STUDY IN ORGANOMETALLIC TRANSITION METAL SILICON CHEMISTRY

PART I. THE QUEST FOR A CATIONIC η^3-SILAPROPENYL METAL COMPLEX. PREPARATION OF VINYLSILANE TRANSITION METAL COMPLEXES

PART II. INSERTION OF TRANSITION METAL SPECIES INTO SUBSTITUTED (CYCLOBUTADIENE) TRICARBONYLIRON COMPLEXES

By

PARVIZ RADNIA

Bachelor of Science in Chemistry

Pars College

Tehran, Iran

1976

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
July, 1981

STUDY IN ORGANOMETALLIC TRANSACTION METAL SILICON CHEMISTRY

PART I. THE QUEST FOR A CATIONIC η^3-SILAPROPENYL METAL COMPLEX. PREPARATION OF VINYLSILANE TRANSITION METAL COMPLEXES

PART II. INSERTION OF TRANSITION METAL SPECIES INTO SUBSTITUTED (CYCLOBUTADIENE) TRICARBONYLIRON COMPLEXES

Thesis Approved:

Thesis Adviser

K. D. Berlin

J. Paul Devlin

Ulrich K. Melcher

Norman N. Durham
Dean of the Graduate College

ACKNOWLEDGMENTS

I would like to thank Dr. Jeffrey S. McKennis for providing the opportunity to pursue this research. In addition, thanks are due my committee members, Drs. K. D. Berlin, J. F. Devlin, U. K. Melcher, and N. Purdie for their time and advice in the planning of the program and the evaluation of this work.

The financial assistance in the form of teaching assistantships by the Chemistry Department, Oklahoma State University for the period January 1977 - January 1981, and the summer research fellowships from the Gulf Oil Corporation Foundation and the Dr. J. F. Johnston Fellowship fund for the summers 1980 and 1981, is sincerely acknowledged with gratitude.

I am extremely grateful to Dr. J. F. Devlin for his generous help in obtaining the FT-IR spectral data.

I would like to thank Mr. Norman B. Perreira for his remarkable effort in designing an inlet for the mass spectrometer and his help in obtaining the spectral data. The technical assistance of Mr. Stan O. Sigle in obtaining NMR spectral data is also gratefully acknowledged.

I also thank Dr. E. M. Holt for providing the X-ray crystallography data.

TABLE OF CONTENTS

Chapter Page

PART II

LIST OF TABLES

Table Page

PART I

PART II

LIST OF FIGURES

Figure Page

PART I

PART II

PART I

THE QUEST FOR A CATIONIC η^3-SILAPROPENYL METAL COMPLEX. PREPARATION OF VINYLSILANE TRANSITION METAL COMPLEXES

CHAPTER I

INTRODUCTION

The ability of transition metals to form organo derivatives was known as far back as 1824, when a Danish pharmacist, W. Z. Zeise, reported the isolation of a compound, $PtCl_2 \cdot C_2H_4$, which is now known to be a dimer with a chlorine bridge.[1] Despite this early work, chemistry of olefin-metal compounds only began to be appreciated during the 1950's. Now it has become evident that mono-, di-, and polyene acyclic and cyclic, conjugated, unconjugated, and cumulated aromatic and nonaromatic hydrocarbons and heteroatomic compounds form complexes with transition metals.[2] The formation of such complexes has contributed greatly to our understanding of chemical bonding. It was postulated theoretically and confirmed experimentally that certain unstable organic compounds can be stabilized significantly by forming complexes with transition metals. Typical examples of these complexes are shown in Figure 1. The role of transition metals in stabilizing reactive compounds can be explained by the nature of their bonding. The most generally useful and most accepted description of this type of bonding for transition metal-olefin complexes is the Dewar-Chatt MO description.[3]

In this description the bonding is assumed to consist of two interdependent components (Figure 2). One component involves the overlap of filled π-orbitals of the olefin with σ-type acceptor orbitals

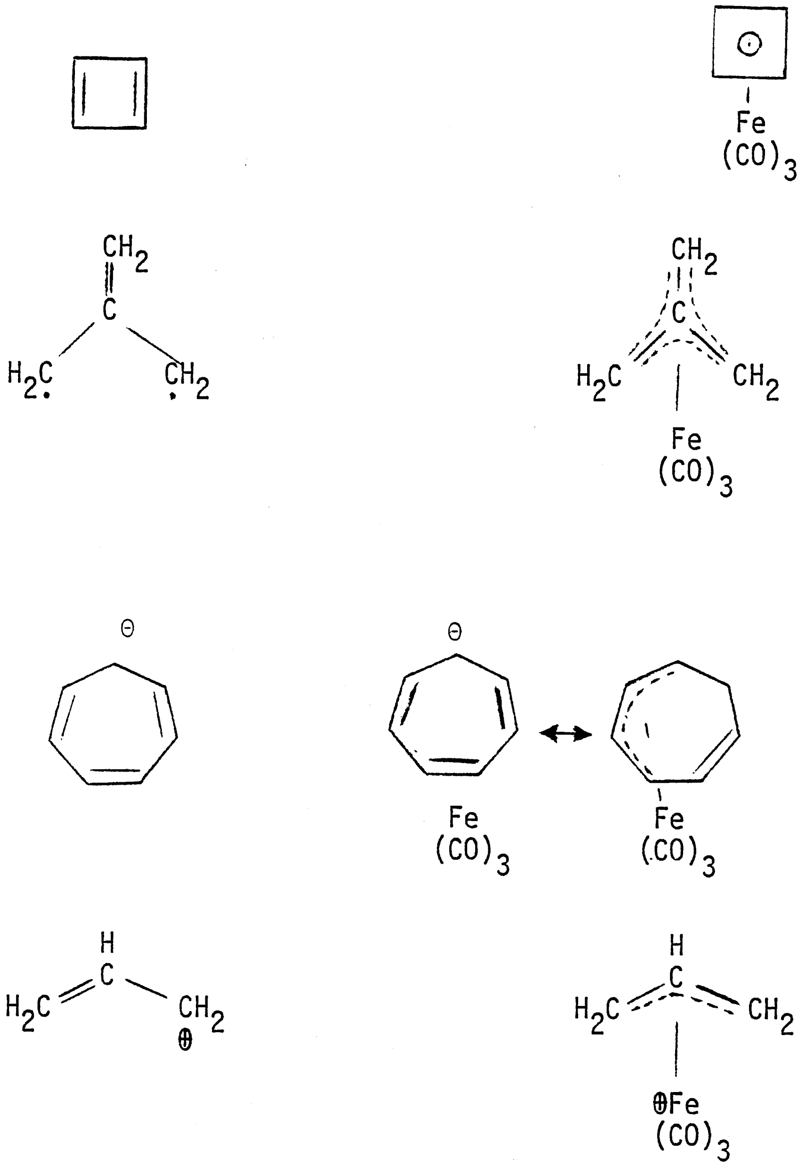
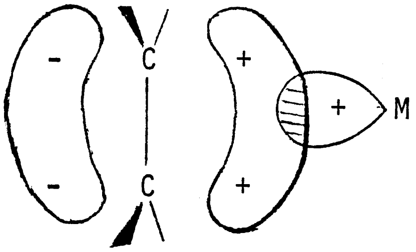
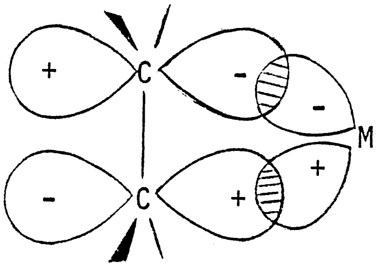


Figure 1. Examples of Unstable Organic Compounds with Their Corresponding Stable Complexes.



Donation from filled π-orbitals on Ligand to vacant metal orbital.



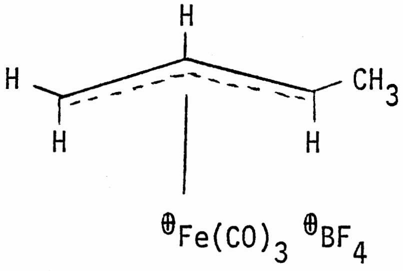
Back-donation from filled metal orbital to acceptor π*-orbital on ligand.

Figure 2. Diagrams Showing the Molecular Orbital View of Olefin-Metal Bonding.

of the metal; this component is referred to as "forward-coordination". The second component, "back-donation", involves the flow of electrons from filled metal d_{xz} or other p_π-d_π hybrid orbitals into the antibonding π-orbitals of the olefin. Both the donation of π-bonding electrons to the metal σ-orbital and the introduction of electrons into the π*-antibonding orbital weaken the π-bonding in the olefin and thus stabilize reactive olefins, e.g., cyclobutadiene. In the case of ionic compounds, e.g., the allylcarbonium ion and the cyclopentadienyl anion, all have relatively low lying molecular orbitals and can participate in forward-coordination or back-donation bonding. Thus, the charge on such reactive organic compounds can be delocalized onto the metal and this results in the stabilization of the ions.

Synthetic Approaches to Cationic Trihapto Transition-Metal Complexes

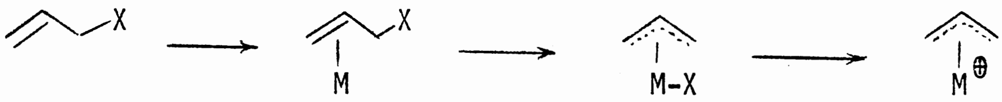
Emerson and Pettit reported the isolation of the first cationic trihapto tricarbonyliron complexes, e.g. cation I., in 1962.

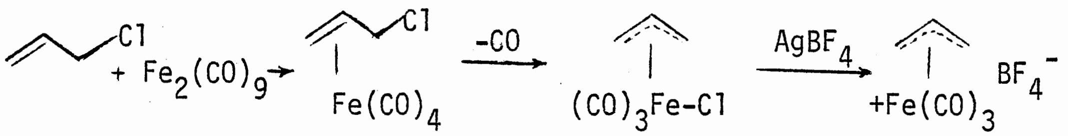


I

Since then, the synthesis and chemistry of trihapto complexes of cations, because of the great significance of cations theoretically and synthetically, have been the subject of extensive investigations, and an enormous number of these types of complexes have been synthesized during the past fifteen years.

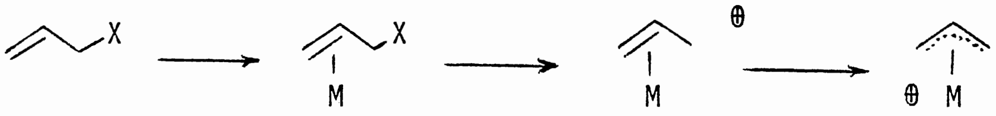
The synthetic approaches used to generate trihapto complexes of cations can be classified according to two general pathways. In the first pathway one starts with an olefin bearing a substituent in an allylic position and forms the corresponding dihapto complex. Then the substituent is rearranged from the allylic position to the metal by photolysis or thermolysis (the formation of the complex and rearrangement of the substituent in some cases can occur in one step). Finally, the substituent is removed by an appropriate chemical reagent as an anion.

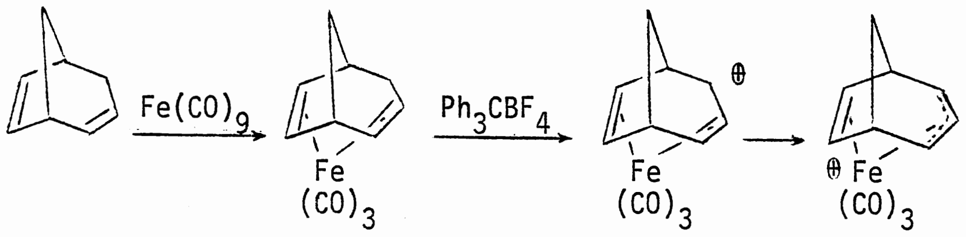




(1, ref. 5)

In the second pathway one forms an olefin complex and then generates a positive charge at an allylic position which causes the metal to move to delocalize the charge onto the metal.





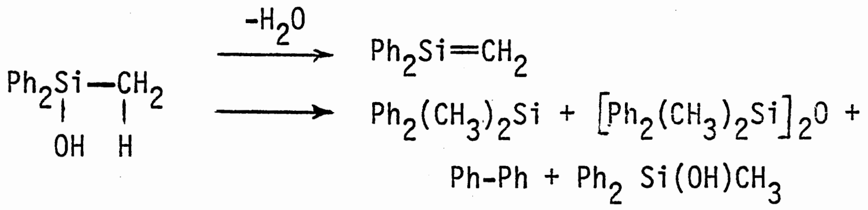
(2, ref. 6)

Elusive Silicon Species

Silicon, a member of Group IVA, is isoelectronic with carbon and consequently forms tetravalent compounds. Although the formation of multiple p_π-p_π bonds is well known property of carbon, and a great body of experimental data is available on organic compounds containing isolated, conjugated, and cumulated carbon double bonds, aldehydes, ketones, imines, and carboxyl compounds, silicon is reluctant to form stable molecules involving p_π-p_π bonding.[7, 8] Also, despite the numerous reports of the detection and/or isolation of a variety of carbonium ions, the existence of silicenium ions, (also referred to as silylenium or silicon cations) still remains questionable.

Multiple Bonded Silicon

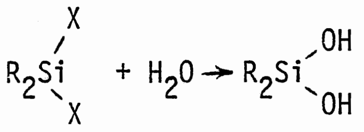
A structure with a multiple bond to a silicon atom was first reported by Gatterman in 1889.[9] A silicon-nitrogen double bond was assigned to compounds obtained in the reactions of ammonia with chlorosilanes. Since then, numerous claims for the synthesis of stable compounds containing silicon multiple bonds have been reported. However, each proposed structure has proven not to be correct. For example, Schlenk and Renning[10] described the synthesis of a stable compound with a silicon-carbon double bond. Their work, however, was reexamined by Kipping[11], who proved that the previous authors had really been dealing with a mixture of a silane and a silanol (Eq. 3).



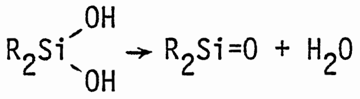
$$Ph_2Si(OH)-CH_2H \xrightarrow{-H_2O} Ph_2Si{=}CH_2$$

$$Ph_2Si(OH)-CH_2H \longrightarrow Ph_2(CH_3)_2Si + [Ph_2(CH_3)_2Si]_2O + Ph\text{-}Ph + Ph_2\,Si(OH)CH_3 \qquad (3)$$

In 1952 Andrianov and Sokolov[12] announced the generation of an unstable species possessing a silicon-oxygen double bond in a mass spectrometer (Eq. 4-6).



