation of "green complex 83" as the major product together with the minor products observed in the reaction of 17b with NaN_3. Reaction with (bicyclo[5.1.0]octatrienyl)irontricarbonyl cation 15 in a variety of aprotic solvents yielded only the monocyclic products, $(C_8H_8)Fe(CO)_3$ (37) and $(C_8H_9N_3)Fe(CO)_3$ 69 (or 70). Reaction of Me_3SiN_3 with (2-methyl π-allyl)irontricarbonyl cation 6b in dry acetone gave almost exclusively, the metal-substituted (2-methyl-π-allyl)azidoirontricarbonyl (80) in excellent yields (50%) in direct contrast to the very low yields (12%) observed for the corresponding reaction with sodium azide.

In all the preceding reactions of Me_3SiN_3 in acetone, the condensation product, 2-methyl-2-hydroxy-4-pentanone (57) was observed to be a minor product. When trimethylsilylazide itself was allowed to react with excess acetone, the condensation product 57 was obtained in 3300% yield with respect to the amount of Me_3SiN_3 used. This suggested that Me_3SiN_3 catalyzed the aldol type of condensation of acetone. Although trimethylsilylazide is known to add to aliphatic aldehydes in the presence of anionic or Lewis acid catalysts, no reactions with ketones have been reported.[73,74]

The failure to cleave Si-Si and Si-O bonds in hexaphenyldisilane and hexamethyldisiloxane respectively in acetonitrile solution of $[(C_6H_7)Fe(CO)_3]BF_4$ (12a) even at elevated temperatures may be partially due to the extreme insolubility of $Ph_3SiSiPh_3$ in acetonitrile and the great thermodynamic stability of Si-O bonds in hexamethyldisiloxane. Also in hexamethyldisiloxane the two lone pairs of electrons are probably involved in pπ-dπ interactions with the vacant d-orbitals on the adjacent silicon atom and hence unavailable to a weak electrophile such the cyclohexadienyl ring in 12a. Vinyltrimethylsilane failed to transfer the vinyl group to the cation 12a under the prevailing circumstances. This may be due not only to the decreased π-electron density on the olefinic carbons because of the involvement of the π-electrons in (p-d)π bonding with vacant d-orbitals on silicon, but also due to the decreased tendency of silicon to undergo nucleophilic attack. Surprisingly, however, allyltrimethylsilane proves to be an excellent allyl anion synthon. Use of an allyl anion synthon such as allyltrimethylsilane definitely represents a better way of transferring the allyl group exclusively to the organic ring compared to the possible use of the highly reactive allyl anion. The ease of transfer of the allyl group to a weak nucleophillic species such as the cyclohexadienyl ring in 12a possibly reflects the electron-donating hyperconjugative effect of the Me_3Si-moiety through "vertical stabilization".[81] It is not clear if allyl transfer from allyltrimethylsilane to 12a occurs by electrophilic ipso-attack or γ-attack on the allyl system (Figure 17). The reaction of 12a with a substituted allyltrimethylsilane under the same conditions could, in principle, pin down the exact mechanism operating in the observed allyl transfer.

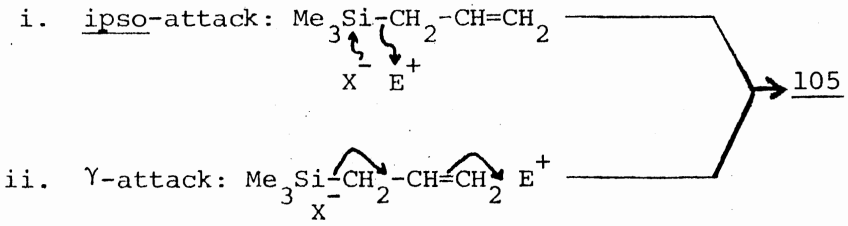
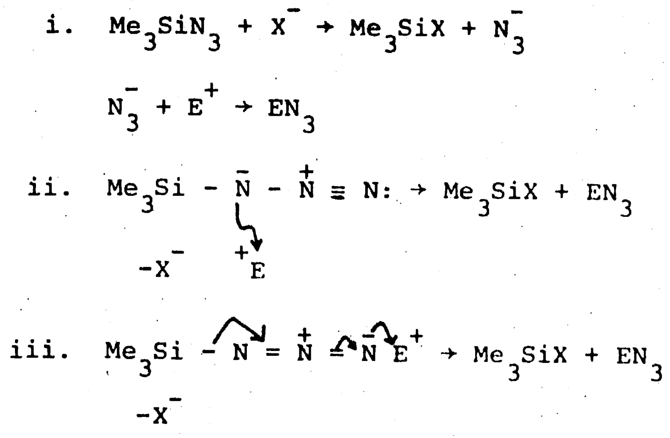


Figure 17. Possible Modes of Allyl Transfer From Allyltrimethylsilane ($E^+=[(C_6H_7)-Fe(CO)_3]^+$)

Trimethysilylazide proved to be an excellent azido anion synthon especially for azide transfers to cationic centers in aprotic solvents. In all the reactions with π-enyl irontricarbonyl cations, trimethylsilylazide was generally as effective as an azide ion and proved to be a better alternative to effect the azide transfer to iron in (2-methyl-π-allyl)irontricarbonyl cation 6b compared to sodium azide. In view of the extreme thermal stability (stable up to 350°C) coupled with the high solubility in all organic solvents, trimethylsilylazide promises to be an excellent substitute for HN_3 and azide ion in the synthesis of organic and organometallic azides. The mechanism of azide transfer from trimethylsilylazide to a cationic center (e.g., E^+) is not clear. The three possible modes of azide transfer from Me_3SiN_3 include: anion-catalyzed generation of a steady-state concentration of azide ion; electrophilic ipso- attack at the α-nitrogen or γ-attack at the end nitrogen (Figure 18).



i. $Me_3SiN_3 + X^- \rightarrow Me_3SiX + N_3^-$

$N_3^- + E^+ \rightarrow EN_3$

ii. $\underset{-X^-}{Me_3Si} - \underset{+E}{\overset{-}{N}} - \overset{+}{N} \equiv N: \rightarrow Me_3SiX + EN_3$

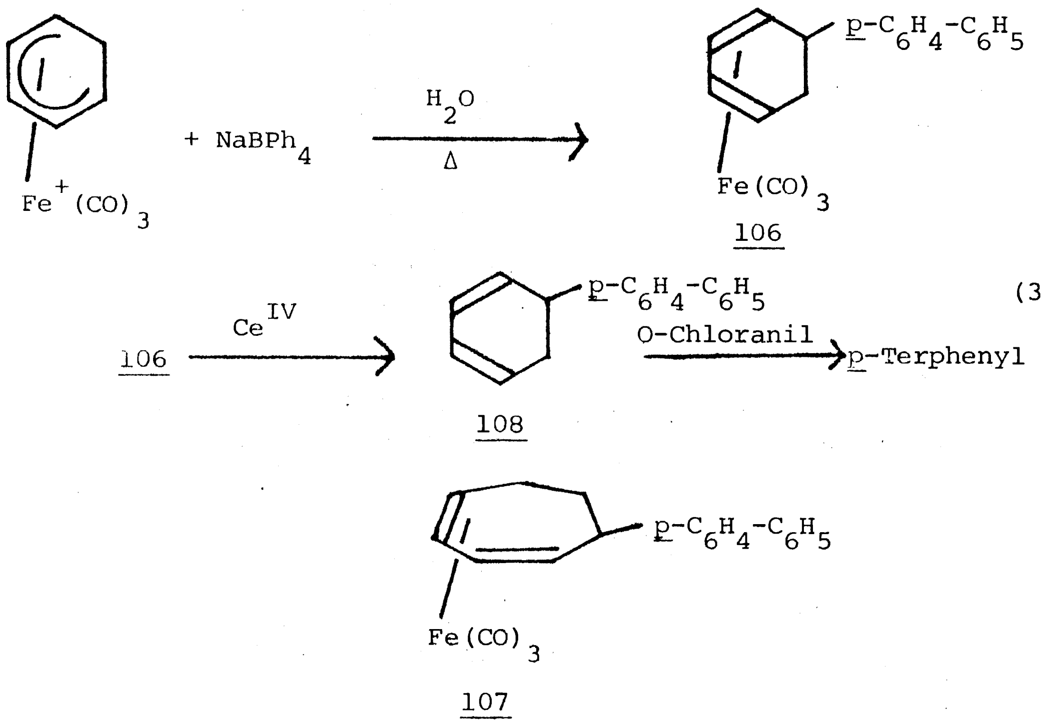
iii. $\underset{-X^-}{Me_3Si} - N = \overset{+}{N} = \overset{-}{N}\,E^+ \rightarrow Me_3SiX + EN_3$

Figure 18. Possible Mechanisms of Azide Transfer From Me_3SiN_3

Use of ^{15}N-labeled Me_3SiN_3 could, in principle, reveal the exact mechanism of azide transfer.

Reaction of Tetraphenylboron Anion With (Dienyl)irontricarbonyl Cations

The present investigations aimed at the possible use of tetraphenylboron anion as a phenyl anion synthon by reacting $NaBph_4$ with $[(C_6H_7)Fe(CO)_3]BF_4$ (12a) and $[(C_7H_9)Fe(CO)_3]BF_4$ (13) in water-hexane solvent system at 90°C, surprisingly, resulted in the formation of (5-p-biphenylylcyclohexa-1,3-diene)irontricarbonyl (106) and (5-p-biphenylylcyclohepta-1,3-diene)irontricarbonyl (107) in *ca.* 35-65% and 9% yields, respectively. The structure elucidation of the biphenylyl complex 106 was accomplished by the oxidative liberation of the free ligand, 5-p-biphenylyl-1,3-cyclohexadiene (108) in quantitative yield using ceric ammonium nitrate, followed by dehydrogenation to p-terphenyl using chloranil (Equation 3.4).



(3.4)

In view of the reports of the facile oxidation of Ph_4B^- by oxygen[82,83] as well as by a variety of metallic species,[84-87] to yield biphenyl and in view of the reported ability of the cationic complex 12a to react by electrophilic substitution with various benzenoid species,[25] a mechanism involving aromatic electrophilic substitution of biphenyl was of immediate concern (Mechanism I).

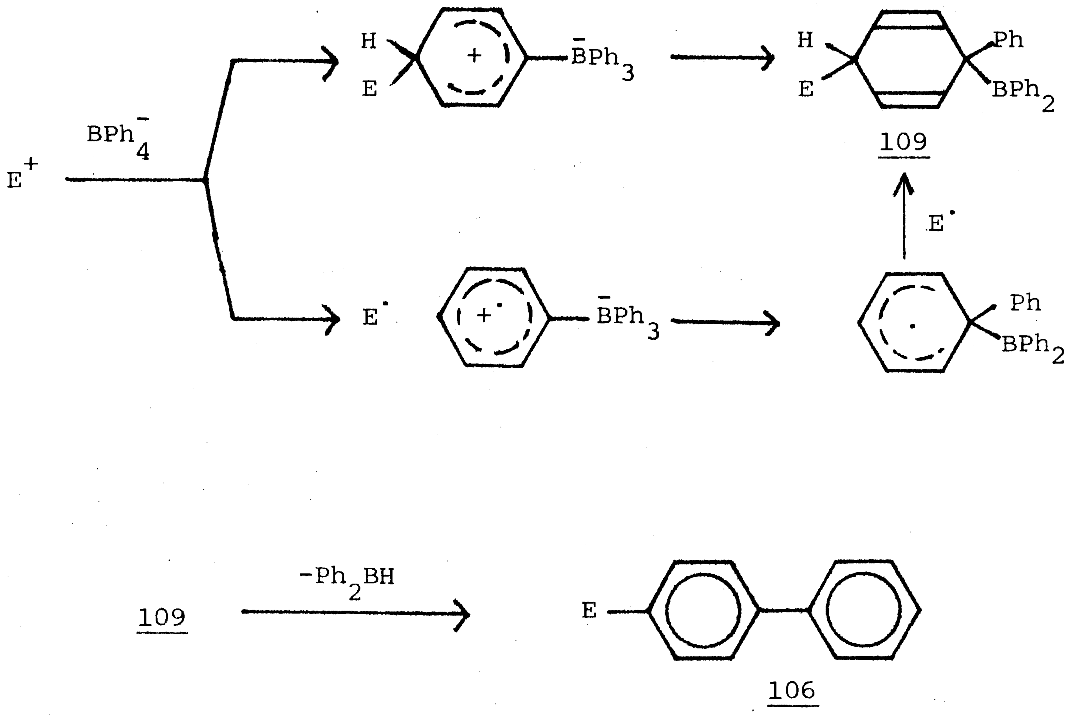
Mechanism I

$$\begin{tikzcd}[column sep=small] 12a\ + & \mathrm{Ph\text{-}Ph} \arrow[r] & 105 \\ & \mathrm{Ph_4B^-} \arrow[u, "\mathrm{ox.}"'] & \end{tikzcd}$$

However, such a mechanism was ruled out by the failure of the cationic complex 12a to react with biphenyl in either the water-hexane solvent system or acetonitrile.

A more tenable mechanistic pathway (Figure 18) involves an electrophilic attack by the cyclohexadienyl ring in 12a upon the phenyl group attached to boron in Ph_4B^- followed by intramolecular nucleophilic attack by another phenyl group[88] to give the E and Z isomers of 109, the net effect being what has been referred to[75,76] as "amphophilic substitution" of a phenyl group attached to boron. Syn-1,4-elimination of Ph_2BH from the Z-isomer of 109 or anti-1,4-elimination of Ph_2BH from the E-isomer of 109 would result in the formation of the observed biphenylyl complex 105. The formation of the intermediate complex 109 could also be explained in terms of free-radical mechanism[87] (Figure 19).

Mechanism II



$E = (C_6H_7)Fe(CO)_3$

Figure 19. Mechanism of Biphenyl Transfer to 12a From BPh_4^-

The amphophilic nature of the phenyl group of Ph_4B^- which results in biphenylyl transfer, is of interest in view of the alternate possibility of observing only electrophilic *ipso* or *para* attack on a phenyl group with subsequent deboronation which would result in phenyl rather than biphenylyl transfer.[89] There was, however, no evidence for the formation of (5-phenyl-1,3-cyclohexadiene)$Fe(CO)_3$, the expected product of phenyl transfer.

At the present time the biphenylyl transfer reaction appears to be limited to those π-complexed cations which are stable to the aqueous media used, since the use of non-aqueous, aprotic media such as THF or acetonitrile afforded complex mixtures of products.

CHAPTER IV

THE SIGNIFICANCE OF THE CURRENT FINDINGS

The preceding experimental investigations of the reactions of cationic π-enyl irontricarbonyl complexes with a variety of selected nucleophiles represents the only reasonably broad, systematic study undertaken so far. The outcome of the current exploratory study is extremely useful in understanding the nature of the reactions and revealed a host of new discoveries which were unexpected based on the knowledge of literature.

The Ring Size

For the first time an attempt has been made to study the effect of the coordinated organic ligand upon the chemical behavior of π-complexed transition-metal carbonyl cations. This was achieved by reacting a single anionic nucleophile, an azide ion, under similar conditions with a series of π-enyl irontricarbonyl cations in which the size of the π-complexed organic ring was varied while the rest of the molecule was kept constant.

Although all cyclic (pentadienyl)irontricarbonyl complexes would be expected to closely resemble one another in their reactions with a common nucleophile, the current findings suggest that the changes in the ring-size dramatically influence the magnitudes of the relative electrophilicities of the metal, the carbonyl carbon, and the organic ligand.

As a consequence, the chemistry of each (pentadienyl)irontricarbonyl cation is distinct. Formation of two types of dimeric complexes from the reactions of the analogous cyclohexadienyl and cycloheptadienylirontricarbonyl cations 12a and 13, respectively, with acetonitrile can also be attributed to the effect of ring-size of the coordinated organic ligand upon the chemical behavior of the cationic complex.

Role of the Metal

For the first time, the reactivity of a π-enyltricarbonyl complex containing a Group VI metal (molybdenum) has been compared with that containing a Group VIII metal (iron). The reactions of $[(\eta^7\text{-}C_7H_7)\text{-}Mo(CO)_3]BF_4$ (17b) and $[(\eta^5\text{-}C_7H_7)Fe(CO)_3]BF_4$ (16) with sodium azide as well as with Me_3SiN_3, suggest that the molybdenum complex 17b is much more susceptible to nucleophilic attack at the metal than the iron complex 16. The results also suggest that electron-transfer reactions at the metal are more likely to occur with a π-enyltricarbonylmolybdenum complex, e.g., 17b, than with an iron complex, e.g., 16.

Also in the present study, the possibility of involvement of axial and equatorial attack of the nucleophiles at the metal center in a π-enyl irontricarbonyl complex has been suggested, although experimental verification of such a supposition is not available.

Reactions With Aprotic Solvents

The formation of $(C_8H_8)Fe(CO)_3$ (37) from (bicyclo[5.1.0]octatrienyl)tricarbonyliron tetrafluoroborate (15); the formation of neutral products from $[(C_7H_7)Fe(CO)_3]BF_4$ in acetone (16), and the formation of the C-C and M-M bonded dimers 90 and 99 from the (cyclohexadienyl)irontricarbonyl cation 12a and the (cycloheptadienyl)irontricarbonyl cation 13, respectively, in CH_3CN in the absence of added nucleophiles were not documented prior to this study. They are representative of some of the idiosyncrasies of the respective cationic π-complexes.

Formation of Ring-Substituted Products

The results from the reactions of sodium azide with $[(C_6H_7)Fe(CO)_3]^+$ (12a), $[(C_7H_9)Fe(CO)_3]^+$ (13), $[(C_7H_7)Fe(CO)_3]^+$ (16) and $[(5.1.0\text{-}C_8H_9)Fe(CO)_3]^+$ (15) can be best explained in terms of competitive nucleophilic additions at the metal, the carbonyl carbon, and the organic ligand, leading to the formation of different final products. Thus exo-substitution on the ring appears to be the result of direct nucleophilic addition at the organic moiety. This is in direct contrast with the suggested initial addition of the azide ion to the metal in (cycloheptadienyl)irontricarbonyl cation 13 followed by rearrangement from metal to the ring to give the exo-substituted complex 58 (Equation 1.4); our reinvestigation of the reaction clearly questions the validity of such an assumption. The reactions of methoxide and t-butoxide ions with (cyclohexadienyl)irontricarbonyl cation 12a in the corresponding alcoholic solvents can also be best explained by competitive nucleophilic additions at the metal, the carbonyl carbon, and the organic moiety. This is also in direct contrast to the claim suggesting initial nucleophilic addition by methoxide ion at the carbonyl carbon in (cyclohexadienyl)irontricarbonyl cation 12a prior to the formation of the ring-substituted product 87 with exo-stereochemistry.

Solvent and Temperature Dependence of the Reactions

The most dramatic discovery of the current investigation is the solvent and temperature dependence of the reactions of (dienyl)irontricarbonyl complexes with oxyanions. For example, entirely different products were obtained when the reaction between $[(C_6H_7)Fe(CO)_3]^+$ (12a) and methoxide ion was carried out in protic as compared to aprotic solvents. Similarly, different products were obtained when the reaction between sodium azide and (bicyclo[5.1.0]octatrienyl)irontricarbonyl cation 15 was carried out in aqueous and non-aqueous solvents. Formation of predominantly ring-substituted products from the reactions of (cyclohexadienyl)irontricarbonyl cation with oxyanions in acetonitrile at low temperatures suggests variation of the relative electrophilicities of various sites on the cationic complex 12a with the reaction temperature. Such variation of the site of nucleophilic attack with reaction temperature has been demonstrated for the first time in the current investigation.

Electron-Transfer Reactions Versus Ionic Reactions

Formation of $(C_6H_8)Fe(CO)_3$ (98) and (5,5'-di-1,3-cyclohexa-1,3-diene)hexacarbonyldiiron (90) from the $[(C_6H_7)Fe(CO)_3]^+$ cation 12a and formation of (5,5'-dicycloheptadiene)hexacarbonyldiiron (99) from $[(C_7H_9)Fe(CO)_3]^+$ cation 13 in the reactions of the cations with acetonitrile at elevated temperatures suggests the ease of electron transfer reactions at the metal. Formation of the dimers $[(\eta^4\text{-}C_6H_7)Fe(CO)_3]_2$ (90) and $[(\eta^5\text{-}C_6H_7)Fe(CO)_2]_2$ (89) from the reactions of (cyclohexadienyl)irontricarbonyl cation 12a with nucleophiles $Y\text{-}O^-$ (Y=H, CH_3, $C(CH_3)_3$, $Si(CH_3)_3$) and Ph_3Si^- in aprotic solvents represents the first documentation of the formation of such dimers during nucleophilic additions. The observed dimerization also provides the first documentation of the involvement of electron-transfer reactions competitive with ionic coupling in the addition of anionic nucleophiles to (cyclohexadienyl)irontricarbonyl cation 12a. Discovery of the ability to suppress the former type of reactions either by bubbling oxygen through the reaction mixture or by the use of low reaction temperatures may prove of future help in enhancing the synthetic utility of the nucleophilic addition reactions with key oxyanions. The exclusive formation of ring-substituted products from the reaction of phenoxide ion with (cyclohexadienyl)irontricarbonyl cation 12a in acetonitrile suggests that electron-withdrawing substituents on the nucleophilic atom bearing the negative charge reduce the tendency of the anion to react with the cationic complex by electron-transfer.

Enhancement of the Synthetic Potential by the Use of Anion Synthons

In view of the extensive reductive coupling reactions of cyclic (dienyl)tricarbonyliron cationic complexes 12a and 13 with several anionic nucleophiles, the demonstrated use of anion synthons to transfer a nucleophile selectively to the organic ring is of great future help in the utilization of transition-metal π-complexed cations in organic synthesis. The demonstrated transfers of allyl and azido groups from allyltrimethylsilane and azidotrimethylsilane, respectively, to a cationic center (e g., 12a) in the absence of added anionic catalysts represent the first examples of the use of the respective organosilicon compounds as anion synthons. The behavior of tetraphenylboron anion, commonly regarded as an inert ion and used in the analysis of metals, as a biphenylyl anion synthon constitutes the first organic synthetic use of the anion and implies enormous synthetic potential for tetraarylboron anions.

CHAPTER V

EXPERIMENTAL

All reactions involving organometallic compounds were performed under either nitrogen or argon which had been passed through a drying column packed with molecular sieves (3A) and Drierite. The glassware was thoroughly dried in an oven (kept at 120°C) before assembly and allowed to cool under dry inert gas atmosphere. The reagent grade solvents were invariably deoxygenated by purging with argon before use. Acetonitrile and tetrahydrofuran were further dried with phosphorous pentoxide and either lithium aluminum hydride or sodium benzophenone ketyl, respectively, at continuous reflux and were freshly distilled just before use. Reagent grade acetone, dichloromethane and pentane were generally used after they were deoxygenated. However, when anhydrous and oxygen-free reaction conditions were demanded, the deoxygenated reagent grade acetone was dried over anhydrous potassium carbonate for several days. Dichloromethane was dried by distillation from calcium hydride. For chromatographic purposes activated acid-washed alumina (kept in oven at 300°C) and 60-200 mesh silica gel were generally used unless stated otherwise.

Melting points were obtained from a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton magnetic resonance spectra were taken on a Varian XL-100 (15) High Resolution NMR spectrometer, a Varian A60 NMR spectrometer, and a Hitachi Perkin-Elmer R-24B spectrometer with tetramethylsilane (TMS) used as an internal standard. ^{13}C spectra were obtained on the Varian XL-100 (15) NMR spectrometer equipped with a Nicolet TT-100 PFT accessory operating at 25.2 MHz. Infrared spectra were recorded on a Beckman-8A spectrometer. Low resolution mass spectra were obtained on a CEC 21-100B Double Focusing Mass spectrometer and high resolution mass spectra were obtained on a CEC21-110B mass spectrometer with NOVA Data Acquisition System. Elemental analysis was obtained from Chemalytics, Inc., Tempe, Arizona.

Preparations

Triphenylmethyl Tetrafluoroborate (1)[90]

Triphenylmethanol (9 g, 35 mmol) was dissolved in propionic anhydride (90 ml) with slight warming, and aqueous tetrafluoroboric acid (48%, 9 ml) was added dropwise to the warm solution until yellow solid began to precipitate. During the addition of the rest of the tetrafluoroboric acid, the temperature was maintained at 20°C. Triphenylmethyl tetrafluoroborate (1) was collected as a finely divided yellow solid (11 g, 95%), washed with anhydrous ether (3 x 50 ml), and stored under vacuum in a desiccator.

(Cyclohexa-1,3-diene)irontricarbonyl (98)

A mixture of 1,3-cyclohexadiene (10 g, 0.13 mol) and diironenneacarbonyl (21 g, 0.06 mol) in deoxygenated benzene (100 ml) was refluxed for 4 h. The reaction mixture was filtered and the solvent distilled *in vacuo*. The resulting yellow oil was chromatographed on activated acid-washed alumina. Elution of the light-yellow band with Skelly B, followed by removal of the solvent gave the complex $(C_6H_8)Fe(CO)_3$ as a yellow oil (6 g, 50%) mp 8-9°C; IR (pentane): 2040 s, and 1980 vs cm^{-1} (C≡O stretch); ^{1}H-NMR (CS_2): δ 5.2 (m, 2H, $H_{2,3}$), 3.18 (m, 2H, $H_{1,4}$) and 1.68 (bs, 4H, $H_{5,6}$); ^{13}G-NMR ($DCCl_3$): δ 85.3 (d, J_{CH}=160 Hz, $C_{1,4}$), 23.9 (t, J_{CH}=130 Hz, $C_{5,6}$) and 211.8 (s, Fe $(C{\equiv}O)_3$) ppm. The spectral data and physical constants agreed well with the reported data[91,20] for the complex.