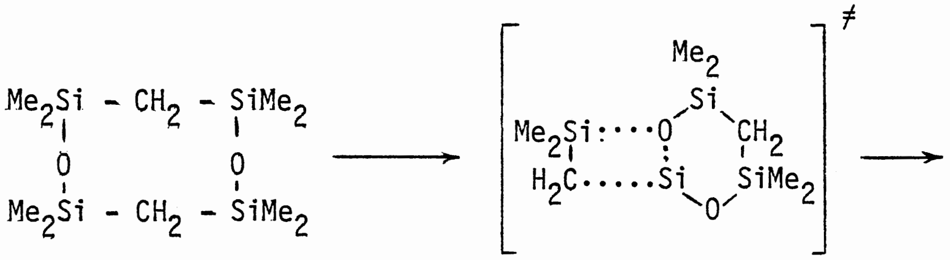
(4)

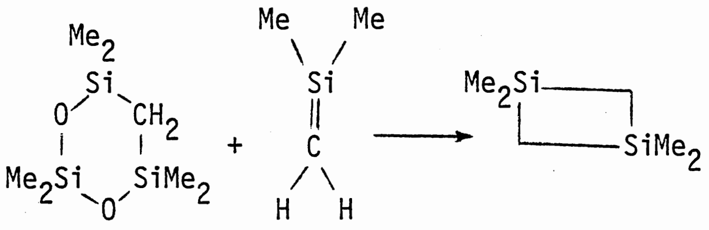


(5)

$$n\ R_2Si{=}O \rightarrow (R_2SiO)_n \qquad (6)$$

In recent years, additional reports have appeared concerning the transient formation of silicon analogs of unsaturated carbon compounds, such as from the pyrolysis of eight membered cyclocarbosiloxanes containing siloxane and silamethylene groups (Eq. 7). All the approaches chosen for the synthesis of a multiple bonded silicon have been collected in a recent review by Gusel 'Nikov and Nametkin.[13]



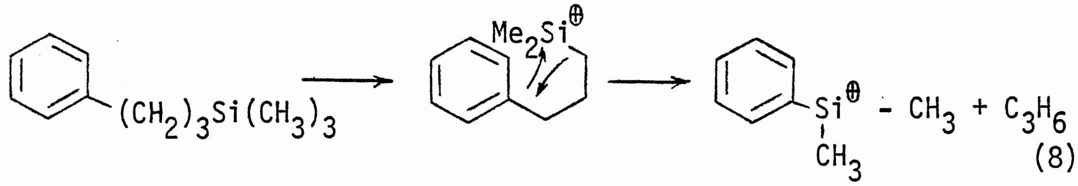


(7)

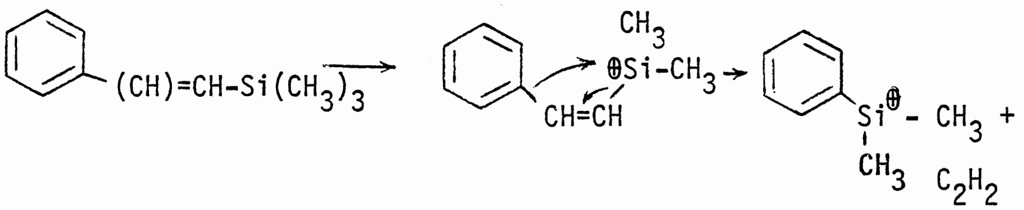
These reports support the notion of the inherent instability of such species.[14]

Silicenium Ion

Considering the Pauling electronegativities of silicon and carbon (1.8 and 2.5, respectively), one would expect ion formation for silicon to be at least as easy as that for carbon, that is for the formation of $R_3C^{\oplus}$. This is true for the formation in the gas phase.[15, 16] For example, in the mass spectroscopic study of 1-(trimethylsilyl)-3-phenylpropane and β-(trimethylsilyl)-styrene, formation of silicenium ions was detected, and further evidence was provided by observation of metastable ions.[17]



(8)



(9)

However, in solution all attempts to obtain silicenium ions, R_3Si^+, have failed. Different methods which have demonstrated the existence of carbonium ions have been applied to demonstrate the existence of trivalent positively charged silicon species. These methods are: (a) detection by physicochemical measurements, (b) preparation of stable salts, and (c) intervention as an intermediate in reaction mechanisms.

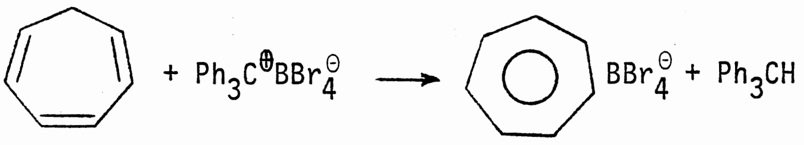
Conductivity measurements indicate no appreciable ionization of Ph_3SiCl in pyridine, nitrobenzene-aluminium tribromide, or liquid sulfur dioxide.[18] In contrast these solvents cause ionization of Ph_3CCl.[18, 19]

Attempts using silicon compounds[20] in place of carbon compound also have been made to repeat reactions which lead to stable carbonium ion salts, but no salts containing the silicenium ion were isolated (Eqs. 10 and 11).

$$\mathrm{Ph_3SiBr + BBr_3 \not\longrightarrow Ph_3Si^{\oplus}BBr_4^{\ominus}} \tag{10}$$

$$\mathrm{Ph_3CBr + BBr_3 \longrightarrow Ph_3C^{\oplus}BBr_4^{\ominus}} \tag{11}$$

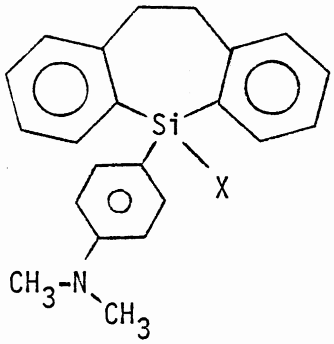
Since Si-H bonds (ΔH = 70-76 kcal/mole) are weaker than C-H bonds (99 kcal/mole), triphenylsilane has been tried as a hydride source in its reaction with trityl cation, a common hydride acceptor (Eq. 12). Unfortunately hydride transfer did not occur; instead the formation of the bromosilane was observed (Eq. 13).



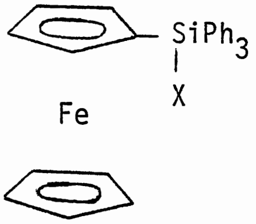
(12, ref. 21)

$$\mathrm{Ph_3Si{-}H + Ph_3C^{\oplus}BBr_4^{\ominus} \longrightarrow Ph_3SiBr + Ph_3CH + BBr_3} \tag{13, ref. 22}$$

In spite of the failure to demonstrate the existence of a stable silicenium ion, this species has often been invoked as a reaction intermediate.[23] Also, the hydride transfer from compounds containing a Si-H bond to an existing carbonium ion has been studied several times, but none of the results favor a mechanism involving Si-H bond ionization.[24] Extensive study of the racemization of optically active silanes bearing different substituents in a variety of solvent systems has been done. The resulting data are not consistent with a $R_3Si^{\oplus}$ intermediate with a trigonal planar structure; however, the data are in agreement with a scheme involving coordination of the solvent with the silicon atom.[25] In 1975 two reports of the generation of silicenium ions in methylene chloride at low temperature were reported by Corey.[26] In both cases an electronically stabilized silicenium ion was conceivably produced by hydride abstraction from silicon using triphenylmethyl perchlorate in methylene chloride at low temperature to produce with silane <u>II</u>, a yellow-green solution, and with <u>III</u>, a dark-green solution. When the cold triphenylmethyl perchlorate-silane solutions were added to a solution of sodium borodeuteride in diglyme, immediate decoloration was observed, and a high yield of triphenylmethane and the deuterated silanes <u>II</u> or <u>III</u> were obtained. However,

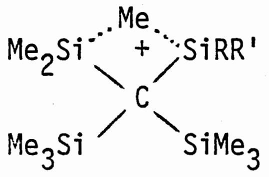


II



III

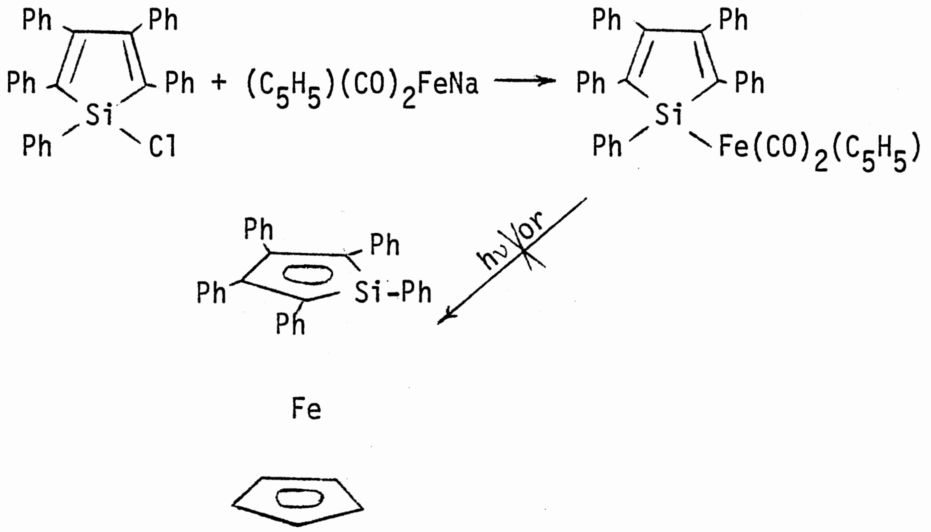
both reactions were reexamined by Barton[27], who discovered that not only silanes II and III, but a wide variety of silyl hydrides, react with triphenylmethyl perchlorate to instantaneously decolorize the solution and afford triphenylmethane and the silyl perchlorate. Also the silyl perchlorate $Et_3Si-OClO_3$ was shown to react immediately and quantitatively with $NaBH_4$ to afford Et_3Si-H under similar conditions as reported previously. Therefore, it was concluded that all of the evidence presented by Corey can be reproduced with systems for which there is no particular reason to presume silicenium ion involvement. Recently the reaction of compounds of the type $(Me_3Si)_3CSiRR'X$ (where X = I or H; R and R' = Me, Et, or Ph) with electrophilic reagents in alcohols and acids (or mixture of these) was studied by Eaborn.[28] The results were interpreted in terms of the formation of a cationic intermediate by abstraction of $X^{\ominus}$ from the silane by the electrophile. A structure IV involving a methyl group bridging two silicon atoms was suggested for this cation.



IV

Stabilization of Reactive Silicon Species by Transition Metals

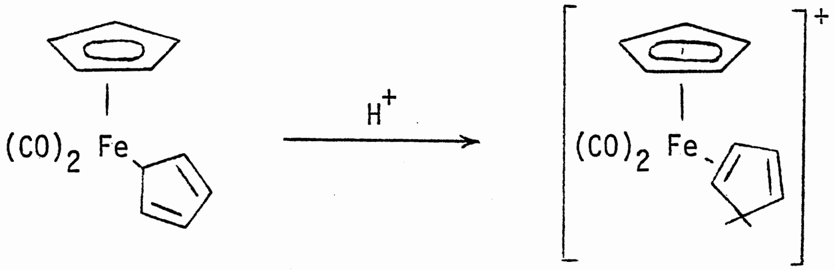
Because of the failure to generate stable multiple bonded silicon species and the ambiguity regarding the existence of silicenium ions, the coordination of silanes to transition metals and the investigation of the chemistry of the resulting complexes have become an extensive research area. In 1969 several compounds possessing silicon sigma bonded to transition metal carbonyls were synthesized by Curtis.[29] In an attempt to rearrange these to π-bonded sandwich compounds, they were heated and photolyzed. But neither photolysis nor thermolysis gave the expected π-sandwich complex (Eq. 14).[30]



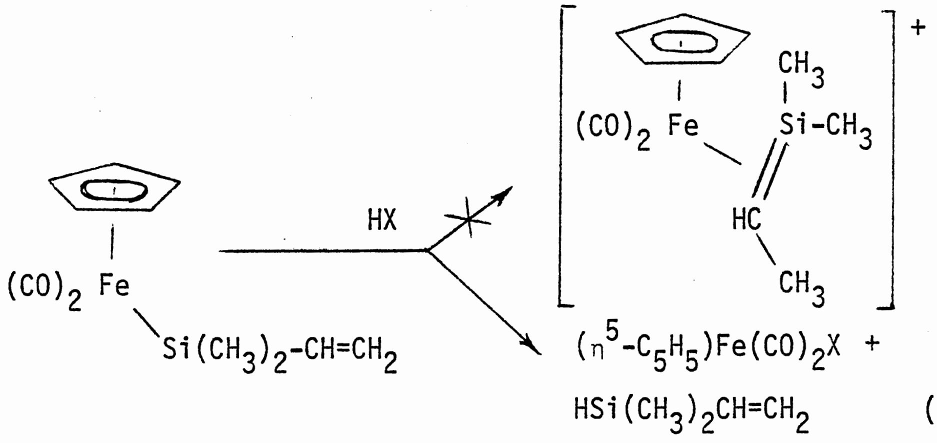
(14)

In 1970 Fitch reported the synthesis of η^4-dimethyldivinylsilanetricarbonyliron by treating the corresponding silane with dodecacarbonyltriiron.[31] The IR spectrum of the complex was reorted to have peaks at 2010 and 1995 cm^{-1} in addition to the expected metal carbonyl peaks (2065, 1982, and 1967 cm^{-1}). The two additional peaks were explained by either the presence of pentacarbonyliron or a type of tautomeric motion in which the silicon atom may occupy two positions in the molecule one of which would require an iron-silicon interaction. In order to further examine the interaction of transition metals with silicon, complexes of the type: $(CH_3)_3MCH{=}CH_2\cdot CuCl$ and $(CH_3)_2M(CH{=}CH_2)_2\cdot 2CuCl$, (M = Si and Sn) were synthesized.[32] These complexes were reported to be extremely stable compared to their carbon analogues, and in the case of the divinyl complexes, they appear to be among the most stable olefin copper (I) chloride complexes. The unusual stability of these complexes was explained by the interaction between the π^*-orbital and an empty d-orbital, such as $d_{x^2-y^2}$ or d_{z^2}, on the Group IV metal which delocalizes electron density onto the Group IVA metal by the backbonding of the transition metal. A direct d-d orbital interaction between the copper atom and the Group IVA atom was considered as another alternative.