(Cyclohexadienyl)irontricarbonyl Tetrafluoroborate (12a)[92]

To a magnetically stirred solution of $(C_6H_8)Fe(CO)_3$ (98) (6 g, 0.03 mol) in dichloromethane (30 ml), solid triphenylmethyl tetrafluoroborate (1) (9.5 g, 0.03 mol) was added and the stirring was continued for 30 min. The yellow crystalline precipitate (8 g, 91%) was collected and washed successively with dichloromethane and diethyl ether; mp 201-202°C (dec) (lit.[92] mp 190°C (dec)); IR (CH_3CN): 2110 s and 2060 vs cm^{-1} ($Fe(CO)_3$).

(Cycloheptadienyl)irontricarbonyl Tetrafluoroborate (13)[93]

The complex 13 was obtained by dropwise addition of a solution of aqueous tetrafluoroboric acid (48%) (3 ml) in propionic anhydride (6 ml) to a magnetically stirred solution of (cycloheptatriene)irontricarbonyl (1.5 g, 6.0 mmol) in propionic anhydride (6 ml) kept at 0°C. The mixture was stirred for 10 min and poured into anhydrous diethyl ether (150 ml). (Cycloheptadienyl)irontricarbonyl tetrafluoroborate (13) was collected as yellow crystalline solid (1.5 g, 71%) and washed with diethyl ether; mp 210-214°C (dec) (lit.[93] mp dec 150°C); IR(CH_3CN): 2110 s, 2060 vs and 1975 w cm^{-1} ($Fe(C\equiv O)_3$).

(2-Methyl-π-allyl)chloroirontricarbonyl (81; R=CH_3, X=Cl)[94]

Diironenneacarbonyl (23 g, 0.06 mol) and 2-methylallyl chloride (23 g, 0.26 mol) were stirred in Skelly B (100 ml) at 40-45°C for one hr. The dark brown reaction mixture was filtered and the filtrate concentrated to few ml (ca 10 ml). Cooling the concentrate to 0°C followed by filtration yielded (2-methyl-π-allyl)chloroirontricarbonyl (81) as yellow-brown crystals (3.6 g, 26%). Two crystallizations from pentane yielded the pure complex as golden-yellow crystals; mp 91-92°C (lit.[94] mp 91-92°C); IR (Pentane): 2100 s, 2050 vs and 2010 vs cm^{-1} ($C\equiv O$); ^{1}H-NMR(CS_2): δ 4.28 (s, 2H, syn $H_{1,3}$), 3.2 (s, 2H, anti $H_{1,3}$) and 2.0 (s, 3H, CH_3); ^{13}C-NMR ($DCCl_3$): δ 26.0 (q, CH_3, J_{CH}=161 Hz), 120.8 (s, C_2), 204.6 (s, $C\equiv O$) and 206.7 (s, $C\equiv C$); ppm mass spectrum m/e (rel. intensity): 230 (M^+), 194 (1), 174 (3), 167 (12), 146 (8), 139 (9), 111 (17), 55 (21), 39 (21) and 28 (100). The H^1-NMR and IR data agreed well with the reported data.[95,66]

(2-Methyl-π-allyl)irontricarbonyl Tetrafluoroborate (6b)[95]

To a magnetically stirred solution of (2-methyl-π-allyl)chloroiron tricarbonyl (0.5 g, 2.2 mmol) in dry tetrahydrofuran (20 ml) at 0°C, silver tetrafluoroborate (0.4 g, 2 mmol) dissolved in tetrahydrofuran (15 ml) was added, and the resulting solution was kept in the dark for 20 min. The precipitated silver chloride was collected and washed with additional tetrahydrofuran (25 ml). The solvent was removed from the filtrate *in vacuo* and the resulting yellow oil was subjected to high vacuum (0.005 mm Hg) to remove traces of the coordinated solvent. The crude product was washed with anhydrous ether to remove any unreacted starting material. The cationic complex, (2-methyl-π-allyl)irontricarbonyl tetrafluoroborate (6b) was obtained as a hygroscopic, fruity-smelling, bright-yellow solid (0.43 g, 70%); mp 120-122°C (lit. mp not reported); IR(KBr): 2080 s, 2010 vs ($Fe(CO)_3$) and 1620 w (C=C) cm^{-1}.

Tropylium Tetrafluoroborate (4)

Triphenylmethyl tetrafluoroborate (34 g, 0.1 mol) was dissolved in dichloromethane (200 ml), and cycloheptatriene (10 g, 0.11 mol) was added dropwise over a period of 2 h. The reaction mixture was magnetically stirred for one hour at room temperature. The white microcrystalline precitate (18 g, 98%) of tropylium tetrafluoroborate (4) was collected, washed with ether; mp 260-262°C (dec) (lit.[5] mp 264°C (dec). The crude product was used in the next step without further purification.

7-Methoxycycloheptatriene[96]

Sodium methoxide (6 g, 0.11 mol) was dissolved in methanol (100 ml); the solution was cooled to 15-20°C. Solid tropylium tetrafluoroborate (4) (17 g, 0.1 mol) was added to the cooled, stirred solution in small batches. The reaction was highly exothermic and a fine, silky white precipitate of sodium tetrafluoroborate separated after the reaction mixture had been stirred for 45 min at room temperature. Pentane (100 ml) was added to the reaction mixture, and the organic layer was washed with distilled water (4 x 75 ml). The aqueous extracts were reextracted with pentane (4 x 25 ml), and the organic extracts were combined and dried over anhydrous magnesium sulfate. Removal of pentane in vacuo, followed by vacuum distillation (44°C, 7 mm Hg) of the crude yellow product (11 g, 95%) yielded pure 7-methoxycycloheptatriene as a colorless liquid; ^{1}H-NMR (CS_2): δ 3.15 (m, 1H, H_7), 3.25 (s, 3H, OCH_3), 5.25 (dd, 2H, $H_{1,6}$), 6.06 (dm, 2H, $H_{2,5}$) and 6.5 (t, 2H, $H_{3,4}$); ^{13}C-NMR ($DCCl_3$): δ 56.2 ($-OCH_3$), 77.8 (C_7), 122.8 (C_1, C_6), 126.0 (C_2, C_5) and 130.7 (C_3, C_4) ppm. The ^{1}H-NMR spectrum and physical properties agreed with the literature data[96].

(7-Methoxycycloheptatriene)irontricarbonyl (110)[62]

Diironenneacarbonyl (5.4 g, 18 mmol) and 7-methoxycycloheptatriene (2 g, 16 mmol) were mixed in benzene and refluxed for 6 h. The reaction mixture was filtered and the solvent removed in vacuo. The extremely air-sensitive and thermally unstable dark-red oily product mixture was heated under vacuum (0.005 mm Hg) at 45°C for 4 h to remove unchanged free ligand. Attempts to separate (7-methoxycycloheptatriene) irontricarbonyl (110) into its exo and endo isomers and to remove (bis(π-allyl)-7-methoxycycloheptatriene)diironhexacarbonyl by column chromatography (silica gel or alumina) failed owing to the reaction of the adsorbents with the complexes. The ^{1}H-NMR spectra of the eluted fractions did not indicate the presence of methoxyl groups which were present before the crude mixture was subjected to the chromatographic techniques. However, the product mixture could be separated by column chromatography using a charcoal-celite (1:4) column. Unfortunately, chromatography using this column proved to be very tedious and time-consuming. Attempts to obtain the pure (tropylium)irontricarbonyl tetrafluoroborate (16) from the crude product mixture without ever isolating (7-methoxycycloheptatriene)irontricarbonyl (110) proved to be successful as described below. The ^{13}C-NMR analysis of the product mixture suggests the following data for (7-methoxycyloheptatriene)irontricarbonyl. ^{13}C-NMR ($DCCl_3$): δ 54.0 (C_1), 56.6 ($O-CH_3$), 63.5 $C_4(C_1)$, 71.80 (C_7), 83.3 $C_2(C_3)$, 94.0 ($C_3(C_2)$, 125.5 (C_6) and 130.8 (C_5) ppm.

(Tropylium)irontricarbonyl Tetrafluoroborate (16)[62]

The product mixture (0.93 g) from the above reaction and aqueous tetrafluoroboric acid (48%, 1 ml) were separately dissolved in propionic anhydride (10 ml and 5 ml, respectively), and the two solutions were mixed at 0°C. Occasionally the reaction was very exothermic. Instantaneous precipitation of a yellow solid upon mixing the reactants occurred. The yellow crystalline solid (0.3 g) was collected, washed with propionic anhydride (10 ml) followed by diethyl ether (50 ml) and dried; mp 110°C (lit.[62] mp 112°C).

(Bicyclo[5.1.0]octatrienyl)irontricarbonyl Tetrafluoroborate (15)[97,98]

(Cyclooctatetraene)irontricarbonyl (37) (3 g, 0.012 mol) in acetic anhydride (20 ml) was treated with aqueous tetrafluoroboric acid (48%, 10 ml) in ice-cold acetic anhydride (25 ml). The color of the mixture immediately changed from dark red to pale yellow. The reaction mixture was immediately poured into diethyl ether (300 ml). The yellow precipitate was collected by filtration and dried under vacuum to give pale-yellow crystals of the cationic complex 15; mp 150°C (dec) (lit.[96] mp 150°C (dec).

Although the cationic complex 15 is stable for several days at room temperature, samples of 15 kept in refrigerator at 0°C over a period of five to six months contained small amounts (~7%) of $C_8H_8Fe(CO)_3$ (37) mixed with the cationic complex.

Reactions of Sodium Azide With π-Complexed Cations

The general procedure involved addition of sodium azide to a solution of the π-complexed cation in the chosen solvent. The progress of the reaction was monitored by obtaining IR spectra at regular intervals. Upon completion of the reaction the solvent was removed *in vacuo*, the neutral products taken up in pentane, and the crude product was subjected to purification techniques.

With (Cyclohexadienyl)irontricarbonyl Tetrafluoroborate (12a)

The general procedure was followed by stirring 0.2 g (0.65 mmol) of the complex 12a and 0.082 g (1.26 mmol) of sodium azide in 20 ml reagent grade acetone for 22 h at room temperature. Th IR absorption bands at 2110 and 2060 cm^{-1} characteristic of 12a disappeared with a concomitant rapid growth of new peaks at 2085, 2040 and 1985 cm^{-1}. The color of the reaction mixture changed from bright yellow to pale yellow in about an hour, pale yellow to dark red in about 4 h and from clear dark red to dark brown in about 10 h. During and after the formation of the brown color, deposition of brown solid from the reaction mixture was observed. IR spectra taken after 90 min did not show any further changes. Filtration and workup of the reaction mixture yielded 0.15 g (92%) of impure (exo-5-azidocyclohexa-1,3-diene)irontricarbonyl (56) as a yellow oil. After vacuum sublimation (27°C, 0.005 mm Hg) of the crude product onto a cold finger kept at -78°C (Dry Ice-acetone), the pure azido complex 56 was obtained as a pale-yellow crystalline solid; mp 31-32°C; IR (Pentane): 2085 s (-N_3, ν_{asym}), 2045 s and 1985 vs (Fe(CO)$_3$ cm^{-1}; ^{1}H-NMR (CS_2): δ 1.52 (dt, 1H, $H_{6,exo}$), 2.26 (m, 1H, $H_{6,endo}$), 2.98 (m, 2H, $H_{1,4}$), 3.8 (dt, 1H, H_5) and 5.28 (m, 2H, $H_{2,3}$); ^{13}-C-NMR ($DCCl_3$): δ 30.7 (t, J_{CH}=132 Hz, C_6), 59.5 (d, J_{CH}=151 Hz, $C_4(C_1)$), 58.2 (d, J_{CH}=158 Hz, $C_1(C_4)$), 56.1 (d, J_{CH}=165 Hz, C_5), 87.3 (d, J_{CH}=174 Hz, $C_3(C_2)$) and 84.1 (d, J_{CH}=174 Hz, $C_2(C_3)$) ppm; mass spectrum m/e (rel. intensity): 261 (5, M^+), 233 (6), 203 (2), 177 (14), 134 (9), 122 (3), 103 (3), 93 (40), 78 (100) and 66 (50); Anal. calcd for $C_9H_7FeN_3O_3$: C, 41.41; H, 2.71; N, 16.1. Found: C, 41.37; H, 2.64; N, 13.97.

TLC (silica gel) analysis (eluent Skelly B) of the progress of the reaction suggested the initial formation of only the azido complex 56 (R_f = 0.63). During the formation of the red color another component with an R_f value of 0.90 was formed. When the red color was replaced by a dark brown color, only one component with an R_f value of 0.67 could be detected. The R_f value for (exo-5-azidocyclohexadiene)irontricarbonyl (56) under similar conditions was 0.6.

When the reaction between sodium azide and 12a was performed in acetone dried with anhydrous potassium carbonate, the color changes and IR spectral changes during the progress of the reaction were the same as those observed for the reaction in reagent grade acetone. However, the red color lasted longer under dry conditions and dissipated quickly upon addition of few milliliters of water to the reaction mixture. Product analysis of the reaction suggested a complicated mixture of products. The IR spectra of the partially separated fractions possessed absorptions at 2200, 2120, 1960, 1700 and 1600 cm^{-1} besides the absorption bands due to the exo-azido complex 56; ^{1}H-NMR spectra of the partially separated fractions exhibited additional proton signals at 6.94 (t), 6.48 (t) and 6.28 (d) in the intensity ratio 2:1:2; at 5.3 (m), 3.33 (m) and 3.15 (m) in the ratio 2:1:2 and also at 3.84 (m), 2.04-2.4 (m), and 0.9-1.6 (m), the intensity of which could not be computed.

Among the several reaction products obtained from the reaction in dry acetone, 2-hydroxy-2-methyl-4-pentanone (57) was invariably found in trace amounts. The ketone 57 was separated from the product mixture in vacuo (0.005 mm Hg, 27°C); IR (film): 3400-3600 vs, 2920 s and 1700 vs cm^{-1}; ^{1}H-NMR (CS_2): δ 1.22 (s, 6H), 2.15 (s, 3H), 2.58 (s, 2H), 3.94 (s, 1H); ^{13}C-NMR ($DCCl_3$): δ 209.6 (s, C_4), 69.4 (s, C_2), 54.5 (t, J_{CH}=125 Hz, C_3), 31.8 (q, J_{CH}=125 Hz, C_5), 29.4 (q, J_{CH}=125 Hz, C_1 and CH_3) ppm. The ^{1}H-NMR and IR data for the ketone 57 agreed exceeding well with the published data. The residue left after the removal of the ketone 57 was extracted with dichloromethane; the extracts filtered, and hexane added to the filtrate. The dark-red viscous oil which precipitated upon addition of hexane possessed a strong IR absorption band at 2220 cm^{-1}. Attempts to obtain the proton nmr spectrum of the dark-red viscous material failed. Nevertheless, the data suggested the isocyanate structure 61 for the red viscous material. The solution of pentane-soluble products left after the separation of the dark-red oils possessed IR absorption at 2120, 2080, 2030-2060, 1980-2000 and

1600 cm^{-1}. Chromatography of the solution either on alumina or silica-gel column made in Skelly B yielded only (exo-5-azidocyclohexadiene)-irontricarbonyl (56).

When the reaction between sodium azide (0.13 g, 2.0 mmol) and 12a (0.3 g, 1.0 mmol) was conducted in dichloromethane (30 ml) freshly distilled from P_2O_5, the color of the reaction mixture remained yellow throughout the entire reaction period (22 h), and (exo-5-azidocyclohexadiene)irontricarbonyl (56) was the only product detected and isolated. Exo-5-azidocyclohexa-1,3-diene)irontricarbonyl (56) (0.16 g, 0.62 mmol) upon reaction with triphenylmethyl tetrafluoroborate (1) (0.19 g, 0.58 mmol) in dichloromethane (8 ml) instantaneously yielded the yellow precipitate (0.15 g, 84%) of (cyclohexadienyl)irontricarbonyl tetrafluoroborate (12a), which was identified by IR spectroscopy and mixture-melting-point with authentic 12a. A light-yellow solid was obtained from the filtrate obtained in the preceding step. Extraction of the yellow solid with pentane followed by recrystallization of the resulting solid from the same solvent yielded trityl azide; mp 54-57°C (dec) (lit.[99] mp 60-63°C dec); IR (CH_2Cl_2): 2100 cm^{-1} (N_3, ν_{asym}). The data obtained for the trityl azide agreed well with the published data.[99]

With (Cycloheptadienyl)irontricarbonyl Tetrafluoroborate (13)

The reaction between 13 (0.3 g, 1.0 mmol) and sodium azide (0.065 g, 1.0 mmol) in reagent grade acetone (25 ml) led to the same color and spectral changes during the reaction period (18 h) as those observed in the preceding reaction in acetone. After the usual workup (exo-5-

azidocyclohepta-1,3-diene)irontricarbonyl (58) was obtained as a yellow oil (0.23 g, 86%) contaminated with trace amounts of 2-hydroxy-2-methyl-4-pentanone (57) and unidentified azido complexe(s). The ketone 57 was separated from the crude product *in vacuo*. Pure (*exo*-5-azidocycloheptadiene)irontricarbonyl (58) was obtained as a yellow oil from the residue by vacuum distillation (0.005 mm Hg, 44°C) onto a cold-finger kept at -78°C (Dry Ice-acetone) IR (Pentane): 2085 (N_3, ν_{asym}), 2040 and 1980 ($Fe(CO)_3$) cm^{-1}; ^{1}H-NMR (CS_2): δ 5.3 (m, 2H, $H_{2,3}$), 3.6 (dd, 1H, H_5), 2.8-3.1 (m, 2H, $H_{1,4}$) and 1.0-2.2 (m, 4H, $H_{6,7}$); ^{13}C-NMR ($DCCl_3$): δ 27.8 ($C_7(C_6)$), 28.9 ($C_6(C_7)$), 56.4 (C_5), 58.8 ($C_1(C_4)$), 62.6 ($C_4(C_1)$), 86.8 ($C_2(C_3)$), 89.6 ($C_3(C_2)$) and 210.2 ($Fe(CO)_3$) ppm. The IR and ^{1}H-NMR spectra for the *exo*-azido complex 58 agreed well with the published data.[51]

The IR and ^{1}H-NMR spectra of the minor organometallic product(s) were similar to those of the major product, suggesting the isomeric nature of the products. The ^{1}H-NMR spectrum of the product mixture containing the major and the minor products possessed a multiplet centered at 5.5 δ which was ascribed to the minor component(s). The fully decoupled ^{13}C-NMR spectrum of the minor product(s) possessed the following signals: ^{13}C-NMR ($DCCl_3$): δ 210.5 ($Fe(CO)_3$), 120-140, 89.3, 87.9, 61.7, 55.8, 55.5, 51.2, 33.5, 30.0, 29.6, 22.4 and 14.1 ppm. The data suggested that (*endo*-5-azidocyclohepta-1,3-diene)irontricarbonyl (63) was the major component in a mixture of possibly three minor products; the other two possible components are (η^3-cycloheptadienyl)azidoirontricarbonyl (59) and (*exo*-2-azido-η^3-cycloheptadienyl)irontricarbonyl. The minor products were extremely air-sensitive and thermally unstable even at 0°C. They were yellow immediately after isolation, but turned red upon standing, and finally decomposed to brown iron oxides.

When the progress of the reaction between 13 and sodium azide in acetone was monitored by TLC (silica gel) with Seklly B as the eluent, bands with R_f values at 0.61 and 0.84 were observed prior to formation of the red color (1.5 h). Attempts to isolate the red material by stopping the reaction when the red color appeared to reach maximum intensity (three hours) were unsuccessful.

The reported reaction between 13 and sodium azide in dichloromethane was reinvestigated by magnetically stirring a suspension of 0.3 g (1.0 mmol) of the cationic complex 13 and 0.065 g (1.0 mmol) of sodium azide in 25 ml of dichloromethane for 40 min (the reported time period for the completion of the reaction was 30 min). The reaction mixture was yellow throughout the reaction period and did not turn red as claimed. The IR spectral changes purportedly observed during the progress of the reaction also were not detected. Workup of the reaction after the stated period led to 92% (0.28 g) recovery of the unchanged cationic complex 13, identified by its IR spectrum and melting point. The IR spectrum of the pentane solubles (5 mg) did not suggest the presence of any metal-carbonyl complex. When the same reaction was monitored by TLC (silica gel) over a period of 4h, a major band with an R_f value of *ca.* 0.5 and a minor band with an R_f value of *ca.* 0.80 were detected at all times.

With (Tropylium)irontricarbonyl Tetrafluoroborate (16)

The general procedure was followed; a suspension of the tropylium complex 16 (0.1 g, 0.3 mmol) and sodium azide (0.02 g, 0.3 mmol) in freshly distilled anhydrous THF at room temperature was magnetically stirred for 5h. Slow appearance of IR absorption bands at 2085, 2045 and 1985 cm^{-1} was observed during the progress of the reaction. The reaction was judged to be complete when the yellow suspended solid was replaced by a clear, pale-yellow solution. Upon workup, (exo-7-azido-cycloheptatriene)irontricarbonyl (67) was isolated exclusively as an air-sensitive yellow oil (0.08 g, 90%). IR (Pentane): 2085, 2045 and 1985 cm^{-1}; ^{1}H-NMR ($DCCl_3$): δ 2.78 (m, 1H, H_1), 3.0 (m, 1H, H_4), 4.02 (t, 1H, H_7), 4.98 (ddm, 1H, H_6), 5.66 (m, 2H, $H_{2,3}$), 6.0 (m, 1H, H_5); ^{1}H-NMR (acetone-d_6): δ 3.0 (m, 1H, H_1), 3.2 (m, 1H, H_4), 4.18 (t, 1H, H_7), 5.02 (ddd, 1H, H6), 5.9 (m, 2H, $H_{2,3}$) and 6.1 (m, 1H, H_5); ^{13}C-NMR ($DCCl_3$): δ 52.8 (C_1(C_4)), 57.0 (C_4(C_1)), 65.0 (C_7), 88.2 (C_2(C_3), 97.2 (C_3(C_2)), 121.4 (C_6) and 134.6 (C_5) ppm. The crude (7-azido-cycloheptatriene)irontricarbonyl (67) (0.07 g, 0.25 mmol) obtained in the preceding reaction, when allowed to react with $(Ph_3C)BF_4$(1) (0.08 g, 0.25 mm) in dichloromethane at 0°C for 25 min as described elsewhere, yielded $[(C_7H_7)Fe\text{-}(CO)_3]BF_4$ (16) (0.06 g, 70%) and trityl azide (0.03 g, 45%).

With (Bicyclo[5.1.0]Octatrienyl)irontricarbonyl Tetrafluoroborate (15)

i. In Non-Aqueous Solvents. A mixture of the cationic complex 15 (0.3 g, 0.9 mmol) and sodium azide (0.055 g, 0.9 mmol) in acetone was stirred magnetically for 3h. The color of reaction mixture turned from yellow to red during the reaction period. The color change was accompanied by rapid disappearance of the IR bands characteristic of the cationic complex 15 and rapid appearance of new bands at 2030 and 1985

cm^{-1}. A weak IR band at 2085 cm^{-1} could also be detected during the progress of the reaction. Upon workup, a dark-red crystalline solid was obtained. The crude product was chromatographed on an alumina column; elution with hexane yielded two bands. The major band was red and was eluted first, closely trailed by a minor yellow band. The first band yielded a red crystalline solid (0.11 g, 51%) which was identified as (cyclooctatetraene)irontricarbonyl (37); mp 89-91°C (lit.[100] mp 93-95°C); IR (Pentane): 2055 and 1990 cm^{-1}; ^{1}H-NMR (CS_2): δ 5.16; ^{13}C-NMR ($DCCl_3$): δ 99.7 ppm. The data obtained for $(C_8H_8)Fe(CO)_3$ agreed exceedingly well with the published data.[100] The second band yielded a small amount of yellow solid contaminated with $(C_8H_8)Fe(CO)_3$ (37). mp 85-90°C; IR (Pentane): 2080, 2045 and 1990 cm^{-1}; ^{1}H-NMR ($DCCl_3$): δ 5.8-6.2 (m, 2H), 5.1-5.5 (m, 2H), 3.24 (m, 3H) and 2.05 (dm, 2H); ^{13}C-NMR ($DCCl_3$): δ 30.6, 56.7, 58.6, 58.8, 86.6, 92.3, 117.9 and 135.2 ppm; mass spectrum: m/e (rel. intensity) 287 (M^+), 259, 245, 231, 216, 203, 175, 161, 149, 135 (92), 121 (95), 105 (100) and 91. The available data suggested (endo-1-azido-2,4,7-cyclooctatriene)irontricarbonyl (69) or (endo-1-azido-2,4,6-cyclooctatriene)irontricarbonyl (70) as possible structures for the minor component.