A typical reaction of σ-allyl complexes is their facile protonation with acids to afford cationic π-olefinic metal complexes (Eq. 15).[33] Despite the generality of this route, treatment of the σ-vinylsilane complex η^5-$C_5H_5(CO)_2FeSi(CH_3)_2CH{=}CH_2$ with acid did not produce the anticipated cationic complex, rather the vinylsilane was replaced by the conjugate base of the acid (Eq. 16).[34]

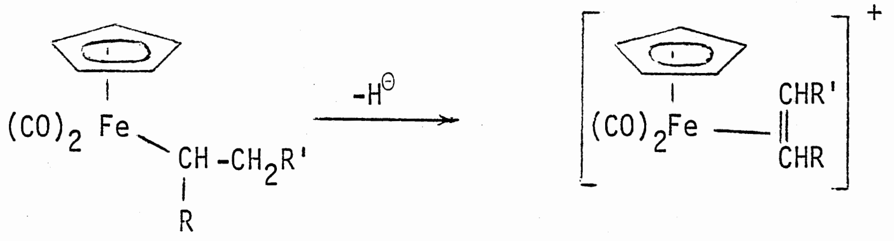


(15)



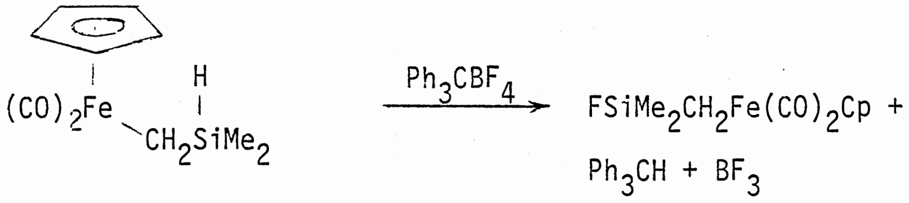
(16)

Another approach to generate π-ethylenic complexes involves the hydride abstraction from σ-alkyl complexes (Eq. 17).[35]



(17)

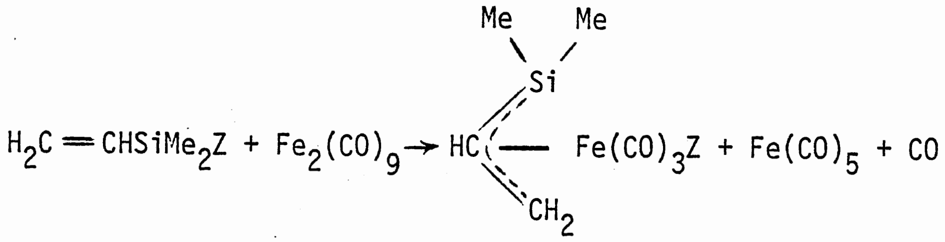
To modify the above route, $HSi(CH_3)_2-CH_2Fe(CO)_2Cp$ was synthesized by Bulkowski[36], but reaction of this complex with Ph_3CBF_4 as the hydride abstracting reagent did not give the desired complex. The only reaction was fluorination of the Si-H bond producing the new fluorosilylmethyl complex $FSi(CH_3)_2CH_2Fe(CO)_2Cp$.



(18)

In 1976 Sakurai and his co-workers reported the synthesis of the η^3-silapropenyltricarbonyliron complexes VIa and VIb by reacting enneacarbonyldiiron with vinylpentamethyldisilane (Va) and 1,2-divinyltetramethyldisilane (Vb).[37] These complexes represented the first stable compounds of doubly bonded silicon (Eq. 19).

The structures of the complexes were determined from various spectroscopic data. The porton NMR spectra of the complexes show three $Si-CH_3$ signals with relative intensities of 1:3:1. These signals were assigned to the protons of the anti-CH_3, $Si(CH_3)_3$, and syn-CH_3 groups by reference to the spectral data of the related π-allyliron complexes.[38] The proton decoupled ^{13}C-NMR spectra of the complexes were



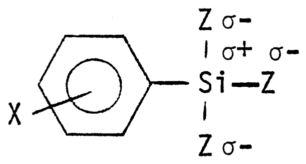
Va, Z = $(CH_3)_3Si$ VIa, Z = $(CH_3)_3Si$
b, Z = $(C_2H_3)Me_2Si$ b, Z = $(C_2H_3)Me_2Si$ (19)

reported to show three C-Si signals with relative intensities of 1:3:1. The mass spectra of the complexes were reported to show the corresponding molecular ion and successive loss of three CO molecules. In the IR spectra of the complexes (thin film) an absorption at 1315 cm^{-1} with medium intensity was detected. The C═C stretching frequency in the π-allyl complex is known to appear at a frequency about 100 cm^{-1} lower than that of the free C═C bond.[39] Since the stretching frequency of an uncoordinated Si═C bond was reported by Barton and McIntosh[40] to be 1407 cm^{-1}, the peak at 1315 cm^{-1} was assigned to a coordinated Si═C bond. However, the results of this thesis show the proposed structure is in error (see ahead).[41]

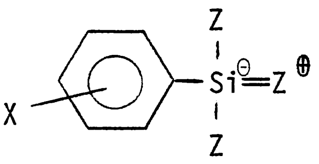
Spectroscopic Evidence for the Presence of p_π-d_π Dative Bonds

The possibility that partial multiple bonding might occur in compounds of the second and higher row elements was pointed out by Pauling[42], who suggested this phenomenon in order to account for the shortening of Si—X and Si—O bonds. Since then a vast number of reports has been published to either confirm or deny the existence of p_π-d_π bonds in the explanations of the unexpected behavior of silicon compounds.

The ^{29}Si-NMR spectra of a series of substituted methylsilanes have been studied by Hunter and Reeves.[43] They concluded that the compounds $M(CH_3)_n(OR)_{4-n}$ give opposite trends for the M chemical shift compared to that of the corresponding carbon analogues. When M is carbon, the addition of an -OR group is strongly deshielding; while, when M is silicon, the effect is strongly shielding after the first -OR group. Similar behavior had also been observed for the attachment of nitrogen and fluorine atoms.[43] The authors assumed that "an increase in π-bonding manifests itself as a shielding effect whereas increasing the polarity of the sp^3 orbitals causes deshielding." Ernst and co-workers[44] studied the ^{29}Si-NMR chemical shifts of a number of aryltrifluoro-, aryltrichloro-, aryltriethoxy-, and aryltrihydrosilanes, and reported that, in contrast to the chemical shift trends in aryltrihydro- and aryltrimethylsilanes, aryltrifluro-, aryltrichloro-, and aryltriethoxysilanes gave downfield shitfs with increasing electron donation by meta and para substituents on the phenyl ring. The authors mentioned that arguments similar to those given by Hunter and Reeves[43] could be used to rationalize these observations.



VIIa



VIIb

Resonance structure VIIb would be stabilized by electron withdrawal by X, leading to an increase in π-bonding and, as a consequence, shielding of the silicon nucleus. This shielding overcompensates for the deshielding effect produced by an increase in the polarization of the Si—Z bond from electron withdrawal by X in VIIa. Resonance contributor VIIb would not be expected to contribute significantly to the ground state description of the phenyltrihydro- and phenyltrimethylsilane, and consequently normal electronic effects should be observed. Indeed such a simplistic explanation appears attractive, but semiempirical quantum chemical (CNDO/2) calculations[44] of electron density at silicon for phenyltrifluoro-, phenyltrihydro-, and phenyltrimethylsilanes indicated no unusual reversal in the density trends to account for the observations.

The results of several studies of the NMR spectra of substituted methysilanes were thought to be best explained in terms of p_π-d_π bonding between silicon and electronegative substituents. For example, the smaller than expected downfield shifts of the proton resonances in hexamethyldisiloxane[45] and tris(trimethylsilyl)amine[46] relative to those in tetramethylsilane, the smaller downfield shifts with increasing n in the series $(CH_3)_{4-n}MCl_n$ and $(CH_3)_{3-n}MCl_n$ when M is silicon than when M is carbon[47], the decrease in shielding along the series $(CH_3)_3$-SiX, X = F, Cl, Br, I; and the increase in $J\,(^{29}SiH)$ in $(CH_3)_3{}^{29}SiX$ along the series $CH_3 < F < Cl < Br < I$[48] all have been explained in terms of p_π-d_π bonding.

Ebsworth and Frankiss studied several substituted methylsilanes and related alkanes.[49] They reported that the β-proton shielding in the series of compounds CH_3SiH_2X decreases along the series X = H, N, O, F, (which is consistent with increasing inductive deshielding), but increases along the series X = I, Br, Cl, F which is similar to the effect observed in the trimethylsilylhalides, and has been explained in terms of increasing p_π-d_π bonding between silicon and the halogen atoms in the order I<Br<Cl<F. However, the same effect was observed in ethyl, isopropyl, t-butyl[50], and cyclohexyl[51] halides, and since it occurs in compounds in which the α-atom is carbon, Ebsworth and Frankiss believed it is unlikely to be caused by p_π-d_π bonding and concluded that there is apparently no unusual bonding in the silicon compounds. Whether it is unjustified to use these reported effects as evidence in favor of the occurrence of π-bonding in silicon compounds or not still remains unanswered.

Transmission of Electronic Effects in Coordinated π-Systems

The bonding between olefinic ligands and the transition metals is best described by the Dewar-Chatt model.[3] Based on this model, the stability of the complexes could be expalined by: (a) interaction between the filled olefinic π-molecular orbitals with the empty orbitals on the metal, and (b) interaction of vacant olefinic antibonding, π^*-molecular orbitals with filled hybrid atomic orbitals of the metal. Thus the stability of olefin-transition metal complexes and the transmission of electronic effects in coordinated π-systems are not only dependent on the substituents of the π-system, but also are dependent upon the metal. For example, stability constant studies show that conjugated C═C systems such as in crotonic acid form less stable complexes than ethylene with platinum and silver.[52] Conversely substituents which conjugate with the bonding C═C system appear to stabilize the olefin-metal bond in the case of iron.

As a general rule formation of a complex between an olefinic π-system and a transition metal causes the lowering of the C═C stretching frequency by 60-150 cm^{-1} [53] and the upfield displacement of the vinyl proton chemical shifts.[54] Both observations can be explained by the description of bonding proposed by Dewar and Chatt. The removal of electrons from the bonding π-orbital of the ethylene and the placing of electrons into the antibonding π*-orbital of the ethylene would weaken the C═C bonding and give rise to more single bonded character.

The presence of substituents in substituted ethylenes can effect the olefin-metal bond strength by steric interactions or by changing the energies of the π- and π*-orbitals. In the case of conjugating substituents a considerable change in the energies of the π- and π*-orbitals occurs. A number of conjugated olefin tetracarbonyliron complexes have been prepared; for example, $(RHC{=}CHX)Fe(CO)_4$ where X = CN, COOH, CHO, and $-HC{=}CH_2$.[55] It has been argued that the apparent increase in olefin-metal bond strength for conjugated olefins occurs, because the energies of the olefinic electrons more nearly match the energies of the iron electrons than in the case of ethylene and non-conjugated olefins.

CHAPTER II

STATEMENT OF THE PROBLEM

The manner in which the stabilities and reactivities of organic species are modified by coordination to transition metals has received considerable attention over the past several years. One of the most interesting and synthetically useful applications in this area has involved the preparation of extraordinarily stable transition metal complexes of highly reactive species which are not normally stable at ambient temperature.

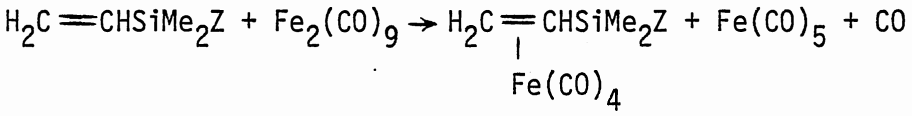
In view of the paucity of the information regarding multiply bonded silicon compounds, as indicated in the Introduction, the preparation of stable transition metal complexes of highly reactive elusive silicon species and the examination of the physical and chemical properties of such complexes would significantly enhance the knowledge of the chemistry of the free silicon species. As indicated earlier, several attempts have previously been made to prepare such complexes by rearrangement of σ-silicon-metal complexes to their corresponding π-complexes. However, all these attempts have been unsuccessful.

In view of the known stabilities of the (η^3-propenyl)tetracarbonyliron cation and its halide derivative, the preparation (or transient generation) of <u>dihapto</u> complexes of substituted vinylsilanes was to be pursued as possible precursors to (η^3-1-silapropenyl)tetra (or tri)carbonyl complexes (neutral or postively charged). The cationic trihapto-silapropenyl metal complexes were of special interest since they would embody the features of both a coordinated silicenium ion and a doubly bonded silicon species. The dihapto complexes of substituted vinyldimethylsilanes would, in their own right, be of theoretical interest in terms of providing an opportunity to study the effect of transition metal complexation upon the transmission of electronic effects in a series of substituted vinylsilanes. The role of p_π-d_π bonding in silicon compounds has been widely debated, and consequently the physical and chemical properties of such complexes would clarify the importance of p_π-d_π bonding in the free, as well as, complexed silicon species.

CHAPTER III

RESULTS AND DISCUSSION

Complexes of several vinylsilanes, as precursors for possible formation of a coordinated silicon-carbon double bond or silicenium ion, were prepared by reacting enneacarbonyldiiron with vinylsilanes (Eq. 20). The spectroscopic data for all of the vinyl silane complexes are consistent with the <u>dihapto</u> structure, iron being coordinated to the vinyl system.



$$H_2C{=}CHSiMe_2Z + Fe_2(CO)_9 \rightarrow \underset{Fe(CO)_4}{H_2C{=}CHSiMe_2Z} + Fe(CO)_5 + CO$$

Va, Z = $(CH_3)_3Si$ VIII a, Z = $(CH_3)_3Si$
c, Z = Me c, Z = Me
d, Z = OEt d, Z = OEt
e, Z = Cl e, Z = Cl
f, Z = F f, Z = F
g, Z = $OSiMe_2C_2H_3$ g, Z = $OSiMe_2C_2H_3$
h, Z = OH h, Z = OH
i, Z = N_3 i, Z = N_3
j, Z = OPh (20)

All of the vinylsilane complexes which were prepared are yellow, viscous liquids and compared to their carbon analogues, are remarkably stable. For comparison purposes, (ethylene)tetracarbonyliron has been reported to decompose above -40°C.[56] Because the complexes are relatively air sensitive and decompose upon standing at room temperature over a period of 4-5 hr., they are best stored in an inert atmosphere at 0°C. The stabilities of the complexes are roughly correlated with the electronegativity of the substituent on the silicon. The higher the electronegativity of the substituent, the more stable is the complex.