The reaction between sodium azide (0.055 g, 0.9 mmol) and 15 (0.3 g, 0.9 mmol) when performed in anhydrous THF (30 ml) at room temperature for 7h led to the formation of $(C_8H_8)Fe(CO)_3$ (37) as the major product and the (azidocyclooctatriene)irontricarbonyl complex 69 or 70 as the minor product. The ratio $(C_8H_8)Fe(CO)_3$ (37)/$(C_8H_9N_3)Fe(CO)_3$ (69 or 70) was approximately 0.7 as estimated from the analysis of the ^{1}H-NMR spectrum of the product mixture. The same reaction at 0°C for 24 h yielded a ratio of 0.15.

ii. Aqueous Solvents. The reaction between sodium azide (0.1 g, 1.5 mmol) and the cationic complex 15 (0.5 g, 1.5 mmol) in a two-phase water-pentane solvent system (60 ml, 1:2 v/v) at $0^{\circ}C$ for 30 min yielded a third product in addition to the two products obtained in the preceding reaction in aprotic solvents. The new product possessed IR absorptions at 2085, 2045 and 1995 cm^{-1} and proton signals expected for (exo-2-azidobicyclo[5.1.0]cycloocta-3,5-diene)irontricarbonyl (68). When the reaction was carried out at $-20^{\circ}C$ in a solvent system consisting of aqueous acetone (1:1 v/v; 35 ml) and pentane (50 ml) for 2.5h, (exo-2-azidocyclo[5.1.0]octa-3,5-diene)irontricarbonyl (68) was obtained as an yellow solid (92%) which was recrystallized from pentane; mp 61-63$^{\circ}C$; ^1H-NMR: δ 0.1 (q, 1H, H_8), 0.78 (m, 1H, H_1), 1.6 (m, 1H, H_7), 3.0 (tm, 1H, $H_6(H_3)$), 3.6 (t, 1H, $H_3(H_6)$), 4.35 (tm, 1H, H_2) and 5.0-5.5 (m, 2H, $H_{4,5}$). In view of the instability of the bicyclic azido complex 68, additional data for the structural assignment such as ^{13}C-NMR, mass spectrum and elemental analysis could not be obtained. However, the assignment of the proton signals was made by comparison with the published spectra[49] of the analogous bicyclic complexes.

With (2-Methyl-π-allyl)irontricarbonyl Tetrafluoroborate (6b)

To a magnetically stirred solution of the π-allyl complex 6b (0.1 g, 0.35 mmol) in acetone (dried over anhyd. K_2CO_3) at $0^{\circ}C$, an equivalent amount of sodium azide was added. The crude product obtained from the workup, was extracted with pentane (40 ml) and filtered. The filtrate was concentrated and cooled to $-20^{\circ}C$. Air-sensitive, bright-yellow crystals of (2-methyl-π-allyl)azidoirontricarbonyl (80) (0.01 g, 9%)

were obtained, mp 68-69°C.

IR (Pentane): 2100s, 2050 vs and 2010s ($Fe(CO)_3$), 2030s ($-N_3$, ν_{asym}) cm^{-1}; ^1H-NMR ($DCCl_3$): δ 1.96 (s, 3H, $\underline{CH}_3$), 2.65 (s, 2H, <u>anti</u> $H_{1,3}$) and 4.3 (s, 2H, <u>syn</u> $H_{1,3}$); ^{13}C-NMR ($DCCl_3$): δ 26.5 ($\underline{CH}_3$), 67.5 $C_{1,3}$), 121.0 (C_2) and 204.9 ($Fe(CO)_3$) ppm; mass spectrum (m/e, rel. intensity): 237 (M^+, <1), 209 (<1), 195(12), 167(47), 139(35), 111(100), 95(29), 71(73), 55(82), 56(75) and 39(80).

With (Tropylium)molybdenumtricarbonyl Tetrafluoroborate 17b)

To a magnetically stirred solution of the molybdenum complex <u>17b</u> (0.25 g, 0.7 mmol) in distilled water (25 ml), an equivalent amount (0.05 g) of sodium azide was added, and the stirring was continued for 30 min. The dark-green reaction mixture was extracted with ether (250 ml) followed by dichloromethane (50 ml). The organic extracts were dried over anhyd. Na_2SO_4, and the solvents were removed <u>in vacuo</u>. A green solid was obtained from both the extracts.

The green solid from the dichloromethane extract was dissolved in a minimum amount of dichloromethane and hexane was added. Fine, green needles of (cycloheptatrienyl)isocyanatomolybdenumdicarbonyl (<u>85</u>) (0.02 g, 10%) precipitated, mp 138-139°C; IR (CH_2Cl_2): 2220 vs, 2020s and 1975s cm^{-1}; ^1H-NMR ($DCCl_3$): δ 5.4(s), (acetone-d_6): δ 5.6(s). The "green complex <u>83</u>" was obtained from the supernatant solution and decomposed above 110°C over a wide range. IR(CH_2Cl_2): 2070w, 1860s and 1700s cm^{-1}. Attempts to obtain the ^1H-NMR spectrum of the "green complex <u>83</u>" failed. The "green complex <u>83</u>" was highly unstable in solution and decomposed to a green amorphous solid.

The green solid (55 mg) obtained from the ether extract was reextracted with pentane. Upon filtration and removal of the solvent from the pentane extract a greenish-yellow glue was obtained. IR(Pentane): 2080 vs, 2020w and 1980 vs cm^{-1}; ^{1}H-NMR (CS_2): δ 6.6 (t, 2H), 6.15 (dt, 2H), 5.15 (dm, 2H) and 4.1 (t, 1H). The gluey material (24 mg) was dissolved in dichloromethane (5 ml) and the solution was cooled to 0°C. An equivalent amount of trityl tetrafluoroborate (1) was separately dissolved in dichloromethane (2 ml) and the solution was cooled to 0°C. The two solutions were mixed at 0°C and the reaction mixture was stirred magnetically for 30 min. Instantaneous precipitation was not observed as seen earlier (*vide infra*). However, the IR spectra taken during the progress of the reaction suggested the formation of trityl azide and the cationic complex 17b. Removal of the solvent *in vacuo* followed by extraction of the residue with pentane yielded trityl azide identified by its melting point and IR spectrum.

Solvent Interactions of (Bicyclo[5.1.0]Octatrienyl)-irontricarbonyl Tetrafluoroborate (15)

Solutions of the bicyclic π-complexed cation 15 (0.1 g, 0.03 mmol) in each of the solvents acetone, dichloromethane, acetonitrile and THF were stirred magnetically and the reaction was followed by IR. The color of the reaction mixture gradually changed from yellow to red. The IR absorption bands characteristic of the (diene)irontricarbonyl complexes gradually appeared at the expense of bands due to the cationic complex 15. Removal of the solvent, followed by extraction with pentane yielded $(C_8H_8)Fe(CO)_3$ (37) as the sole neutral complex. The results are presented in Table I.

Reactions of Oxy-anions With $[(C_6H_7)Fe(CO)_3]BF_4$ (12a)

Reactions of oxy-anions with 12a in CH_3CN were carried out by one addition of an equivalent amount of the oxy-anion to a stirred solution of 12a (0.453 g, 1.5 mmol) in 35 ml freshly distilled acetonitrile kept at the specified temperature (Table II). The resulting heterogeneous mixture was stirred for the time period required as judged from the IR spectra obtained at regular intervals during the progress of the reaction. The residue left after removal of acetonitrile *in vacuo*, was first extracted with pentane (50-75 ml) followed by dichloromethane (20-25 ml). The pentane extract was chromatographed on a silica gel column. The sequence of the eluants used during the chromatography was Skelly B, benzene and ether. The results of the additions of various oxyanions to 12a in CH_3CN are presented in Table II.

The reactions of potassium hydroxide, sodium methoxide, potassium *tert*-butoxide and sodium trimethylsilanolate with 12a in CH_3CN led to rapid development of a red color, accompanied by the appearance of new IR absorption bands at *ca*. 2040, 1970-1990 and 1755 cm^{-1}. Upon workup a yellow oil was obtained from the pentane extract and a dark-red, slimy crystalline solid from the dichloromethane extract. The red crystalline solid was identified as bis(η^5-cyclohexadienyl)diirontetracarbonyl ("M-M dimer 89"), mp > 155°C (dec.) (lit.[19] mp 165°C dec.) IR (CH_2Cl_2): 2045w, 1975 vs and 1755 cm^{-1}. Attempts to obtain the ^1H-NMR spectrum of the M-M dimer 89 failed owing to the instability of the complex in solution.

Chromatography of the yellow oil obtained from the pentane extract, upon elution with Skelly B, yielded light-yellow crystals of (5,5'-

dicyclohexa-1,3-diene)diironhexacarbonyl ("C-C dimer" 90). The C-C dimer 90 was recrystallized from pentane, mp 120-121°C (lit.[20] mp 120-122°C and 165-168°C[101]); IR(hexane): 2040 and 1985 cm^{-1}; ^{1}H-NMR (CS_2): δ 5.32 (m, 4H, $H_{2,3}$, $H_{2',3'}$), 2.98 (m, 4H, $H_{1,4}$, $H_{1',4'}$), 1.56-1.98 (m, 4H, $H_{5,5'}$, $H_{6,6'\ endo}$), 0.98-1.38 (m, 2H, $H_{6,6'\ exo}$); ^{13}C-NMR ($DCCl_3$): δ 27.9 (t, J_{CH} 130 Hz, $C_6(C_{6'})$), 28.7 (t, J_{CH} 130 Hz, $C_{6'}$ (C_6)), 59.5 (d, J_{CH}=160 Hz, $C_1(C_{1'})$), 59.7 (d, J_{CH}=160 Hz, $C_{1'}(C_1)$), 64.4 (d, J_{CH}=160 Hz, $C_4(C_{4'})$), 64.7 (d, J_{CH}=170 Hz, $C_{4'}(C_4)$), 85.0 (d, J_{CH}=170 Hz, C_2, $C_{2'}$, C_3, $C_{3'}$, 45.6 (d, J_{CH}=140 Hz, $C_5(C_{5'})$, 46.0 (d, J_{CH}=140 Hz, $C_{5'}(C_5)$), 27.9 (t, J_{CH}=130 Hz, $C_6(C_{6'})$, 28.7 (t, J_{CH}=130 Hz, $C_{6'}(C_6)$ ppm; mass spectrum; m/e (rel. intensity), 438 (M^+,3), 409(15), 382(18), 380(15), 352(35), 324(29), 296(41), 267(59), 240(6), 219(88), 210(35), 191(71), 162(41), 134(100) and 111(29).

The second yellow band obtained by elution with a 1:1 Skelly B/benzene mixture yielded impure (5,5'-oxy-dicyclohexadiene)diironhexacarbonyl (92) as an yellow oil which crystallized slowly in a refrigerator. Recrystallization from pentane afforded a pure sample of the ether complex 92, mp 104-105°C (lit.[58] mp 104°C); IR(hexane): 2040, 1980 and 1945 cm^{-1}; ^{1}H-NMR(CS_2): δ 5.4 (m, 4H, $H_{2,3}$, $H_{2',3'}$), 3.8 (dt, 2H, $H_{5,5'}$), 2.82 (m, 4H, $H_{1,4}$, $H_{1',4'}$), 2.14 (m, 2H, $H_{6,6'\ \underline{endo}}$) and 1.2-1.6 (m, 2H, $H_{6,6'\ \underline{exo}}$); ^{13}C-NMR($DCCl_3$): δ 31.3 (t, J_{CH}=130 Hz, $C_6(C_{6'})$), 31.9 (t, J_{CH}=130 Hz, $C_{6'}(C_6)$), 55.4 (d, J_{CH}=165 Hz, $C_{1'}(C_1)$), 55.6 (d, J_{CH}=160 Hz, $C_1(C_{1'})$), 60.6 (d, J_{CH}=165 Hz, $C_4(C_{4'})$, 60.7 (d, J_{CH}=165 Hz, $C_{4'}(C_4)$), 75.8 (d, J_{CH}=145 Hz, $C_5(C_{5'})$), 75.3 (d, J_{CH}=145 Hz, $C_{5'}(C_5)$), 84.7 (d, J_{CH}=175 Hz, $C_{2,2'}(C_{4,4'})$) and 87.1 (d, J_{CH}=175 Hz, $C_{4,4'}(C_{2,2'})$), ppm.

The third band, eluted from the column with a benzene-ether mixture, was a colorless oil. Recrystallization of the oil from pentane, gave white, flat, needle-like crystals of (5-hydroxycyclohexa-1,3-diene)-irontricarbonyl (91), mp 50-51°C, (lit.[20] mp 50-51°); IR(hexane): 3610(OH), 2040s, 1980 vs, and 1945s ($Fe(CO)_3$) cm^{-1}; ^1H-NMR($DCCl_3$): δ 5.5 (m, 2H, $H_{2,3}$), 3.92 (m, 1H, H_5), 2.92 (m, 2H, $H_{1,4}$), 2.26 (m, 1H, $H_{6,endo}$) and 1.22-1.58 (m, 2H, $H_{6,exo}$ and OH). The melting point and ^1H-NMR spectrum agreed well with those reported for the 5-hydroxycyclohexa-1,3-diene complex 91 obtained by the reduction of (cyclohexadienone)irontricarbonyl.[20] The proton signal at 3.92 δ assigned to H_5 suggests endo-substitution on the ring.

The pale-yellow, fourth band, eluted with ether, was a light-yellow oil. Recrystallization from pentane afforded pale yellow crystals which melted over a wide range of temperature (50-75°C); IR (hexane): 3610w (OH), 2040s and 1980 vs cm^{-1}; ^1H-NMR($DCCl_3$): 5.52 (dt, 2H), 4.36 (d, 1H), 2.98 (m, 2H), 2.36 (m, 1H) and 1.4-1.6 (m, 2H). The IR and ^1H-NMR spectral data suggested a (exo-5-hydroxycyclohexa-1,3-diene)irontricarbonyl structure. The data agrees well with that reported for (5-hydroxycyclohexa-1,3-diene)irontricarbonyl (91) obtained from the addition of sodium bicarbonate to 12a in water.

Addition of sodium trimethylsilanolate to 12a in acetonitrile at 0°C did not lead to the formation of a red color during the reaction period (15 min). However, when the reaction mixture was allowed to come to room temperature prior to the removal of the solvent, slow appearance of a red color could be observed. Upon workup (exo-5-trimethylsiloxycyclohexa-1,3-diene)irontricarbonyl (95) was obtained as a yellow oil (0.45 g, 92%). Vacuum sublimation (31°C, 0.002 mmHg) of the crude product yielded pure siloxy complex 95 as a light-yellow solid, mp 49-51^{o}C; IR (hexane): 2040s, 1980 vs and 1960w, 1035s and 970s cm^{-1}; ^{1}H-NMR(CS_2): δ 0.6(s, 9H, Si($\underline{CH}_3$)$_3$), 1.43 (dt, 1H, $H_{6,\underline{exo}}$), 2.2 (m, 1H, $H_{6,\underline{endo}}$), 2.86 (m, 2H, $H_{1,4}$), 4.22 (dt, 2H, $H_{2,3}$); ^{13}C-NMR($DCCl_3$): δ 0.02 (q, J_{CH}=118 Hz, Si($\underline{C}H_3$)$_3$), 33.6 (t, J_{CH}=130 Hz, C_6), 55.4 (d, J_{CH}=155 Hz, C_1(C_4)), 63.8 (d, J_{CH}=160 Hz, C_4(C_1)), 69.5 (d, J_{CH}=150 Hz, C_5), 84.6 (d, J_{CH}=170 Hz, C_2(C_3)) and 87.1 (d, J_{CH}=170 Hz, C_3(C_2)); mass spectrum: m/e (rel. intensity) 308 (M^+,0.1), 307, 298, 280, 250, 222(100), 231, 207, 197, 192, 180, 178, 168, 163, 152, 135, 85, 76, 58 and 48; Anal. calcd for $C_{12}H_{16}FeO_4Si$:C, 46.76; H, 5.24 found: C, 46.80; H, 5.13. The reaction between $[(C_6H_5)_3C]BF_4$ (<u>1</u>) (0.17 g, 0.5 mmol) and <u>95</u> (0.16 g, 0.5 mmol) led to the isolation of $[(C_6H_7)Fe(CO)_3]BF_4$ (<u>12a</u>) in 82% yield (0.13 g).

Addition of potassium phenoxide to <u>12a</u> in acetonitrile at room temperature did not lead to either the formation of a red color or the isolation of the dimers <u>89</u> and <u>90</u>. After 8.5 h the cationic complex <u>12a</u> was recovered unchanged in 64% yield. The ^{1}H-NMR spectrum of the pentane soluble yellow oil suggested the presence of predominantly phenol and (5-phenoxycyclohexa-1,3-diene)irontricarbonyl (<u>94</u>) mixed with traces of the ether complex <u>92</u>. The IR and ^{1}H-NMR spectra agreed well with those reported for <u>94</u>.[58]

During the addition of sodium methoxide to <u>12a</u> in acetonitrile in the presence of oxygen, the color of the reaction mixture remained yellow. The IR band at 1755 cm^{-1} characteristic of the M-M dimer <u>89</u> could not be detected. However, a weak absorption band at 1715 cm^{-1} was detected during the progress of the reaction. Upon workup, only (<u>exo</u>-5-methoxycyclohexa-1,3-diene)irontricarbonyl (<u>87</u>) was isolated as a yellow oil (46%), ^{1}H-NMR(CS_2)[19]: δ 5.4 (m, 2H, $H_{2,3}$), 3.71 (dt, 1H,

H_5), 3.1)S, 3H, $O\underline{C}H_3$), 2.8-3.16 (m, 2H, $H_{1,4}$), 2.0-2.3 (m, 1H, $H_{6,\underline{endo}}$) and 1.38-1.52 (m, 1H, $H_{6,\underline{exo}}$); ^{13}C-NMR($DCCl_3$): δ 30.8 (t, J_{CH}=135 Hz, C_6), 55.7 (V, J_{CH}=140 Hz, $O\underline{C}H_3$), 56.3 (d, J_{CH}=155 Hz, $C_1(C_4)$), 59.2 (d, J_{CH}=155 Hz, $C_4(C_1)$), 78.1 (d, J_{CH}=145 Hz, C_5), 84.8 (d, J_{CH}=170 Hz, $C_2(C_3)$) and 87.3 (d, J_{CH}=170 Hz, $C_3(C_2)$) ppm.

Occasionally a weak absorption band at 1715 cm^{-1} was observed during the reaction of $NaOCH_3$ and *12a* in the absence of oxygen, but could not be detected in the separated fractions. During the progress of the reaction between potassium hydroxide and *12a* in acetonitrile, a weak absorption band at 1820 cm^{-1} which increased with time, was observed. However, it was not detected in the pentane or dichloromethane extracts.

Addition of sublimed potassium *tert*-butoxide to *12a* in *t*-butanol (25 ml) at *ca.* 28°C led to the precipitation of a red-crystalline solid during the progress of the reaction. Upon workup and chromatography the same products obtained from the reaction in acetonitrile were isolated. In addition, elution with benzene of a pale-yellow band that immediately followed the band due to the ether complex *92* yielded, after recrystallization, pale yellow crystals (0.035 g, 8%) of (5-*t*-butoxycyclohexa-1,3-diene)irontricarbonyl (*93*), mp 45-50°C; ^{1}H-NMR (CS_2): δ 5.3-5.5 (m, 2H, $H_{2,3}$), 3.92 (dt, 1H, H_5), 2.8 (m, 2H, $H_{1,4}$), 1.98-2.18 (m, 1H, $H_{6,\underline{endo}}$), 1.3-1.46 (m, 1H, $H_{6,\underline{exo}}$) and 1.04 (s, 9H, $-OC(\underline{C}H_3)_3$); ^{13}C-NMR ($DCCl_3$): δ 28.5 ($\underline{C}H_3$), 33.2 (C_6), 55.8 ($C_1(C_4)$), 63.5 ($C_4(C_1)$), 69.5 (C_5), 73.6 ($\underline{C}(CH_3)_3$), 84.7 ($C_2(C_3)$) and 86.8 ($C_3(C_2)$) ppm. The proton signal for H_5 at 3.92 δ, suggests the stereochemistry of *tert*-butoxy group on the ring to be *exo*.

Preparation of the Triphenylsilyl Anion

Hexaphenyldisilane (0.35 g, 0.7 mmol) was suspended in freshly distilled anhydrous THF (20 ml) (distilled first from sodium-benzophenone followed by final distillation from LAH), and lithium wire (high-sodium content) (3 x 0.2 cm) was added. The lithium wire was cut into small pieces under the solvent. The reaction mixture was stirred vigorously for 8-24 h. The initiation of the reaction was indicated by the formation of a light-yellow colored solution, which turned yellowish green and finally dark brown. The reaction was stopped upon the disappearance of the white solid (hexaphenyldisilane), and the solution was used immediately.

Reaction of Triphenylsilylanion With 12a

The triphenylsilylanion solution was filtered under dry, inert atmosphere into a magnetically stirred solution of 12a (0.4 g, 1.3 mmol) in acetone kept at -78°C. The reaction mixture was stirred at -78°C for 30 min and at room temperature for 45 min. The reaction mixture turned red at room temperature. Upon removal of the solvents, a dark-red crystalline solid was obtained. Pentane extraction of the residue yielded a yellow oil (0.1 g) the ^{1}H-NMR spectrum of which suggested presence of predominantly the "C-C dimer" 90. The Dichloromethane extraction, led to the isolation of the M-M dimer 89 as the major product of the reaction.

Reaction of 12a With CH_3CN

A solution of 12a (0.88 g, 2.87 mmol) in freshly distilled acetonitrile (80 ml) was refluxed (85°C) for 1.5 h and the progress of the reaction was monitored by obtaining IR spectra at regular intervals. The conversion of cationic to neutral irontricarbonyl complexes was complete in one hour. Removal of the solvent in vacuo followed by extraction of the residue with dichloromethane (80 ml) yielded a yellow solution. The dichloromethane extract was washed with water; dried over anhyd. Na_2SO_4 and the solvent removed in vacuo. An yellow solid mixed with a yellow oil was obtained (0.29 g). The crude product was dissolved in a minimum volume of pentane at 33°C and the resulting solution was cooled to -20°C. The precipitated pale-yellow needles of (5,5'-dicyclohexadiene)diironhexacarbonyl ("C-C dimer" 90) (0.07 g, 11%) were collected. The supernatant solution from recrystallization yielded (cyclohexadiene)irontricarbonyl (98) as a yellow oil (0.25 g, 34%). The products were identified by their melting points and spectra (vide infra).

Reaction of 12a With CH_3CN in the Presence of O_2

Dry oxygen was passed through a solution of 12a (0.3 g, 1.0 mmol) in acetonitrile (30 ml), and the reaction mixture was refluxed for 5 h. IR spectra taken during the reaction period remained unchanged, suggesting the presence of only the cationic species 12a. After 5 h the reaction mixture was brown owing to the deposition of a brown solid. After filtration and removal of the solvent in vacuo, a bright yellow solid was obtained, which was successively washed with pentane and ether. No neutral irontricarbonyl complexes were detected either in the pentane or the ether extract. The yellow solid (0.24 g, 80% recovery) was identified as 12a by its melting point and IR spectrum.

Reaction of $[(C_7H_9)Fe(CO)_3]BF_4$ (13) With CH_3CN

A solution of 13 (0.4 g, 1.25 mmol) in freshly distilled CH_3CN (40 ml) was refluxed for 5 h. The conversion of the IR absorption bands at 2110 and 2060 cm^{-1} to bands at 2040, 1975 and 1750 cm^{-1} was slow, but complete in 5 h. The color of the reaction mixture changed from yellow to dark red during the reaction period. After filtration and removal of the solvent in vacuo a dark-red solid was obtained. The solid was extracted with pentane and the extract was chromatographed on a neutral alumina column made in Skelly B. Elution with the same solvent yielded a small amount of an unidentified yellow oil (0.02 g). Extraction of the residue remaining from the pentane extraction with dichloromethane yielded bis(η^5-cycloheptadienyl)diirontetracarbonyl (99) (0.083 g, 33%) as a dark-red crystalline solid, which was recrystallized from dichloromethane-pentane, mp 170-185°C (dec., lit.[19] mp 198°C) UV(λ_{max}): 495 nm; IR(CH_2Cl_2): 2040w, 1975 vs and 1750s cm^{-1}. The IR spectrum and the melting point agreed well with the published data.[19]

Reaction of $[(C_7H_9)Fe(CO)_3]BF_4$ (13) With CH_3CN in the Presence of O_2

Refluxing the solution of 0.35 g (1.1 mmol) of 13 in 35 ml of acetonitrile for 5 h in the presence of oxygen led to the recovery of the unchanged cationic complex 13 in 46% yield. The IR spectra taken during the reaction period did not suggest the formation of neutral organometallic products.

Reactions of Organosilicon Compounds With 12a and 13

Hexamethyldisiloxane, vinyltrimethylsilane and allyltrimethylsilane were separately reacted with 12a by heating excess of the organosilicon compound with 0.5 g (1.6 mmol) of 12a in CH_3CN (30 ml) at $45^\circ C$ for 24 h. The reaction mixture was filtered; the solvent was removed *in vacuo* and the residue was extracted with pentane followed by acetone.

Attempted reactions of hexamethyldisiloxane and vinyltrimethylsilane with 12a led to the recovery of unchanged 12a in 82% (0.41 g) and 92% (0.46 g) yields, respectively. The IR spectra of the pentane extracts in both reactions did not possess any metal carbonyl absorptions. Reaction of allyltrimethylsilane with 12a under the same conditions yielded exclusively (5-allylcyclohexa-1,3-diene)irontricarbonyl (105) (0.26 g, 62%) as a yellow oil; IR(CH_2Cl_2): 2040, 1970 [$(Fe(CO)_3$] and 1640 (C=C) cm^{-1}; ^{1}H-NMR (CS_2); δ 5.65 (m, H, $-CH_2-\underline{H}C=CH_2$), 5.26 (m, 2H, $H_{2,3}$), 4.8-5.0 (m, 2H, $C=C\underline{H}_2$), 3.0 (m, 2H, $H_{1,4}$), 2.0 (m, 4H, H_5, $H_{6,\underline{endo}}$, $-\underline{CH}_2-CH=CH_2$) and 1.3 (m, 1H, $H_{6,\underline{exo}}$); ^{13}C-NMR ($DCCl_3$): δ 211.8(s), 136.7 (d, J_{CH}=145 Hz, $H\underline{C}=CH_2$), 115.7 (t, J_{CH}=160 Hz, $HC=\underline{C}H_2$), 85.4 (d, J_{CH}=170 Hz, $C_3(C_2)$), 84.4 (d, J_{CH}=170 Hz, $C_2(C_3)$), 66.4 (d, J_{CH}=160 Hz, $C_4(C_1)$), 59.4 (d, J_{CH}=160 Hz, $C_1(C_4)$), 43.9 (t, J_{CH}=130 Hz, $-\underline{C}H_2-CH=CH_2$), 37.8 (d, J_{CH}=130 Hz, C_5) and 30.0 (t, J_{CH}=130 Hz, C_6) ppm. The ^{1}H-NMR and IR spectra agreed very well with the published data for the allyl complex 105.[21]

Excess of trimethylsilylazide was added to a magnetically stirred solution of 12a (0.3 g, 1.0 mmol) in reagent-grade acetone (25 ml) at room temperature and the stirring was continued for 20 h. Upon workup (exo-5-azidocyclohexadiene)irontricarbonyl (56) (0.13 g, 53%) was isolated occasionally contaminated with traces of the ketone 57. The reaction mixture was pale yellow throughout the reaction period. The IR bands due to the cationic complex 12a at 2110 and 2060 cm^{-1} were completely replaced by absorption bands at 2085, 2045 and 1985 cm^{-1} within 2 h.