The enhanced stability of the vinylsilane complexes compared to the carbon analogues has also been observed by Fitch and co-workers.[57] They have argued that the vinylsilane complexes are stabilized through a mechanism which enhances their ability to accept back-donated electron density from the metal such as by an interaction between the π^*-orbital of the olefin and a d-orbital of suitable symmetry on the silicon atom. Using the same argument the observed stability of the vinylsilane complexes prepared in this study and the effect of the substituents on the stability can be explained. The perturbation interaction of the π- and π^*-orbitals of the olefin with a d-orbital of suitable symmetry on the silicon atom lowers both the π- and π^*-orbitals of the olefin leading to enhancement of the back-donation of electrons by the iron, thus stabilizing the complex. The introduction of more electronegative substituents on silicon contracts and lowers the energy of the d-orbitals which results in greater overlap between the π^*-orbital of the olefin and a d-orbital of the silicon. Consequently, the capacity of the olefin π^*-orbital to accept the back-donated electron density from the iron increases and leads to stabilization of the complex. The other alternative is the direct involvement of an iron d-orbital with a d-oribital of suitable symmetry on the silicon atom which also could cause the stabilization of the complexes. The more electronegative the substituent is, the more contracted the d-orbitals on the silicon are. Thus, a greater overlap between filled metal d-orbital and silicon empty d-orbital leads to the greater stabilization.

Spectroscopic Characterization

IR Spectral Data

The IR spectra (Table I) of all of the complexes prepared possess three metal carbonyl stretching bonds at room temperature. However, the IR spectra of the complexes at low temperature, $90^{o}K$, show a shoulder at 2010-2040 cm^{-1} in addition to the other three metal carbonyl stretching frequencies which is consistent with the presence of tetracarbonyl species.

The IR spectra of the azide, chloride, and fluoride complexes all show peaks corresponding to a Si-Z or Z stretching frequency which is consistent with the preservation of the vinyldimethylsilane structure upon coordination. Interestingly, these stretching frequencies do not change appreciably by coordination of the vinylsilane to the metal: c.f. N_3 2140 (complex) and 2143 (free ligand) cm^{-1}; Si-Cl 470 and 470 cm^{-1}; Si-F 864 and 878, 895 cm^{-1}.[58]

The IR spectra of all the complexes exhibit an IR absorption band with medium to weak intensity at 1317-1324 cm^{-1}. The IR spectrum of (ethylene)tetracarbonyliron is also reported to have peak at 1317 cm^{-1}.[59] It is reasonable to assign this peak to a CH_2 deformation.

TABLE I

SELECTED IR DATA FOR SUBSTITUTED (η^2-VINYLDIMETHYLSILANE)TETRACARBONYLIRON COMPLEXES VIII (cm^{-1})[a]

Me	$SiMe_3$	OEt	$OSiMe_2C_2H_3$[b]	OPh[b]	OH[b]	F	Cl	N_3[b]
2058 m	2083 m	2088 m	2088 m	2085 s	2082 s	2091 m	2090 m	2085 m, 2140
2040 s,sh	2030 s,sh	2040 s,sh	2010 s,sh	2010 s,sh	2005 s,sh			
2000 vs	1997 vs	2000 vs	1990 vs	1980 vs	1990 vs	2012	2000 vs	2000 vs
1971 vs	1973 vs	1975 vs	1968 vs	1900 vs	1970 vs	1974 vs	1980 vs	1970 vs
				1597 m				
1404 w	1400 w	1390 w	1400 w	1490 s	1400 w	1400 w	1407 w	1405 w
1320 m	1317 m	1325 m	1316 m	1317 m	1319 m	1315 m	1316 m	1317 m
1259 m	1245 s	1253 s	1256 s	1253 s	1252 s	1255 s	1254 s	1260 s
1249 s								
1201 m	1200 m	1197 m	1195 m	1198 m	1195 m	1196 m	1195 m	1196 m
		1104 s						
		1070 s	1032 s	1025 m	1030 m	1039 m	1042 m	1037 m
853 s	835 s	838 s	830 s	910 s	830 s	864 s	844 s	839 s
837 s						841 s	812 s	815 s
	800 s	792 s	784 s		774 s	795 s	790 s	790 s
635 s	637 s	637 vs				638 s	695 s	
616 m	617 w	618 s	627 vs		624 m	624 m	615 m	625 s
592 s	595 m	598 s				598 s	594 m	

---

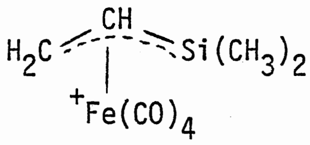
[a] Thin films (5-10 mm) at 90°K, unless otherwise indicated. Spectra recorded at room temperature were only slightly different.

[b] Thin films at room temperature.

Mass Spectral Data

All the vinylsilane complexes are sensitive to elevated probe and ion-source temperatures and easily lose carbon monoxide. Thus, special care is necessary for obtaining an accurate mass spectrum. We designed a special probe which would introduce the complex directly to the ion source chamber through a molecular leak. Also with repeatedly scanning at different temperatures, we were able to optimize the ion source temperature.

All of the vinyldimethylsilane complexes examined by mass spectroscopy show mass peaks corresponding to the tetracarbonyliron complex and fragments from subsequent loss of four carbon monoxide molecules (Table II). Moreover, in all cases the mass fragment corresponding to (M^+-Z) (m/e 253) is detected, which is evidence for the existence of the (η^3-1-silapropenyl)tetracarbonyliron cation IX in the gas phase. The existence of a silicenium ion in the gas phase has been reported previously.[16]



IX

NMR Spectral Data

The ^{13}C-chemical shifts of the vinyl carbon atoms of the complexes (Table III) appear at higher field than those of the corresponding free ligands (Table IV); they are consistent with a η^2-tetracarbonyliron structure and were assigned from the inspection of the proton coupled

TABLE II

MASS SPECTRAL DATA FOR SUBSTITUTED (η^2-VINYLDIMETHYLSILANE)-TETRACARBONYLIRON COMPLEXES*

m/e	CH_3	$SiMe_3$	OEt	Cl	F
P	268(9.1)	326(12.8)	298(8.1)	288(2)	272(8.3)
P-Me	253(3.0)	311(3.5)	283(8.8)	273(1.5)	---------
P-Z	253(3.0)	253(3.5)	253(6.6)	253(4.0)	---------
P-CO	240(6.1)	298(9.9)	270(30.9)	260(17)	244(8.3)
P-2CO	212(14)	270(36.1)	242(50)	232(36)	216(14.6)
P-3CO	184(33)	242(48.9)	214(27.9)	204(74)	188(29.2)
P-4CO	156(69)	214(73)	186(100)	176(79)	160(100)
P-Fe(CO)$_4$	100(19)	158(30.5)	---------	120(100)	104(8.3)
P-Fe(CO)$_4$, Me	85(100)	143(39.7)	115(74.3)	--------	---------
		85(87.2)	184(44.9)		
		(P-Fe(CO)$_4$, $SiMe_3$)	(P-3CO,2Me)		
		73(100)			
		($SiMe_3$)			

*Values in parentheses are relative intensities.

spectrum. The upfield shifts of the C_α absorption upon coordination are conspicuously constant, ~95 ppm; however, the upfield shifts of C_β absorption range from ~88 to 97 ppm. The chemical shifts of the vinyl carbon atoms of the complex linearly correlate well with

TABLE III

^{13}C-NMR CHEMICAL SHIFT DATA FOR SUBSTITUTED (η^2-VINYLDIMETHYLSILANE) TETRACARBONYLIRON COMPLEXES VIII*

Z	C_α	C_β	C_{Si}	M-CO		
Me	45.1	41.8	0.26	211.7		
$SiMe_3$	44.7	41.9	-1.37;-4.46	211.7	$SiMe_3$: -2.24	
$OSiMe_2C_2H_3$	43.7	40.6	2.41; 0.11	211.2	C_α:139.1 C_β:131.6	$SiMe_2$: 1.66; 1.45
OH	43.2	40.5	1.63; 1.31	211.2		
OEt	42.4	40.7	-0.26;-0.62	211.1	CH_2: 58.7	$CH_{3'}$: 18.3
OPh	40.4	40.2	0.56;-0.03	210.6	$C_{1'}$:154.4 $C_{2'}$:129.3	$C_{3'}$:119.6 $C_{4'}$:121.3
Cl	40.6	39.6	3.90; 2.63	210.1		
F	38.6	39.4;39.2	0.35;-0.32 0.23;-0.38	210.2		
N_3	37.7	39.3	-0.76;-1.89	210.0		

*Chemical shifts are in ppm relative to TMS in $DCCl_3$.

TABLE IV

^{13}C-NMR CHEMICAL SHIFT DATA FOR SUBSTITUTED VINYLDIMETHYLSILANES V*

Z	C_α	C_β	C_{Si}
CH_3	140.2	130.6	-1.57
$SiMe_3$	138.7	130.6	-2.30;-4.49
$OSiMe_2C_2H_3$	139.4	131.4	0.55; 0.41
OH	138.6	132.1	-0.30;-0.41
OEt	137.4	132.8	-2.1
Cl	135.9	133.8	1.57
F	135.1;135.8	134.0;134.2	-1.33;-1.96
N_3	133.6	134.6	-2.75;-2.83

*Chemical shifts are in ppm, relative to TMS in $DCCl_3$.

those for the analogous carbons in the free ligand. By plotting the C_α and C_β chemical shifts in the complex against the analogous shifts for the carbons in the ligand, straight lines are obtained with correlation coefficients of 0.97 and 0.95 and slopes of 1.19 and -0.62, respectively (Figure 3 and 4). The positive value of the slope for the graph of $C_{\alpha C}$ versus $C_{\alpha F}$ represent the similarity of the transmission of electronic effects at C_α in these two systems; however, the negative slope value of the plot of $C_{\beta C}$ versus $C_{\beta F}$ indicates that the transmission of electronic effect at C_β has been inverted upon coordination. Such

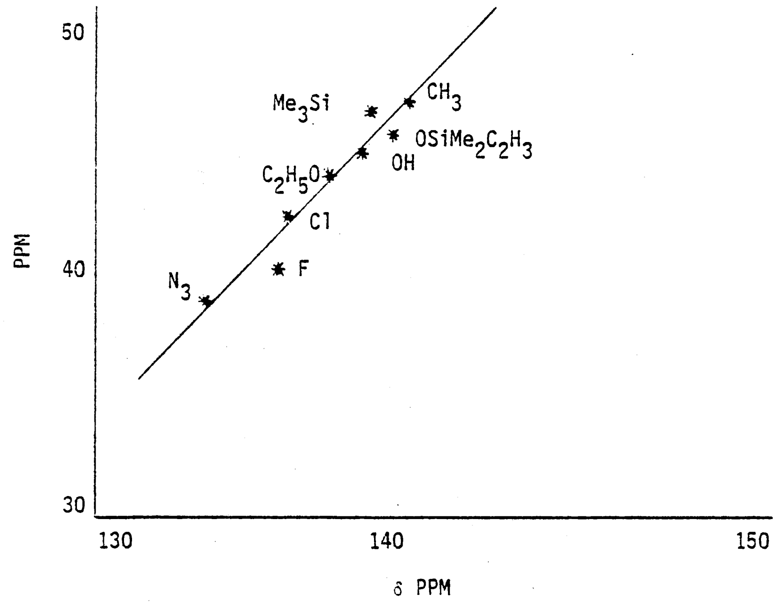


Figure 3. ^{13}C-NMR Chemical Shifts: δ C_α in Complex, $C_{\alpha}C$, vs. δ C_α in Free Ligand, $C_{\alpha}F$.

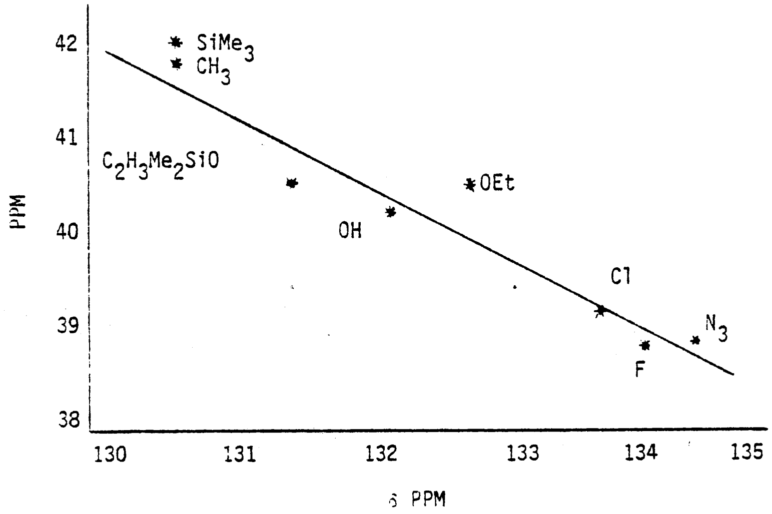


Figure 4. ^{13}C-NMR Chemical Shifts: δ C_β in Complex, $C_{\beta}C$, vs. δ C_β in Free Ligand, $C_{\beta}F$.

inversion is due to the back-donation of electrons from the metal to this carbon. Although the ^{13}C-chemical shift values of C_α and C_β do not correlate to a high degree with the electronegativity of the substituents in either the complexes or in the free ligands, the relative magnitude of the shifts of the vinyl carbon atoms in both systems suggests that the substituent effect is primarily inductive in nature. The comparison of the ^{13}C-chemical shifts of the vinyldimethylsilanes with those of the related hydrocarbons, $H_2C{=}CH\text{-}CH_2Z$,[60] shows an increase in the shielding of the C_α atom, ranging from 0.9 to 1.4 ppm, and a decrease in the shielding of the C_β atom, ranging from 17.1 to 20.2 ppm. Similar behavior has also been observed by Yuriev and coworkers for the trisubstituted vinylsilanes $H_2C{=}CHSiZ_3$, Z = CH_3, OEt, and Cl,[61] and has been explained based on p_π-d_π interaction. The coupling constant values (Table V) point to the similarity of the structure of vinylsilanes and their tetracarbonyl complexes.

Since the contributions to the chemical shift changes induced by the substituent are generally either a result of inductive, field or resonance effects, the use of linear free-energy relationships has found great utility in the study of substituent effects in NMR spectroscopy.[62] We have attempted to correlate the ^{13}C-chemical shifts of vinyldimethylsilanes and their tetracarbonyliron complexes with several physical constants (Tables VI-IX) in hopes of learning about the relative importance of these interactions and the mechanisms through which the substituent effects are transmitted. A two (or more) parameter equation such as Equation 21 was used, where δ is the ^{13}C-chemical shift of a particular carbon, A is an inductive effect parameter, and B is a resonance effect parameter. Such correlation was evaluated for the

TABLE V

COUPLING CONSTANT DATA FOR SUBSTITUTED VINYLSILANE AND THEIR COMPLEXES*

Z	$J_{C\text{-}Si\text{-}C\text{-}H}$	$J_{C_\alpha H_a}$	$J_{C_\beta H_b}$	$J_{C_\beta H_a}$
		Vinylsilanes		
CH_3	118.7	142.8	158.0	12.2
$SiMe_3$	119.9	142.6	158.3	12.3
$OSiMe_2C_2H_3$	118.4	142.8	158.0	12.0
OH	118.4	140.4	158.3	11.7
OEt	118.7	141.4	158.1	11.8
Cl	121.1	146.9	159.4	11.3
F	119.4	143.2	158.9	11.8
N_3	120.6	142.0	159.2	11.3
		Vinylsilane Complexes		
CH_3	118.6	141.7	157.7	3.2
$SiMe_3$	-----	141.2	157.4	3.0
$OSiMe_2C_2H_3$	118.5	142.7	156.8	5.4
OH	118.7	143.1	158.6	4.5
OEt	119.3	136.2	158.6	4.8
OPh	119.2	137.1	159.0	5.2
Cl	121.0	137.4	158.4	3.6
F	119.9	138.3	159.5	3.9
N_3	120.6	139.6	158.1	5.1

*Values are in Hz.

TABLE VI

RESULTS OF THE LINEAR REGRESSION OF THE ^{13}C-CHEMICAL SHIFTS OF VINYLSILANES* $\delta 13C = aA + bB + 1$

Position	a	b	a/b	i	r	Std. Dev.
C^1_α	-7.40 (-8.53)	-------	-------	138.96 (139.99)	0.824 (0.977)	1.41 (0.49)
C^1_β	6.16 (6.19)	-------	-------	131.12 (130.87)	0.957 (0.989)	0.52 (0.24)
C^2_α	-9.93 (-9.00)	-4.43 (-1.36)	2.24 (6.62)	138.23 (139.60)	0.901 (0.986)	1.21 (0.47)
C^3_β	6.94 (6.32)	1.36 (0.38)	5.10 (16.60)	131.34 (130.98)	0.970 (0.991)	0.48 (0.27)
C^3_α	-9.71 (-9.03)	-2.79 (-0.87)	3.48 (10.40)	138.11 (139.55)	0.927 (0.988)	1.04 (0.44)
C^3_β	6.93 (6.34)	0.93 (0.26)	7.45 (24.4)	131.40 (131.00)	0.978 (0.991)	0.42 (0.26)
C^4_α	-11.15 (-10.22)	-5.29 (-2.56)	2.11 (3.99)	138.20 (139.31)	0.875 (0.956)	1.35 (0.81)
C^4_β	8.52 (7.38)	2.19 (1.27)	3.89 (5.81)	131.33 (131.18)	0.935 (0.964)	0.71 (0.53)

*Values in parentheses correspond to values with compounds Va and Vi excluded. Values a and b are correlation factors, i is the intercept, and r is the correlation coefficient.

(1) $\delta^{13}C + a\sigma_I + i$

(2) $\delta^{13}C = a\sigma_I + b\sigma_R + i$

(3) $\delta^{13}C = a\sigma_I + b\sigma_{R^+} + i$

(4) $\delta^{13}C = aF + bR + i$

TABLE VII

RESULTS OF THE LINEAR REGRESSION OF THE ^{13}C-CHEMICAL SHIFTS OF VINYLSILANES*

$\delta^{13}C = aA + bB + cC + i$

Position	a	b	c	i	r	Std. Dev.
(Si-$\underline{C}H_3$)^1	7.83 (5.90)	-------	-------	-2.02 (-1.77)	0.841 (0.772)	1.40 (1.26)
(Si-$\underline{C}H_3$)^2	9.14 (6.57)	2.29 (1.98)	-------	-1.64 (-1.19)	0.861 (0.802)	1.47 (1.45)
(Si-$\underline{C}H_3$)^3	9.13 (6.43)	1.57 (0.93)	-------	-1.54 (-1.30)	0.873 (0.792)	1.41 (1.48)
(Si-$\underline{C}H_3$)^4	11.14 (7.97)	3.24 (2.15)	-------	-1.70 (-1.40)	0.841 (0.854)	1.56 (1.27)
(Si-$\underline{C}H_3$)^5	(9.14)	(-5.92)	(-5.87)	(-9.45)	(0.854)	(1.79)
(Si-$\underline{C}H_3$)^6	(9.02)	(-3.27)	(-5.58)	(-9.09)	(0.865)	(1.73)

*Values in parentheses correspond to values with compounds $\underline{Va}$ and $\underline{Vi}$ excluded. Values a and b are correlation factors, i is the intercept, and r is the correlation coefficient.

(1) $\delta^{13}C = a\sigma_I + i$

(2) $\delta^{13}C = a\sigma_I + b\sigma_R + i$

(3) $\delta^{13}C = a\sigma_I + b\sigma_{R^+} + i$

(4) $\delta^{13}C = aF + bR + i$

(5) $\delta^{13}C = a\sigma_I + b\sigma_R + cEs + i$

(6) $\delta^{13}C = a\sigma_I + b\sigma_{R^+} + cEs + i$

TABLE VIII

RESULTS OF THE LINEAR REGRESSION OF THE ^{13}C-CHEMICAL SHIFTS OF VINYLSILANE COMPLEXES

$$\delta^{13}C = aA + bB + i$$

Position	a	b	a/b	i	r	Std. Dev.
C^1_α	-10.12 (-10.78)	-------	------	44.30 (45.04)	0.893 (0.956)	1.32 (0.76)
C^1_β	-4.16 (-4.26)	-------	------	41.53 (41.66)	0.970 (0.985)	0.27 (0.17)
C^2_α	-12.45 (-11.23)	-4.00 (-1.34)	3.11 (8.38)	43.63 (44.65)	0.929 (0.961)	1.19 (0.83)
C^3_β	-4.58 (-4.31)	-0.72 (-0.17)	6.36 (25.4)	41.41 (41.61)	0.977 (0.986)	0.26 (0.19)
C^3_α	-11.97 (-10.94)	-1.79 (-0.21)	6.69 (52.1)	43.69 (44.93)	0.930 (0.956)	1.18 (0.87)
C^3_β	-4.64 (-4.43)	-0.47 (-0.22)	9.87 (20.1)	41.37 (41.55)	0.986 (0.989)	0.20 (0.17)
C^4_α	-14.56 (-12.86)	-5.32 (-2.87)	2.74 (4.48)	43.59 (44.27)	0.894 (0.930)	1.44 (1.10)
C^4_β	-5.79 (-5.21)	-1.23 (-0.70)	4.71 (7.44)	41.45 (41.54)	0.961 (0.987)	0.34 (0.18)

*Values in parentheses correspond to values with complexes VIIIa and VIIIi excluded. Values a and b are correlation factors, i is the intercept, and r is the correlation coefficient.

(1) $\delta^{13}C = a\sigma_I + i$

(2) $\delta^{13}C = a\sigma_I + b\sigma_R + i$

(3) $\delta^{13}C = a\sigma_I + b\sigma_{R+} + i$

(4) $\delta^{13}C = aF + bR + i$

TABLE IX

RESULTS OF THE LINEAR REGRESSION OF THE ^{13}C-CHEMICAL SHIFTS OF VINYLSILANE COMPLEXES*

$\delta^{13}C = aA + bB + cC + i$

Position	a	b	c	i	r	Std. Dev.
$(Si\text{-}\underline{C}H_3)^1$	2.33 (1.69)	--------	--------	-0.40 (0.25)	0.362 (0.251)	1.56 (1.49)
$(Si\text{-}\underline{C}H_3)^2$	1.99 (2.70)	-0.60 (2.96)	--------	-0.50 (1.11)	0.369 (0.442)	1.70 (1.60)
$(Si\text{-}\underline{C}H_3)^3$	1.82 (2.80)	-0.50 (1.40)	--------	-0.57 (1.00)	0.384 (0.451)	1.70 (1.60)
$(Si\text{-}\underline{C}H_3)^4$	3.51 (3.30)	-0.60 (2.34)	--------	-0.78 (0.66)	0.451 (0.458)	1.60 (1.60)
$(Si\text{-}\underline{C}H_3)^5$	(9.00)	(-14.53)	(-13.03)	(-17.13)	(0.965)	(0.57)
$(Si\text{-}\underline{C}H_3)^6$	(5.95)	(-6.27)	(-6.27)	(-7.17)	(0.766)	(1.40)

*Values in parentheses correspond to values with complexes VIIIa and VIIIi excluded. Values a and b are correlation factors, i is the intercept, and r is the correlation coefficient.

(1) $\delta^{13}C = a\sigma_I + i$

(2) $\delta^{13}C = a\sigma_I + b\sigma_R + i$

(3) $\delta^{13}C = a\sigma_I + b\sigma_{R+} + i$

(4) $\delta^{13}C = aF + bR + i$

(5) $\delta^{13}C = a\sigma_I + b\sigma_R + cEs + i$

(6) $\delta^{13}C - a\sigma_I + b\sigma_{R+} + cEs + i$

$$\delta^{13}C = aA + bB + i \qquad (21)$$

^{13}C-chemical shifts of the vinyl carbons in the vinyldimethylsilanes and their complexes, where: (1) $A = \delta_I$, $B = 0$; (2) $A = \delta_I$, $B = \delta_R$; (3) $A = \delta_I$, $B = \delta_{R+}$; and (4) $A = F$, $B = R$. Values for these physical constants are tabulated in Table X. In the study of the linear regression of the ^{13}C-chemical shifts of the methyl carbon atoms an additional parameter, ES (Taft steric parameter),[64] was also considered. The correlation factors, a and b, were determined by regression analysis, viz. a minimization of the difference between the experimental chemical shifts and the chemical shifts calculated using Equation 21. The term i is the intercept of the regression analysis and theoretically corresponds to the calculated shift of a particular carbon in the parent system, Z = H. However, from the values of i tabulated in Table IX it is apparent that the intercept resulting from correlation of the (Si-CH$_3$) ^{13}C-chemical shifts and the parameters, δ_I, δ_R, and ES does not appear to be the ^{13}C-chemical shift of the (Si-CH$_3$) group when Z = H.

From the linear regression data (Tables VI and VIII) for both systems, the inductive effect of the substituents is the major substituent effect on the ^{13}C-chemical shifts of the vinyl carbons. The ratio of the correlation factors, a/b, represents the relative importance of the inductive effect of the substituents. As can be seen from the tables, when there is a good linear correlation, the inductive effect predominates over the resonance by at least a factor of 5. The correlation factors for C_α and C_β of vinyldimethylsilanes are of opposite sign whereas the correlation factors for C_α and C_β of vinyldimethylsilane complexes are of similar sign. These trends are apparent

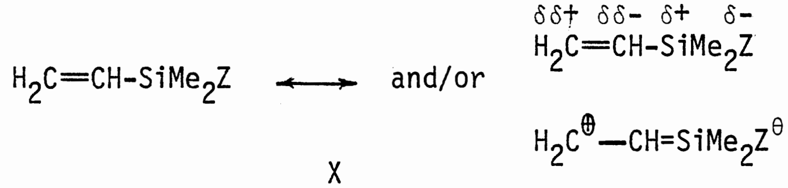
TABLE X

SUBSTITUENTS AND SUBSTITUENT CONSTANTS*

Substituent	σ_I	σ_R	σ_{R^+}	F	R	ES
Me	-0.05	-0.12	-0.206	-0.04	-0.13	-1.24
Cl	0.47	-0.24	-0.435	0.41	-0.15	-0.97
F	0.52	-0.46	-0.767	0.43	-0.34	-0.46
N_3	0.42	-0.27	-0.270	0.30	-0.13	
CH	0.25	-0.62	-1.103	0.29	-0.64	-0.55
OEt	0.27	-0.51	-0.847	0.22	-0.44	-0.55
OPh	0.39	-0.42	-1.289	0.34	-0.35	-0.55
$SiMe_3$	-0.13	0.06	0.037	-0.04	-0.04	

*Ref. 63 and 64.

from the ^{13}C-chemical shifts given in Tables III and IV; the chemical shifts of C_α and C_β change, by changing the substituents, in the opposite direction in vinyldimethylsilanes and in the same direction in the vinyldimethylsilane complexes. A scheme which is consistent with this data involves a resonance contribution and inductive polarization of In the case of the vinyldimethylsilane complexes, the back-donation of



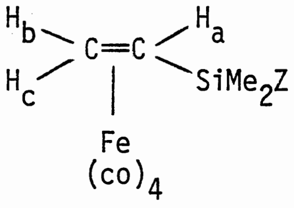
$$H_2C{=}CH\text{-}SiMe_2Z \longleftrightarrow \text{and/or} \begin{array}{l} \overset{\delta\delta+}{H_2C}{=}\overset{\delta\delta-}{CH}\text{-}\overset{\delta+}{SiMe_2}\overset{\delta-}{Z} \\ H_2C^{\oplus}{-}CH{=}SiMe_2Z^{\ominus} \end{array}$$

X

electrons by the metal to the π-system overcomes the electron deficiency on the C_β generated by the substituent effect, thus resulting in the shielding of both C_α and C_β in the complexes. Interestingly, behavior similar to the vinyldimethylsilanes has been observed for the 3-substituted propenes[60], systems in which the presence of p_π-d_π bonding is very unlikely.

No correlation with substituent constants has been observed for the Si-CH_3 ^{13}C-chemical shifts, either in the case of the vinylsilanes or in the case of the vinylsilane complexes.