Addition of excess trimethylsilylazide to a stirred solution of the cationic complex 13 (0.4 g, 1.1 mmol) in acetone (35 ml) at room temperature followed by continued stirring for 20 h led to the same IR spectral changes as in the preceding reaction. The reaction mixture was reddish-orange at the end of the reaction period. After workup (exo-5-azidocycloheptadiene)irontricarbonyl (58) (0.19 g, 55%) was obtained as the major product mixed with traces of the ketone 57 and the same minor product (63) formed in the reaction of 13 with NaN_3 (*vide infra*).

Addition of trimethylsilylazide (0.08 ml) to a stirred suspension of $[(C_7H_7)Fe(CO)_3]BF_4$ (16) (0.15 g, 0.5 mmol) in anhyd. THF (20 ml) at room temperature followed by continued stirring for 2 h led to the formation of a clear pale-yellow solution. Upon workup, (exo-7-azidocycloheptatriene)irontricarbonyl (67) (0.065 g, 50%) was isolated exclusively.

The reaction between (bicyclo[5.1.0]cyclooctatrienyl)irontricarbonyltetrafluoroborate (15) (0.3 g, 0.9 mmol) and trimethylsilylazide (0.2 ml, 2.0 mmol) in anhyd. THF at 0°C for 24 h after workup, yielded a mixture (0.11 g) of $(C_8H_8)Fe(CO)_3$ (37) and the monocyclic azidocomplex 69 or 70 in the ratio $[(C_8H_8)Fe(CO)_3$ (37)/$(C_8H_9N_3)Fe(CO)_3$ (69 or 70)] of 0.125. The same reaction at room temperature for 5 h and 18 h yielded the ratios 0.3 and 0.5 respectively.

The addition of trimethylsilylazide (0.05 ml, 0.36 mmol) to a stirred solution of (2-methyl-π-allyl)irontricarbonyl tetrafluoroborate (6b) (0.1 g, 0.35 mmol) in dry acetone kept at 0°C was followed by continued stirring for one hour at 0°C and 2 h at room temperature. After workup and recrystallization of the crude product from pentane (2-methyl-π-allyl)azidoirontricarbonly (80) was obtained in 50% yield.

The rea-tion between trimethylsilylazide and acetone was performed by stirring 0.07 ml of trimethylsilylazide with 15 ml of dry acetone at room temperature for 1.5 h. Removal of the excess of acetone gave 2 g (3300%) of 2-methyl-2-hydroxy-4-pentanone (57) as a colorless oil.

Reaction of $[(C_6H_7)Fe(CO)_3]BF_4$ (12a) With $NaB(C_6H_5)_4$

To a magnetically stirred solution of the cationic complex 12a (1.0 g, 3.3 mmol) in deoxygenated distilled water (90 ml), chloroform-washed sodium tetraphenylboron (1.12 g, 3.3 mmol) was added. Instantaneous precipitation of a yellow solid was observed. Hexane (80 ml) was added to the reaction mixture and the resulting heterogeneous reaction mixture was heated at 90-95°C (oil bath temp.) for 25 h. The reaction mixture was allowed to come to 45°C and the yellow hexane layer was separated. The aqueous layer was washed with hexane (3 x 25 ml), the organic extracts with water. The organic extracts were combined and dried over anhyd., Na_2SO_4. Upon removal of the solvent, a yellow oil, which crystallized slowly in a refrigerator, was obtained. A minimum amount of pentane (3 ml) was added to the crude product and the solution was cooled to 0°C (40 min.). The yellow crystalline solid (0.8 g, 66%) was collected, recrystallized from hexane and identified as (5-p-biphenylylcyclohexa-1,3-diene)irontricarbonyl (106), mp 120.5-

121.5°C; IR(KBr):2045, 1980, 1475, 835, 770, 730 and 700 cm^{-1}; ^1H-NMR(CS_2): δ 1.5-1.7 (dm, 1H, $H_{6,\underline{exo}}$), 2.1-2.5 (m, 1H, $H_{6,\underline{endo}}$), 3.0-2.8 (m, 2H, $H_{1,4}$), 3.2-3.4 (dt, 1H, H_5), 5.2-5.5 (m, 2H, $H_{2,3}$) and 7.0-7.4 (m, 9H, *p*-biphenylyl H's); ^{13}C-NMR($DCCl_3$); δ 33.5 (t, J_{CH}=130 Hz, C_6) 44.2 (d, J_{CH}=140 Hz, C_5); 60.6 (d, J_{CH}=154 Hz, $C_1(C_4)$), 66.8 (d, J_{CH}=160 Hz, $C_4(C_1)$), 84.3 (d, J_{CH}=170 Hz, $C_2(C_3)$), 86.0 (d, J_{CH}=170 Hz, $C_3(C_2)$), 126.8 (d, J_{CH}=160 Hz, $C_2'(C_2'')$), 126.9 (d, J_{CH}=160 Hz, $C_2''(C_2')$), 127.0 (d, J_{CH}=160 Hz, C_4''), 127.2 (*d*, J_{CH}=160 Hz, C_3''), 128.5 (d, J_{CH}=160 Hz, C_3'), 139.0 (s, C_4'), 140.6 (s, C) and 145.7 (s, C_1'') ppm; mass spectrum: m/e (rel. intensity) 371 (M^+) (< 2), 343 (20), 314 (50), 287 (100) and 231 (80); anal. calcd for $C_{21}H_{16}FeO_3$: C, 67.76; H, 4.34. Found: C, 67.79; H, 4.32.

Reaction of $[(C_7H_9)Fe(CO)_3]BF_4$ (13) With $NaBPh_4$

The reaction with 0.5 g (1.6 mmol) of the cationic complex 13 and 0.54 g (1.6 mmol) of sodium tetraphenylboron in a water-hexane solvent system (50 ml:100 ml) for 24 h at 90-95°C upon workup yielded impure (5-*p*-biphenylylcyclohepta-1,3-diene)irontricarbonyl (107) as a light-yellow solid (0.045 g, 8%), mp 115-118°C; IR(pentane): 2045, 1980, 835 and 770 cm^{-1}; ^1H-NMR ($DCCl_3$): δ 1.4-2.6 (m, 2H, $H_{6,7}$ *exo*), 2.8-3.3 (m, 3H, $H_{1,4}$, H_5), 5.2-5.6 (m, 2H, $H_{2,3}$) and 7.2-7.7 (m, 9H, biphenylyl H's); ^{13}C-NMR ($DCCl_3$): δ 28.5, 32.6, 45.6, 59.0, 62.9, 86.9, 88.8, 126.8, 127.1, 128.2, 128.5, 139.1, 140.8 and 147.9 ppm; mass spectrum: m/3 (rel. intensity): 358 (14, M^+ -CO), 331 (29), 302 (64), 246 (21), 210 (100), 202 (21), 189 (21), 178 (29), 165 (43), 155 (64), 148 (~100), 112 (51), 91 (86), 84 (79) and 77 (93).

Oxidation of (5-*p*-biphenylylcyclohexadiene)-irontricarbonyl (106)

To a stirred solution of 0.1 g (0.27 mmol) of the biphenylyl complex 106 in 10 ml of aqueous acetone (5%), solid ceric ammonium nitrate was added in small quantities until the gas evolution stopped. The reaction mixture was extracted with ether; the ether extract was washed with saturated NaCl solution and dried over anhyd. Na_2SO_4. Upon removal of ether, 5-*p*-biphenylylcyclohexa-1,3-diene (108) was isolated as a white flaky solid (0.6 g, 97%) which was recrystallized from anhyd. methanol, mp 67-68^{o}C; IR(KBr): 1480, 830, 765 and 675 cm^{-1}; ^{1}H-NMR (CS_2): δ 31.6, 39.4, 123.8, 124.4, 125.3, 126.8, 126.9, 127.8, 129.7, 139.1 and 140.8; mass spectrum (FI): m/e 232 (M^{+}, 100) and 233 ($M_{+}1$, 17); Anal. calcd for $C_{18}H_{16}$: C, 93.05; H. 6.95. Found: C, 89.67; H, 7.62.

Dehydrogenation of 5-*p*-biphenylyl-1,3-cyclohexadiene (108)

o-Chloranil (0.075 g, 0.3 mmol) and 5-*p*-biphenyl-1,3-cyclohexadiene (108) (0.075 g, 0.33 mmol) were dissolved in benzene (20 ml) and the resulting solution was refluxed for 12 h. Ether (30 ml) was added to the reaction mixture and the organic layer was successively washed with 10% aq. NaOH (until the washings were clear), water and finally a saturated NaCl solution. The organic phase was dried over anhyd. $NaSO_4$. The solvents were removed and the product was chromatographed on a neutral-alumina column with benzene as the eluent. Shiny-white, and flaky crystals of *p*-terphenyl (0.04 g, 57%) were obtained from the second band, mp 208-210°C (lit. mp 213°C); IR (KBr): 1480, 840, 745 and 685 cm^{-1}; mass spectrum (FI): m/e 230 (M^+, 100) and 231 (M+1, 15).

SELECTED BIBLIOGRAPHY

1. "Carbonium Ions", G. A. Olah and P. Von R. Schleyer, Eds.; John Wiley & Sons, 1976; Vol. 1.

2. Hoffman, K. A.; Kirmreuther, H.; Chem. Rev. 1909, 42, 4856. Gomberg, M.; Cone, L. H., Ann. Chem. 1909, 370, 142, 193.

3. Breslow, R.; Yuvan, C. J. Am. Chem. Soc. 1963, 80, 5991.

4. Doering, W. v. E.; Sanders, M.; Boyton, H. G.; Earhart, H. W.; Wadlerg, E. F.; Edwards, W. R.; Labor, G. Tetrahedron. 1958, 4, 178.

5. Dauben, Jr., H. J.; Gadecki, F. A.; Harmon, K. M.; Pearson, D. L. J. Am. Chem. Soc. 1957, 79, 4557.

6. Rosenberg, Jr., J. L. V.; Mahler, J. E.; Pettit, R. J. Am. Chem. Soc. 1962, 84, 2842.

7. Pettit, R.; Haynes, H. W. "Carbonium Ions", G. A. Olah and P. von R. Schleyer, Eds. John Wiley & Sons, 1976; Vol. 5, Pp. 2263-2302. Abel, E. W.; Tyfield, S. P., "Advances in Organometallic Chemistry"; Academic Press: New York, 1970; Vol. 8, P. 117. Haas, M. A. Organometal. Chem. Rev. A. 1969, 4, 307. Davidson, J. L. Inorg. Reaction Mechanisms (Chem. Soc. Specialist Periodical Reports). 1977, 5, 387.

8. Sidgwick, N. V. J. Chem. Soc. 1923, 123, 275; Trans. Faraday. Soc. 1923, 19, 469; Chem. Ind. 1923, 42, 901, 1203; "The Electronic Theory of Valence", Clarendon Press, Oxford, 1927.

9. Dewar, M. J. S. Bull. Soc. Chim. Fr. 1951, C71. Chatt, J.; Duncanson, L. A. J. Chem. Soc. 1953, 2939.

10. Hoffman, R.; Hoffman, P. J. Am. Chem. Soc. 1976, 98, 598.

11. Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. J. Organomet. Chem. 1976, 107, C40; 120, C25.