The ^{1}H-NMR spectra of all the vinylsilane complexes (Table XI) except <u>VIIc</u> (Z = CH_3) show two Si-CH_3 signals with chemical shifts ranging from 0.00 to 0.54 ppm; with Z = CH_3 only a singlet at 0.18 ppm is observed. The magnetic nonequivalence of the methyl groups on the silicon atom is due to their disastereotopic nature. A similar observation has been reported by Fitch.[57] The NMR signals of the vinyl protons of all of the complexes appear at higher field than those of the free-ligand vinyl protons because of the coordination of the π-system to the iron atom.[54] The assignment of the proton chemical shifts was based on the relative size of the vicinal coupling constants, where $J_{trans} > J_{cis}$.[65] The signal for the <u>cis</u> vinyl proton H_b appears downfield from that for the <u>trans</u>, H_c, as observed with uncoordinated



VIII

TABLE XI

^{1}H-NMR CHEMICAL SHIFT DATA FOR SUBSTITUTED (η^2-VINYLDIMETHYLSILANE)TETRACARBONYLIRON COMPLEXES VIII*

Z	H_a	H_b	H_c	Me	J_{ab}	J_{bc}
$(CH_3)Si$	2.15 dd	3.03 d	2.53 d	0.23,0.00	10.5	14.8
CH_3	2.14 dd	3.04 d	2.58 d	0.18	10.7	14.6
Cl	2.08 dd	2.95 d	2.56 d	0.54,0.47	10.5	13.9
C_6H_5O	1.99 dd	2.95 d	2.66 d	0.35,0.34	10.9	14.3
OH	1.96 dd	2.92 d	2.56 d	0.26,0.23	10.7	14.4
$C_2H_3Me_2SiO$	1.94 dd	2.89 d	2.53 d	0.21,0.115	10.9	14.4
N_3	1.92 dd	2.94 d	2.59 d	0.40,0.34	11.2	14.3
C_2H_5O	1.90 dd	2.90 d	2.56 d	0.22,0.20	11.0	14.5
F	1.81 qd	2.88 dd	2.52 d	0.34,0.31	10.4	14.4

*Chemical shifts are in ppm relative to TMS in CS_2. Coupling constants are in Hz. Hydrogen atoms are designated according to structure VIII.

vinylsilanes.[66] The chemical shifts of both H_a and H_b decrease as the electronegativity of the substituents increases (Figures 5 and 6); however, the chemical shifts of H_c appears to be independent of the substituent (Table XI). Plotting the proton chemical shifts of H_a and H_b against the electronegativities of the substituents gives an excellent straight line with correlation coefficients of 0.96 and 0.96 and slopes of -0.22 and -0.14, respectively (Figures 5 and 6). The chemical shifts of H_a are twice as sensitive as the chemical shifts of H_b toward the

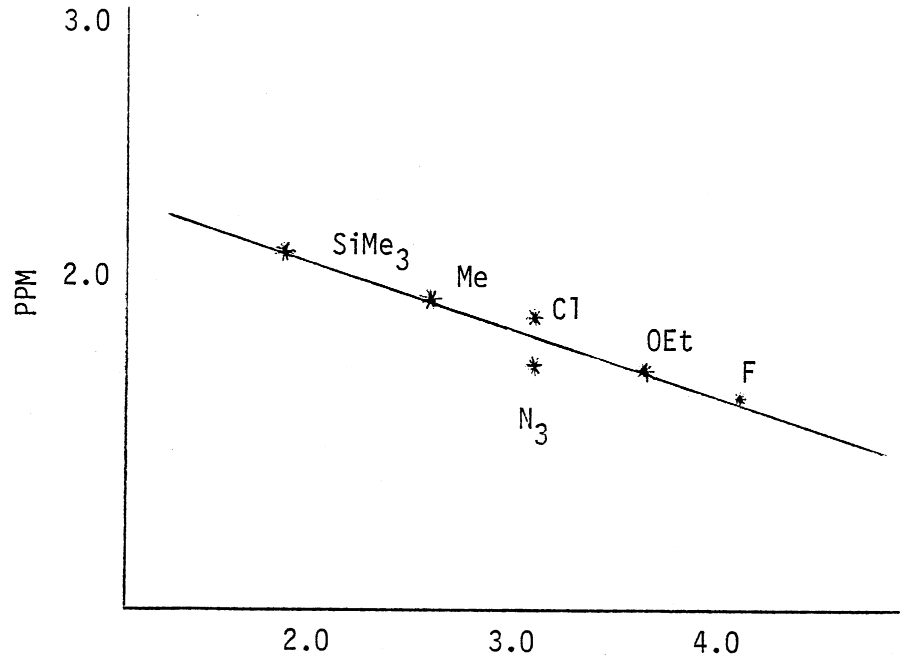


Figure 5. Chemical Shift of H_a vs. the Electronegativity.

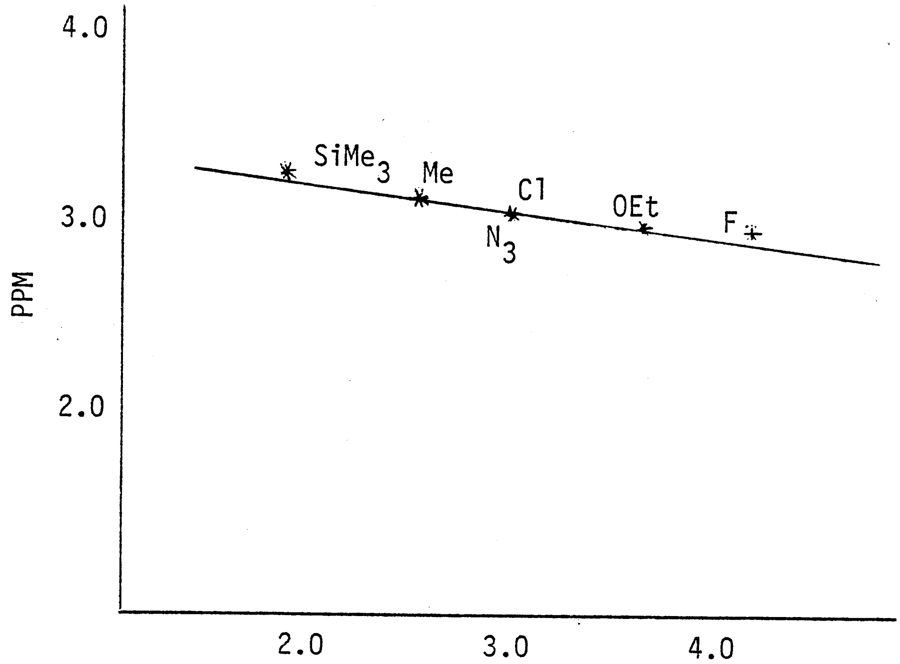


Figure 6. Chemical Shift of H_b vs. the Electronegativity.

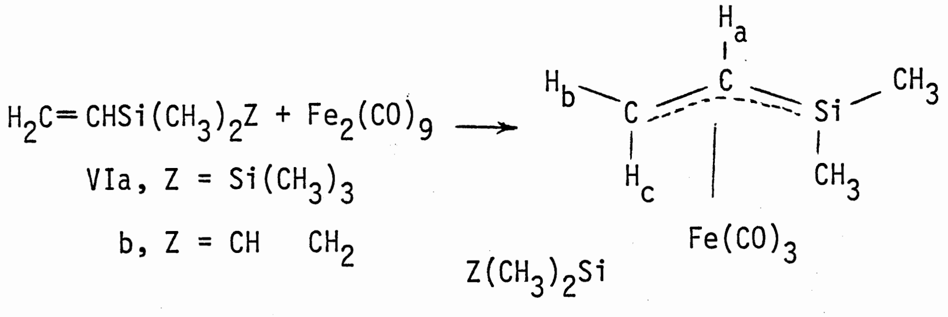
substituent effect. The ^{1}H-chemical shifts of the methyl groups, using the average of the two chemical shifts, correlate linearly with σ_I and ES ($\delta^1H = 0.070\ \sigma_I - 0.29$ ES - 0.12; r = 0.958; STD DEV = 0.04) which implies that the inductive and steric effects of the substituents are the major effects transmitted by the substituent. The greater value of the correlation factor for δ_I(0.70) compared to the value of 0.29 for the ES correlation factor points to the larger contribution of the inductive effect of the substitutent on the $Si{-}CH_3$ proton chemical shift over steric effects.

The sum of the coupling constants lie in the narrow range of 24.4-25.5 Hz. The constancy of the sum of the coupling constants has also been reported by Summitt and co-workers.[66] They explained that since the summation of coupling constants in vinyl systems correlates with the electronegativity of the substituent on the vinyl carbon, such constancy of the sum of the coupling constants in vinylsilanes supports the view that the silicon atom effectively shields the vinyl group, by forming a $p\pi$-$d\pi$ bond, from inductive electronic effects exerted by the substituent. However, the sum of the spin-spin coupling constants of substituted propenes ($H_2C{=}CH{-}CH_2Z$, where Z = H, CH_3[67], OCH_3[68], Cl, Br, I[70]), a system in which the presence of $p\pi$-$d\pi$ bonding is very unlikely, also fall in a narrow range of 27.85-26.19 Hz.

The ^{19}F-chemical shift of the fluorine in the complex [σ_{CDCl_3} = 152.8 ppm (ref. CCl_3F)] is similar to that observed for the fluorine in the free ligand (δ_{CDCl_3} = 162.2 ppm) and in the Me_3SiF (δ_{CDCl_3} = 158 ppm[71]) which supports the conclusion that the structure of the vinylsilane upon coordination is preserved. The ^{1}H-, ^{13}C-, and ^{19}F-NMR spectra of the fluoride complex <u>VIIIf</u> show long range ^{19}F coupling through the silicon which suggests the preservation of Si-F bond upon coordination. The ^{19}F-^{1}H coupling constants are $^{3}J_{F\text{-}Si\text{-}C\text{-}CH_c}$ = 7.0 Hz, $^{3}J_{F\text{-}Si\text{-}H_a}$ = 8.6 Hz, $^{4}J_{F\text{-}si\text{-}C\text{-}CH_b}$ = 1.4 Hz, and $^{4}J_{F\text{-}Si\text{-}C\text{-}CH_c}$ = 0.0 Hz; these values are similar to the values reported for fluorosilanes.[71] Also, the greater long range coupling of fluorine with H_b (<u>trans</u>) compared to that with H_c (<u>cis</u>) has been observed in related systems.[72] The ^{19}F-^{13}C coupling constants for the vinyl carbons, C_α and C_β, in the free ligand are substantial, $J_{F\text{-}Si\text{-}C_\alpha}$ = 17.4 Hz and $J_{F\text{-}Si\text{-}C\text{-}C_\beta}$ = 4.2 Hz; however, the coupling constant of C_β decreases, and in the case of C_α, it vanishes upon coordination to the metal, $J_{F\text{-}Si\text{-}C_\alpha}$ = 0.0 Hz; $J_{F\text{-}Si\text{-}C\text{-}C_\beta}$ = 3.3 Hz. The ^{13}C signal of the silicon methyl carbon in the fluoride free ligand appears as a doublet owning to coupling with fluorine ($J_{F\text{-}Si\text{-}CH_3}$ = 15.5 Hz). In the case of the complex, the situation is more complicated because of the diastereotopic nature of the silicon methyl groups, and slightly different coupling of fluorine with the two diastereotopic methyl carbon atoms is observed, $J_{F\text{-}Si\text{-}(CH_3)_a}$ = 16.9 Hz; $J_{F\text{-}Si\text{-}(CH_3)_b}$ = 15.5 Hz.

Evidence for the Nonexistence of a (η^3-1-Silapropenyl)tricarbonyliron Complex

Recently the preparation of the first (η^3-1-silapropenyl)tricarbonyliron by reacting vinylpentamethyldisilane or 1,2-divinyltetramethyldisilane with $Fe_2(CO)_9$ was reported.[37] Reexamination of the reaction between vinylpentamethyldisilane and $Fe_2(CO)_9$ under the same reaction conditions (solvent, reaction time, work-up, etc.) resulted in the production of the same yellow complex previously reported. The reaction was also performed under the same reaction conditions as used in the



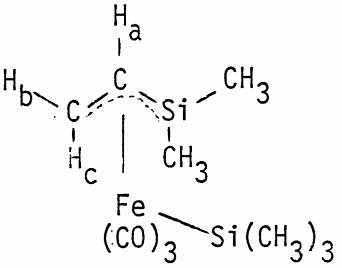
(19)

preparation of the vinyldimethylsilane complexes VIII; the same product was obtained.

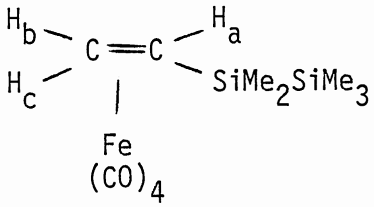
The ^{1}H- and ^{13}C-NMR spectral data (Table XII) of the complex prepared in this study are the same as those reported except with very small and consistent differences in chemical shifts which represent a shift of the spectrum as a whole, or instrumental differences.

The ^{1}H-NMR spectrum shows three peaks at 0.23, 0.12, and 0.00 ppm with relative intensities in the ration of 1:3:1 which had been assigned by Sakurai to the syn-CH_3Si, $(CH_3)_3Si$, and anti-CH_3Si groups, respectively, in the proposed structure VIa.[37] An alternative interpretation of the spectrum which apparently had not been considered by the author is that the complex might possess structure VIIIa which would also give rise to three peaks and the intensity pattern, 1:3:1, due to the diastereotopic methyl groups on the silicon atom adjacent to the coordinated double bond.

The IR spectrum of the yellow liquid prepared in this study at room temperature is essentially the same as that reported for the proposed species VIa with the exception that an additional metal carbonyl band at 2080 cm^{-1} with weak intensity is detected by us. The absence of this peak from the reported IR data was apparently an inadvertent



VIa



VIIIa

TABLE XII

NMR SPECTRAL FOR COMPLEXES "VIa" AND "VIIIa"

VIIIa	VIa[1]
^1H-NMR	
3.03 d, J=10.5 Hz, H_b	3.17 d, J=10.0 Hz, H_b
2.53 d, J=14.8 Hz, H_c	2.67 d, J=15.0 Hz, H_c
2.15 dd, J-10.5;14.8 Hz, H_a	2.29 dd, J-10.0;15.0 Hz, H_a
0.23 s, $Si(CH_3)CH_3$	0.38 s, $Si(CH_3)CH_3$
0.12 s, $Si(CH_3)_3$	0.27 s, $Si(CH_3)_3$
0.00 s, $Si(CH_3)CH_3$	0.15 s, $Si(CH_3)CH_3$
^{13}C-NMR	
211.7 CO	212 CO
44.7 C ,d,J_{CH}=141.2 Hz	46.0 na[3]
41.9 C ,t,J_{CH}=157.4 Hz	43.0 na
-1.4 $Si(CH_3)CH_3$	0.0 $Si(CH_3)CH_3$
-2.2 $Si(CH_3)_3$	-1.0 $Si(CH_3)_3$
-4.4 $Si(CH_3)CH_3$	-3.0 $Si(CH_3)CH_3$

(1) Data from ref. 37

(2) $\Delta = \delta VIa - \delta VIIIa$

(3) na: no assignment made

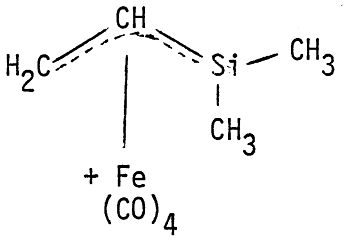
omission. The magnitude of the metal-carbonyl stretching frequencies is consistent with either a tetra- or a tricarbonyl iron complex. However, the IR spectrum of the yellow liquid at 90^{0}K (thin film) shows a shoulder at 2030 cm^{-1} in addition to the other three metal-carbonyl absorptions which is consistent with structure VIIIa. Moreover, we do not detect any appreciable absorption in the region 350-255 cm^{-1} (absorption for the M-SiR_3 stretching frequency has been reported at 300 cm^{-1}, e.g., ν(Fe-Si) for $(CH_2)_3Si(CH_3)_2\ Fe(CO)_4$ has been reported to have the value of 302 cm^{-1} with medium intensity[73]). A peak at 1315 cm^{-1} was assigned to the coordinated Si═C bond in the species VIa. The presence of similar bands in the IR spectra of the vinylsilane complexes analogous to VIIIa (viz., VIIIc-j) (Table I), and also the presence of similar absorption at 1317 cm^{-1} in the IR spectrum (thin film, solid state) of (ethylene)tetracarbonyliron[59] would make the above assignment doubtful. The elemental analysis of VIIIa and the reported values for VIa both cannot be used as a criterion for distinguishing between these two complexes definitively. This is due to the similarity of the deviation of the experimental data with that of the calculated data for both the tri- and tetracarbonyl compounds.

The mass spectrum of the complex was reported to possess the following fragments: m/e (rel. intensity) 298(2.9), 270(4.9), 242(6.8), 214(21.6), 158(23.9), 143(21.0), 85(54.4), 73(100). The presence of the fragment m/e 298 $\left[C_2H_3Si_2(Me_5)Fe(CO)_3{}^+\right]$, the fragments corresponding to the successive loss of three CO groups, and the fragment m/e 73(Me_3Si^+) as the base peak caused the author[37] to conclude that the complex had the structure VIa without considering that the presence of mass 158 corresponds to the vinylpentamethylsilane and the unlikeliness of the generation of vinylpentamethyldisilane from complex VIa. Reexamination of the mass spectrum of the yellow complex "VIa" and examination of the mass spectra of the analogous complexes VIIIc-j provided information about the sensitivity of these complexes to the elevated probe and ionsource temperatures, resulting in the fragmentation and/or decomposition of the complexes in such a way that we were not able to detect the parent peak either. With the design of a special inlet which would permit introduction of the complexes directly into the ionization chamber through a molecular leak and setting the temperature of the ionization chamber at 100-110^oC, the parent mass, which in all cases corresponded to the m/e for (vinylsilane)-Fe(CO)$_4$, became detectable.

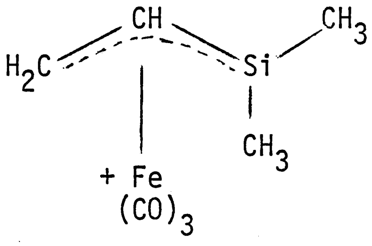
Oxidative elimination of the metal from the complex VIIIa by ceric ammonium nitrate led to formation of the free ligand vinylpentamethyldisilane which was detected by GC. This fact as well as the comparison of the physical constants and spectral data represented above leaves no doubt, not only as to the identity of the complex prepared and that reported by Sakurai, but also as to the structure of the complex which is the tetracarbonyliron complex VIIIa, rather than the tricarbonyliron complex VIa, postulated previously.

Reactions

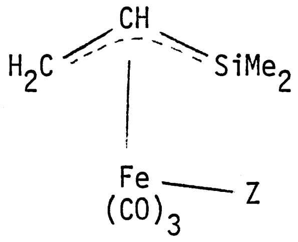
Since the (η^3-propenyl)tricarbonyliron cation and its halide derivatives are well known and reported to be very stable,[74] attempts were made to prepare the analogous (η^3-1-silapropenyl)tricarbonyliron species XI, VI and/or the (η^3-1-silapropenyl)tetracaronyliron species IX. Generation of the cationic complexes IX and XI was of special interest since these complexes incorporate the features of both a coordinated silicenium ion and a doubly bonded silicon species. Attempts to ther-



IX



XI



VI

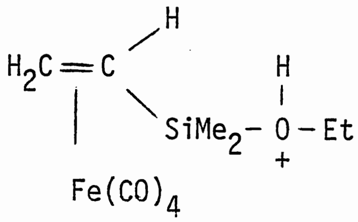
mally rearrange the η^2-chloride complex VIIIe to the complex VI, Z = Cl (see Introduction, p. 6) in either refluxing ether, hexane, or benzene were unsuccessful; only decomposition products and some starting material were obtained.

In an attempt to generate the cationic complex IX or XI, two general approaches were taken: 1) treatment of the ethoxy complex VIIId with acid (see Introduction, p. 6), and 2) treatment of the chloride complex VIIIe with several halide abstracting reagents.

With the hope of preparing cationic complexes by protonation of the ethoxy complex VIIId with the acids: sulfuric, acetic, hexafluorophosphoric, and trifluoroacetic, were examined. Unfortunately, sulfuric acid decomposed the complex rapidly even at -80°C. On the other hand, acetic acid failed to react with the complex even after extended periods at room temperature. Treatment of the ethoxy complex VIIId with hexafluorophosphoric acid generated a new complex. The new complex was detected by the gradual disappearance of bands at 2088, 2000, and 1975 cm^{-1} and the appearance of new bands at 2091, 2012, and 1974 cm^{-1} in the IR spectrum of the reaction mixture at 0°C. The new complex was characterized and found to be the fluoride complex VIIIf. Trifluoracetic acid caused the decomposition of the ethoxy complex at room temperature, but relatively clean reaction was observed at low temperature by ^{1}H-NMR. At -100^{o}C in either Freon-12 (CCl_2F_2) or sulfur dioxide, the addition of trifluoroacetic acid (2 eqv.) to the ethoxy complex resulted in the disappearance of the original Si-CH_3 signals and the appearance of new signals which were centered at 0.31 ppm and downfield by 0.04 ppm from the original signals. The original Si-CH_3 signals in CCl_2F_2 and SO_2 were separated from each other by 0.04 and 0.14 ppm, respectively; however, the new signals were further apart (0.25 ppm) in CCl_2F_2. As the temperature was gradually raised, the signals were reduced in intensity and new more closely spaced signals, 0.11 ppm apart, centered at 0.52 ppm developed. In CCl_2F_2, the transformation was complete at -35^{o}C, but in SO_2 the transformation was more rapid and was accompanied by decomposition even at -70^{o}C.

The conversion of the initially formed species to the final species could be easily detected by the appearance of coordinated vinyl absorption slightly downfield from that of the initial complex. The final complex was not isolated for further characterization owning to its extreme sensitivity towards moisture; it most likely is the trifluoroacetate complex VIII, Z = O_2CCF_3, because of the similarity of its spectrum with that obtained for the complex prepared from the chloride complex VIIIe and sodium trifluoroacetate.

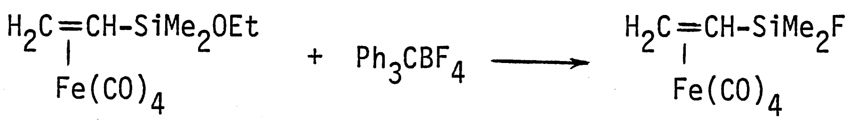
To identify the complex initially formed at low temperature three possible complexes were considered: 1) the η^3-silapropenyl cationic complex IX, 2) the η^3-silapropenyl complex VI, Z = O_2CCF_3, and 3) the protonated ethoxy complex XII. The formation of either IX or VI, Z = O_2CCF_3, necessitates the liberation of ethonol which could then be



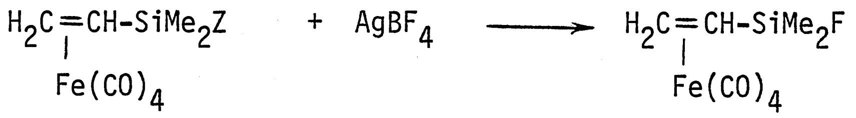
XII

protonated or react further with trifluoroacetic acid. Comparison of the ^{1}H-NMR absorptions for the ethoxy group in the initial complex in CCl_2F_2 at -100^o and -80^{o}C with those obtained for the ethoxy group for solutions of ethanol and ethanol-trifluoroacetic acid in CCl_2F_2 at -100^o or -80^{o}C indicates that ethanol has not been liberated at these temperatures. Moreover, if the initial complex were IX or VI, Z = O_2CCF_3, there should be little if any change in the absorption of the ethoxy group in the conversion of either of these species to the trifluoroacetate VIII, Z = O_2CCF_3. However, as the conversion proceeds a new triplet for a newly formed ethoxy species grows with concomitant reduction in the triplet for the ethoxy group of the initial complex. These observations as well as the fact that the vinyl proton absorptions for the ethoxy complex are only slightly shifted upon the addition of acid at -100^{o}C suggest that the complex initially formed at -100^{o}C is indeed the protonated ethoxy complex XII and not the desired cation IX.

With the hope of preparing the cation IX or XI, the ethoxy complex VIIId was treated with triphenylmethyl tetrafluoroborate and the chloride and fluoride complexes, VIIIe and VIIIf, were treated individually with silver tetrafluoroborate, but in all cases the fluoride complex was generated, in 28%, 16%, and 5-10% yield, respectively (Eq. 22 and 23). Formation of a Si-F bond by treating hydrosilanes and halosilanes with triphenylmethyl tetrafluoroborate[36] and silver tetrafluoroborate,[34] respectively, has been reported previously. Although the cation IX could be an intermediate, cleavage of the Si-Cl bond in concert with the formation of the Si-F bond is also reasonable.



$$\underset{\displaystyle \mathrm{Fe(CO)_4}}{\mathrm{H_2C{=}CH\text{-}SiMe_2OEt}} + \mathrm{Ph_3CBF_4} \longrightarrow \underset{\displaystyle \mathrm{Fe(CO)_4}}{\mathrm{H_2C{=}CH\text{-}SiMe_2F}} \qquad (22)$$

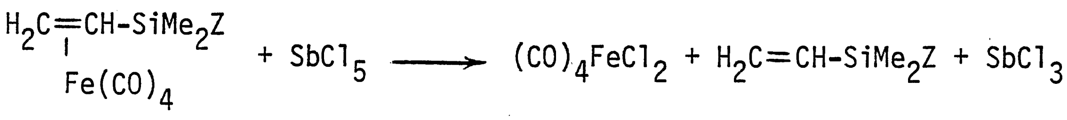


$$\underset{\displaystyle \mathrm{Fe(CO)_4}}{\mathrm{H_2C{=}CH\text{-}SiMe_2Z}} + \mathrm{AgBF_4} \longrightarrow \underset{\displaystyle \mathrm{Fe(CO)_4}}{\mathrm{H_2C{=}CH\text{-}SiMe_2F}} \qquad (23)$$

Z = Cl, F

The chloride complex VIIIe was also treated with silver nitrate and thallium nitrate; however no evidence for the generation of a cationic intermediate was obtained. The starting complex was partially decomposed with the formation of a silver or thallium mirror.

Reaction of the ethoxy VIIId and chloride VIIIe complexes with $SbCl_5$ in CH_2Cl_2 at -78°C, followed by work-up at room temperature resulted in the formation of $(CO)_4FeCl_2$ in 25 and 68% yield, respectively (Eq. 24). The reaction of chloride complex VIIIe with antimony pentachloride was also performed at -100°C in SO_2 in a NMR probe; no evidence for the possible generation of the expected cation was observed. Disappearance of the coordinated vinyl proton absorptions and appearance of uncoordinated vinyl absorptions, simultaneously, was observed over the temperature range of -100° to -20°C.



$$\underset{\displaystyle \mathrm{Fe(CO)_4}}{\mathrm{H_2C{=}CH\text{-}SiMe_2Z}} + \mathrm{SbCl_5} \longrightarrow \mathrm{(CO)_4FeCl_2} + \mathrm{H_2C{=}CH\text{-}SiMe_2Z} + \mathrm{SbCl_3}$$

Z = OEt, Cl (24)

Formation of dichlorotetracarbonyliron is suggestive evidence for the initial attack of antimony pentachloride at the metal leading to the formation of (antimony pentachloride)tetracarbonyliron which is known to decompose to give dichlorotetracarbonyliron.[75]

CHAPTER IV

EXPERIMENTAL

All reactions were carried out under argon which had been passed through a drying column packed with anhydrous calcium sulfate and sodium hydroxide. The glassware was thoroughly dried with a head gun while under an argon atomsphere. All solvents (reagent grade) were obtained from freshly opened bottles and were degassed. Degassing was done by purging the solvents with argon for 10-15 minutes immediately prior to use. Tetrahydrofuran was dried at continuous reflux with lithium aluminum hydride or sodium benzophenone ketyl and was freshly distilled just before use. Dichlorodifluoromethane (Freon 12) and sulfur dioxide were dried by passage through a column packed with 3A molecular sieves. Deactivated acid-washed alumina and 60-200 mesh silica gel were used for chromatographic purposes. Vinyltrimethylsilane, vinyldimethylethoxysilane, vinyldimethylchlorosilane, and 1,3-divinyltetramethyldisiloxane were purchased from Petrarch Systems, Inc. Vinyldimethylfluorosilane, pentamethylchlorodisilane, and vinylpentamethyldisilane were prepared according to published procedures.[76 - 78] Vinyldimethylazidosilane was prepared by nucleophilic addition of sodium azide to vinyldimethylchlorosilane.

Spectroscopic Data

Proton magnetic resonance and ^{13}C-NMR spectra were obtained from a Varian XL-100-15" High Resolution NMR spectrometer equipped with a Nicolet TT-100 FFT accessory (operating at 25.2 MHz for ^{13}C-spectra). All proton chemical shifts are reported relative to tetramethylsilane using carbon disulfide as solvent. The ^{13}C-chemical shifts are reported relative to TMS using chloroform-d^1 as solvent and internal standard, $^{\sigma}DCCL_3$=1970 Hz. Infrared spectra were obtained at ambient temperature using a Beckman-8A spectrometer and at 90°K using a Digilab FTS-20C FT-IR spectrometer, thin film 5-10μm. Low and high resolution mass spectra were obtained on a CEC21-110B mass spectrometer with a Nova Data Acquisition system at 70 ev with an ambient inlet temperature and an ionsource temperature of 100-110°C. The samples were introduced directly into the ionization chamber through a molecular leak. Ultraviolet spectra were obtained on Beckman Model 25 UV spectrophotometer using hexane (spectra grade) as solvent. Spectroscopic data for the substituted vinyldimethylsilanes and their tetracarbonyliron complexes are given in Tables I-V and XI. Elemental analysis was obtained from Phillips Petroleum Co., Bartlesville, Oklahoma. Owing to the proclivity of the vinylsilane complexes towards decomposition, the analyses are not as good as desired.