12. Mahler, J. E.; Pettit, R. J. Am. Chem. Soc. 1963, 85, 3955.

13. Mahler, J. E.; Gibson, D. H.; Pettit, R. J. Am. Chem. Soc. 1963, 85, 3959.

14. McArdle, P.; Sherlock, H. J. Organomet. Chem. 1973, 52, C29.

15. Angelici, R. J.; Busetto, L. J. Am. Chem. Soc. 1969, 91, 3197.

16. Graziani, M.; Busetto, L.; Palazzi, A. J. Organomet. Chem. 1971, 26, 261.

17. Dombek, B. D.; Angelici, R. J. Inorg. Chim. Acta. 1973, 7, 345.

18. Rosan, A.; Rosenblum, M. J. Organomet. Chem. 1974, 80, 103.

19. Hashmi, M. A.; Munro, J. D.; Pauson, P. L.; Williamson, J. M. J. Chem. Soc. A. 1967, 240.

20. Birch, A. J.; Cross, D. E.; Lewis, J.; White, D. A.; Wild, S. B. J. Chem. Soc. A. 1968, 332.

21. Birch, A. J.; Pearson, A. J. Tetrahedron. Lett. 1975, 2379; J. Chem. Soc. Perkin. Trans I. 1976, 954.

22. Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. J. Chem. Soc. Perkin. Trans. I. 1973, 1882. Birch, A. J.; Chamberlain, K. B.; Thompson, D. J. ibid. 1973, 1900.

23. Kane-Maguire, L. A. P. J. Chem. Soc. A. 1971, 1602. Mansfield, C. A.; Kane-Maguire, L. A. P. J. Chem. Soc. Dalton. Trans. 1976, 2187.

24. Ireland, R. E.; Brown, G. G.; Stainford, R. H.; McKenzie, T. C. J. Org. Chem. 1974, 39, 51.

25. Kane-Maguire, L. A. P.; Mansfield, C. A. J. Chem. Soc. Chem. Commun. 1973, 540.

26. Mansfield, C. A.; Al-Kathumi, K. M.; Kane-Maguire, L. A. P. J. Organomet. Chem. 1974, 71, C11.

27. John, G. R.; Kane-Maguire, L. A. P.; Eaborn, C. J. Chem. Soc. Chem. Commun. 1975, 481.

28. Mansfield, C. A.; Kane-Maguire, L. A. P. J. Chem. Soc. Dalton. Trans. 1976, 2192.

29. Franke, F.; Jenkins, I. D. Aust. J. Chem. 1978, 31, 595.

30. Evans, J.; Howe, D. V.; Johnson, B. F. G.; Lewis, J. J. Organomet. Chem. 1973, 61, C48.

31. Johnson, B. F. G.; Karlin, K. D.; Lewis, J.; Parker, D. G. J. Organomet. Chem. 1978, C67.

32. Shu, B. Y.; Biehl, E. R.; Reeves, P. C. Syn. Commun. 1978, 8, 523.

33. Shiavon, G.; Paradesi, C.; Boanini, C. Inorg. Chim. Acta. 1975, 15, L5.

34. Edwards, R.; Howel, J. A. S.; Johnson, B. F. G.; Lewis, J. J. Chem. Soc. Dalton. Trans. 1974, 19, 2105.

35. Deeming, A. J.; Ullah, S. S.; Domingos, A. J. P.; Johnson, B. F. G., Lewis, J.; J. Chem. Soc. Dalton. Trans. 1974, 19, 2093.

36. Munro, J. D.; Panson, P. L. J. Chem. Soc. 1961, 3475.

37. Pauson, P. L.; Smith, G. H. Valentine, J. H. J. Chem. Soc. A. 1967, 1059.

38. Baike, P. E.; Millis, O. S.; Pauson, P. L.; Smith, G. H.; Valentine, J. H. Chem. Commun. 1965, 425.

39. Al-Kathumi, K. M.; Kane-Maguire, L. A. P. J. Organomet. Chem. 1975, 102, C4.

40. Sweigart, D. A.; Gower, M.; Kane-Maguire, L. A. P. J. Organomet. Chem. 1976, 108, C15.

41. John, G. R.; Kane-Maguire, L. A. P.; Sweigart, D. A. J. Organomet. Chem. 1976, 120, C47.

42. Salzer, A. Inorg. Chim. Acta. 1976, 18, L31; ibid. 1976, 17, 221.

43. Munro, J. D.; Pauson, P. L. J. Chem. Soc. 1961, 3484.

44. Munro, J. D.; Pauson, P. L. J. Chem. Soc. 1961, 3479.

45. Al-Kathumi, K. M.; Kane-Maguire, L. A. P. J. Chem. Soc. Dalton. Trans. 1973, 1683.

46. Holmes, J. D.; Pettit, R. J. Am. Chem. Soc. 1963, 85, 2531.

47. Davidson, A.; McFarlane, W.; Wilkinson, G. Chem. Ind. 1962, 820.

48. Aumann, R.; Angen. Chem. Internat. Ed. 1973, 12, 574.

49. Aumann, R. J. Organomet. Chem. 1974, 78, C31.

50. Bryan, E. G.; Burrows, A. L.; Johnson, B. F. G.; Lewis, J.; Schiavon, G. M. J. Organomet. Chem. 1977, 129, C19.

51. Brown, D. A.; Chawla, S. K.; Glass, W. K. Inorg. Chim. Acta. 1976, 19, L31.

52. Cowles, R. J. H.; Johnson, B. F. G.; Josty, P. L.; Lewis, J. Chem. Commun. 1969, 392.

53. John, G. R.; Mansfield, C. A.; Kane-Maguire, L. A. P. J. Chem. Soc. Dalton. Trans. 1977, 6, 574.

54. Brown, D. A.; Chester, J. P.; Fitzpatrick, N. J. J. Organomet. 1978, 155, C21.

55. Birch, A. J.; Jenkins, I. D. "Transition Metal Organometallics in Organic Synthesis", H. Alper., Ed; Academic Press, New York, 1976; Vol. 1, Pp. 1-82.

56. Birch, A. J.; Williamson, D. H. J. Chem. Soc. Perkins I, 1973, 1892.

57. Pelter, A.; Gould, K. J.; Kane-Maguire, L. A. P. J. Chem. Soc. Chem. Commun. 1974, 1029.

58. Nametkin, N. S.; Tyurin, V. D.; Slupczynski, M.; Ivanov, V. I.; Nekhaev, A. I. Roczniki. Chemii. Ann. Soc. Chim. Polonorum. 1976, 50, 1499.

59. Johnson, B. F. G.; Lewis, J.; Randall, G. L. P. J. Chem. Soc. A. 1971, 422

60. Charles, A. D.; Diversi. P.; Johnson, B. F. G.; Karlin, K. D.; Lewis, J.; Rivera, A. V.; Sheldrick, G. M. J. Organomet. Chem. 1977, 128, C31.

61. Pearson, R. G. J. Am. Chem. Soc. 1963, 85, 3533. Pearson, R. G., Songst., J. J. Am. Chem. Soc. 1967, 89, 1827. Pearson, R. G. Survey of Progress in Chemistry. 1969, 5, 1.

62. Mahler, J. E.; Jones, D. A. K.; Pettit, R. J. Am. Chem. Soc. 1964, 86, 3589.

63. Emerson, G. F.; Pettit, R. J. Am. Chem. Soc. 1962, 84, 4591.

64. a) Wuffman, C. E.; Yarnell, C. F.; Wulfman, D. S. Chem. Ind. 1960, 1440. Wulfman, D. S.; Durham, L.; Wulfman, C. E. ibid. 1962, 859. Wulfman, D. S.; Ward, J. J. Chem. Commun. 1967, 276.

    b) Feigel, M.; Kessler, H.; Leibfritz, D.; Walter, A. J. Am. Chem. Soc. 1979, 101, 1943.

65. Brookhart, M.; Davis, E. R. J. Am. Chem. Soc. 1970, 92, 7622.

66. Heck, R. F.; Boss, C. R. J. Am. Chem. Soc. 1964, 86, 2580.

67. Faller, J. W.; Adams, M. A. J. Organomet. Chem. 1979, 170, 71.

68. Randall, E. W.; Rosenberg, E.; Milone, L. J. Chem. Soc. Dalton. Trans. 1973, 1672.

69. Brown, D. A.; Chambers, W. J. J. Chem. Soc. A. 1971, 2083.

70. Minasyan, M. Kh.; Struchov, Yu.T.; Kristskaya, R. I.; Shclembelov, G. A. J. Organomet. Chem. 1968, 14, 395.

71. Mentioned in Reference 50.

72. Birkofer, L.; Ritter, A. Angen. Chem. Internat. Ed. 1965, 4, 417.

73. Birkofer, L.; Kaiser, W. Liebigs. Ann. Chem. 1975, 266.

74. Evans, D. A.; Truesdale, L. K. Tetrahedron Lett., 1973, 49, 4929.

75. Negishi, Ei-ichi. J. Organomet. Chem., 1976, 108, 281.

76. Negishi, Ei-ichi., Merril, R. E. J. Chem. Soc. Chem. Commun. 1974, 860.

77. Negishi, Ei-ichi.; Abramovitch, A.; Merril, R. J. Chem. Soc. Chem. Commun. 1975, 138.

78. Yamamoto, Y.; Maruyama, K. J. Am. Chem. Soc. 1978, 100, 6282.

79. Interalia:Behrens, H.; Wakamatsu, H. Z. Anorg. Allgem. Chem. 1963, 320, 30. Hieber, W.; Schubert, E. H. ibid. 1965, 338, 37. Hieber, W.; Brendel, G. ibid. 1957, 289, 338.

80. Al-Kathumi, K. M.; Kane-Maguire, L. A. P. J. Inorg. Nuclear. Chem. 1972, 34, 3759.

81. a) Eaborn, C. "Organosilicon Compounds." Academic Press: New York, 1960; Pp. 86-113.

    b) Hanstein, W.; Berwin, H. J.; Traylor, T. G. J. Am. Chem. Soc. 1970, 92, 7476.

82. Cooper, J. N.; Powell, R. E. J. Am. Chem. Soc. 1963, 85, 1590.

83. Geske, D. H. J. Phys. Chem. 1959, 63, 1062.

84. Razuvaev, G. A.; Grilkina, T. G. Zh. Obshch. Khim. 1954, 24, 1415.

85. Geske, D. H. J. Phys. Chem. 1962, 66, 1743. Bancroft, E. E.; Blount, H. N.; Janzen, E. G. J. Am. Chem. Soc. 1979, 101, 3692.

86. Abley, P.; Halpern, J. J. Chem. Soc. D. 1971, 1238.

87. Eisch, J. J.; Wilcsek, R. J. J. Organomet. Chem. 1974, 71, C21.

88. Eisch, J. J. Adv. Organomet. Chem. 1977, 16, 67.

89. Perrin, C. L.; Skinner, G. A. J. Am. Chem. Soc. 1971, 93, 3389.

90. Dauben; Honnen; Whiting. J. Org. Chem. 1960, 25, 1442.

91. Hallam, B. F.; Pauson, P. L. J. Chem. Soc. 1958, 642.

92. Fischen, E. O.; Fischer, R. D. Angew. Chem. 1960, 72, 919.

93. Dauben, Jr., H. J.; Bertelli, D. J. J. Am. Chem. Soc. 1961, 83, 497, 5049.

94. Murdoch, H. D.; Weiss, E. Helv. Chim. Acta. 1962, 45, 1927, 1156.

95. Emerson, G. F.; Mahler, J. E.; Pettit, R. Chem. Ind. 1964, 836.

96. Pratt, T. J., Ph.D. Dissertation, University of Washington, 1964.

97. Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. J. Chem. Soc. 1962, 4821.

98. Brookhart, M.; Davis, E. R. Tetrahedron. Lett. 1971, 4349. Brookhart, M.; Davis, E. R.; Harris, D. L. J. Am. Chem. Soc. 1972, 94, 7853.

99. Saunders, Jr., W. H. Ware, J. C. J. Am. Chem. Soc. 80, 1958, 3328.

100. Manuel, T. A.; Stone, F. G. A. Proc. Chem. Soc. 1959, 90; J. Am. Chem. Soc. 1960, 82, 366. Rausch, M. D.; Schrauzer, G. N. Chem. Ind. (London), 1959, 957. Nakamura, A.; Hagihara, N. Bull. Chem. Soc. Japan, 1959, 32, 881.

101. Birch, A. J.; Jenkins, I. D.; Liepa, A. J. Tetrahedron. Lett. 21, 1975, 1723.

VITA

Baireddy Raghava Reddy

Candidate for the Degree of

Doctor of Philosophy

Thesis: REACTIONS OF TRANSITION METAL π-COMPLEXED CATIONS WITH SELECTED NUCLEOPHILES

Major Field: Chemistry

Biographical:

Personal Data: Born in Gadwal, Andhra Pradesh, India, March 10, 1952, the son of Mr. B. SoogiReddy and Mrs. B. Govindamma.

Education: Graduated from Government High School, Gadwal, Andhra Pradesh, India, in 1968; obtained Bachelor of Science in Chemistry from Osmania University, Hyderabad, India, in 1973 and Master of Science in Chemistry from the same University in 1975; completed the requirements for Doctor of Philosophy degree in Chemistry at Oklahoma State University, Stillwater, Oklahoma, USA, in December, 1980.

Professional Experience: Graduate Teaching Assistant, Chemistry Department, Oklahoma State University from August, 1975 to May, 1980.