Preparations

Pentamethylchlorodisilane[77]

Hexamethyldisilane (45 g, 0.31 mol) and concentrated sulfuric acid (163.5 g, sp. gr. 1.84) were placed in a 200-ml, three-neck flask equipped with a mechanical stirrer. The reaction was vigorously stirred under a hood at room temperature for 3.5 hours. Then the reaction mixture was cooled with an ice-water bath, and 24 g (0.45 mol) of anhydrous ammonium chloride was added to the mixture over 30 min with constant stirring. The reaction mixture was stirred for an additional 30 min. Separation followed by simple distillation of the organic layer gave 15 g of crude product. Fractional distillation of the crude product using a vigreux column resulted in the recovery of unchanged hexamethyldisilane (5 g, bp 113-114°C) and pentamethylchlorodisilane 8.6 g (18.9%), bp 134-136°C (lit. bp 134-135°C). The purity of the product was examined by GC (col.: 15% DV 101 Chrom. G; Col. temp. 90°C; inj. temp. 100°C; and flow rate 57 ml/min); the product contained pentamethylchlorodisilane (96%), and hexamethyldisilane (4%).

Vinylpentamethyldisilane (Va)[78]

A 100-ml, three-neck flask equipped with a refluxing condenser was charged with 15 ml of a solution of vinylmagnesium bromide (1.4 M in THF, 0.021 mol). Then pentamethylchlorosilane (3.5 g, 0.021 mol) dissolved in an equal volume of tetrahydrofuran was added dropwise over ~10 min. After the addition was completed, the reaction mixture was refluxes for 15 hours. Then it was cooled and filtered. The solvent was removed *in vacuo*. The residue was extracted with pentane and after solven removal was distilled. Pure vinylpentamethyldisilane was obtained, yield 0.5 g (15%), bp 131-132°C (lit. bp 131-132°C).

Vinyldimethylfluorosilane (Vf)[76]

Antimony trifluoride (6.0 g, 0105 mol) was placed in a 100-ml, three-neck flask equipped both with a dropping funnel containing 4.0 g (0.03 mol) of vinyldimethylchlorosilane and with a column packed with glass helices. The vinyldimethylchlorosilane was added dropwise and vinyldimethylfluorosilane (3.2 g, 92.7%) was collected from the head of the column using a short-path condenser and a cold receiver (Dry-Ice acetone).

Vinyldimethylazidosilane (Vi)

Vinyldimethylchlorosilane (4.4 g, 36.5 mol) was dissolved in tetrahydrofuran (~15 ml) and the resulting solution placed in a 100-ml, three-neck flask furnished with a reflux condenser. To this solution sodium azide (2.4 g, 36.9 mol) was added, and the reaction mixture was refluxed for 5.5 hr. Then it was cooled and the solvent was removed in vacuo. Distillation of the crude product gave 1.44 g (27.3%) of vinyldimethylazidosilane (bp 56-57°C, 31 mm).

Substituted (η^2-Vinyldimethylsilane)-tetracarbonyliron Complexes

The $(H_2C{=}CH\text{-}SiMe_2Z)Fe(CO)_4$ complexes, where Z = Me, Me_3Si, OEt, Cl, and F were prepared following a general procedure. Enneacarbonyldiiron was suspended in diethyl ether and to this solution the corresponding vinylsilane was added. The reaction mixture was stirred at room temperature until the suspended enneacarbonyldiiron had disappeared (4-5 hr). The reaction mixture was filtered through Celite, and the resulting filtrate was concentrated in vacuo using a rotary evaporater to yield a dark green, viscous oil. Vacuum distillation of the oil gave the corresponding tetracarbonyliron complex. In some cases, a second distillation was necessary in order to obtain the pure complex.

In the case of the Z = OEt and Me_3Si substituents complexes VIIId and VIIIa, the crude oil was chromatographed on short columns of alumina and silica gel, respectively. The yellow bands were eluted with pentane. Removal of the solvent in vacuo gave yellow oils which were purified further by vacuum distillation.

(η^2-Vinyltrimethylsilane)tetracarbonyliron (VIIIc)

Vinyltrimethylsilane (1.0 g, 10 mmol) and $Fe_2(CO)_9$ (4.5 g, 12.4 mmol) were used; yield 0.67 g (25%); bp 25-27°C (0.25 mm).

(η^2-Vinylpentamethyldisilane)tetracarbonyliron (VIIIa)

Vinylpentamethyldisilane (550 mg, 3.48 mmol) and $Fe_2(CO)_9$ (440 mg, 1.21 mmol) were used; yield 0.23 g (60%); bp 45°C (0.005 mm); λ_{max}= (hexane) 270(sh)(ε 8800), 236(sh)(14700), 212 nm(23300).

(η^2-Vinyldimethylethoxysilane)tetracarbonyliron (VIIId)

Vinyldimethylethoxysilane (1.0 g, 7.69 mmol) and $Fe_2(CO)_9$ (4.5 g, 12.4 mmol) were used; yield 1.5 g (67%); bp 37-38°C (0.005 mm); λ_{max}= (hexane) 262(sh)(ε 8000), 215 nm(27000). Anal. Calcd. for $C_{10}H_{14}FeO_5Si$: C, 40.28; H, 4.73 Found: C, 40.68; H, 4.71.

(η^2-Vinyldimethylchlorosilane)tetracarbonyliron (VIIIe)

Vinyldimethylchlorosilane (1.5 g, 12.4 mmol) and $Fe_2(CO)_9$ (3.5 g, 9.6 mmol) were used; yield 2.22 g (62%); bp 28-30°C (0.005 mm). Anal. Calcd. for $C_8H_9ClFeO_4Si$: C, 33.3; H, 3.14 Found: C, 35.01; H, 3.95.

(η^2-Vinyldimethylfluorosilane)tetracarbonyliron (VIIIf)

Vinyldimethylfluorosilane (1.6 g, 15.38 mmol) and $Fe_2(CO)_9$ (3.0 g, 8.24 mmol) were used; yield 1.5 g (36%); bp 24°C (0.03 mm). Anal. Calcd. for $C_8H_9FFeO_4Si$: C, 35.3; H, 3.33 Found: C, 37.35; H, 3.80.

Preparation of Complexes from the Chloride Complex and Nucleophile

(η^2-Vinyldimethylfluorosilane)tetracarbonyliron (VIIIf)

(η^2-Vinyldimethylchlorosilane)tetracarbonyliron (VIIIe)(1.0 g, 3.5 mmol) was placed in a 50-ml, three-neck flask containing acetone, and anhydrous sodium fluoride (0.3 g, 7.1 mmol) was added. The reaction mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the resulting oil was extracted with pentane. The pentane was removed and the concentrated crude product was distilled to give the fluoride complex VIIIf 0.753 g (80%); bp 24°C (0.03 mm).

(η^2-Vinyldimethylazidosilane)tetracarbonyliron (VIIIi)

(η^2-Vinyldimethylchlorosilane)tetracarbonyliron (VIIIe) (1.6 g, 5.5 mmol) was dissolved in tetrahydrofuran in a 100-ml, three-neck flask. Sodium azide (0.37 g, 5.7 mmol), dried by heating at 80°C under vacuum for 24 hr, was added. The reaction mixture was stirred at room temperature for 9.5 hr. It was filtered and the solvent was removed *in vacuo*. The resulting oil was extracted with pentane and the extracts were concentrated. Vacuum distillation of the crude product yielded 1.17 g (71.5%) of (η^2-vinyldimethylazidosilane)tetracarbonyliron (VIIIi) (45°C, 0.005 mm). Anal. Calcd. for $C_8H_9FeN_3O_4Si$: C, 32.56; H, 3.07 Found: C, 33.71; H, 3.51.

(η^2-Vinyldimethylphenoxysilane)tetracarbonyliron (VIIIj)

(η^2-Vinyldimethylchlorosilane)tetracarbonyliron (VIIIe)(1.0 g, 3.5 mmol) was placed in a 50-ml, three-neck flask containing tetrahydrofuran and potassium phenoxide (0.46 g, 3.5 mmol) which had been prepared from phenol and potassium hydride. The reaction mixture was stirred at room temperature for 40 hr. At the end of this time, the reaction mixture was filtered through Celite and the solvent was removed *in vacuo*. The resulting oil was extracted with pentane, and the extracts were concentrated to give a yellow oil which was chromatographed on a column packed with alumina. Elution with pentane removed the (η^2-1,3-divinyltetramethyldisiloxane)tetracarbonyliron, which had presumably been generated by hydrolysis of the unchanged chloride complex. Further elution with pentane-benzene (1:1) yielded the phenoxy complex VIIIj. A second chromatography was performed to remove traces of phenol; yield of pure phenoxy complex 35 mg (3.1%).

Preparation of Silanol and Siloxy Complexes (VIIIh and VIIIg)

These complexes were prepared most conveniently by hydrolysis of the chloride (or fluoride) complex by passage through alumina column.

(η^2-Vinyldimethylfluorosilane)tetracarbonyliron (VIIIf)(1.0 g, 3.7 mmol) was placed on a column packed with alumina. Elution with pentane yielded (η^2-1,3-divinyltetramethyldisiloxane)tetracarbonyliron (VIIIg) 0.55 g (85%). Anal. Calcd. for $C_{12}H_{18}FeO_5Si_2$: C, 40.68; H, 5.12 Found: C, 38.16; H, 4.39.

In addition to complex VIIIg a small amount of the starting complex was recovered. Then elution with dichloromethane gave (η^2-vinyldimethylsilanol)tetracarbonyliron (VIIIh)(29.8 mg, 3%), which could be recrystallized from pentane to give an off-white solid, mp 42-43°C.

Reactions

Reaction of (η^2-Vinylpentamethyldisilane)tetracarbonyliron (VIIIa) with Ceric Ammonium Nitrate

(η^2-Vinylpentamethyldisilane)tetracarbonyliron (VIIIa)(22 mg, 0.067 mmol) was placed in a 25-ml, three-neck flask containing aqueous acetone (3 ml acetone and ~0.5 ml water), and the solution was cooled by an ice-water bath. With vigorously stirring, ceric ammonium nitrate was added until no more gas evolution was detected. Then the reaction mixture was transferred to a separatory funnel containing cold water and was extracted with pentane (~5 ml). The pentane solution was analyzed by GC (15% DV 101 Chrom. G. column, column temperature 85°C, injection temperature 100°C, flow rate 57 ml/min), which showed the presence of vinylpentamethyldisilane.

Reaction of (η^2-Vinyldimethylethoxysilane)tetracarbonyliron (VIIId) with Hexafluorophosphoric Acid

(η^2-Vinyldimethylethoxysilane)tetracarbonyliron (VIIId)(2 g, 6.7 mmol) was dissolved in diethyl ether in a 100-ml, three-neck flask. The solution was cooled by an ice-water bath. Then hexafluorophosphoric acid diethyl ether complex (1.48 g, 6.7 mmol) was added dropwise. After the addition of acid was completed, the reaction mixture was warmed to room temperature and stirred for an additional three hours. The two layers were separated, and the ether layer was concentrated *in vacuo*. Pentane was added and the solution was treated with solid sodium bicarbonate until no more carbon dioxide evolution was observed. The solution was filtered and the solvent was removed *in vacuo* affording 1.4 g (75%) of (η^2-vinyldimethylfluorosilane)tetracarbonyliron (VIIIf). The boiling point and spectral data agreed with that for the complex prepared from $Fe_2(CO)_9$ and vinyldimethylfluorosilane.

Reaction of (η^2-Vinlydimethylethoxysilane)tetracarbonyliron (VIIId) with Triphenylmethyltetrafluoroborate

Triphenylmethyl tetrafluoroborate (1.3 g, 3.2 mmol) was dissolved in dichloromethane in a 50-ml, three-neck flask and the ethoxy complex VIIId (1.0 g, 3.4 mmol) was added. The reaction mixture was stirred for five hours at room temperature. An IR spectrum of the reaction mixture gave no evidence for the generation of a cationic complex. The reaction mixture was filtered, and the fitrate was concentrated *in vacuo*. A small quantity of methanol was added to the oily residue, and the insoluble tritylethyl ether was removed by filtration. Removal of the solvent from the filtrate gave 0.25 g (28%) of (η^2-vinyldimethylfluorosilane)tetracarbonyliron (VIIIf), which was identified by comparison of its spectral data with that for the authentic complex.

Reaction of (η^2-Vinyldimethylchlorosilane)tetracarbonyliron (VIIIe) with Silver Tetrafluoroborate

(η^2-Vinyldimethylchlorosilane)tetracarbonyliron (VIIIe)(0.6 g, 2.08 mmol) was added to a stirred suspension of silver tetrafluoroborate (0.9 g, 4.6 mmol) in tetrahydrofuran at 0°C in a 50-ml, three-neck flask.

The reaction mixture was stirred for 30 min at $0^{o}C$ and then for 15 min at room temperature. Then the mixture was filtered. Concentration of the filtrate yielded 89 mg (16%) of a yellow oil which was identical in all respects to (η^2-vinyldimethylfluorosilane)tetracarbonyliron (VIIIf).

The fluoride complex VIIIf was also treated with silver tetrafluoroborate using the same procedure. It decomposed and only 5-10% of the starting complex was recovered.

Reaction of (η^2-Vinyldimethylchlorosilane)tetracarbonyliron (VIIIe) with Antimony Pentachloride

The chloride complex VIIIe (0.3 g, 1.04 mmol) was dissolved in dichloromethane in a 50-ml, three-neck flask, and the solution was cooled to $-78^{o}C$ with a Dry Ice-acetone bath. A solution of antimony pentachloride (0.13 ml, 1.02 mmol) in dichloromethane (~4 ml) was added dropwise to the solution of the complex. During the addition the reaction mixture became orange. After the reaction mixture had been stirred for 15 min, anhydrous diethyl ether (~15 ml) was added. The reaction mixture was stirred for an additional hour, during which time a yellow solid precipitated. The reaction mixture was warmed to room temperature and filtered under argon giving 150 mg (68%) of dichlorotetracarbonyliron, dp $85^{o}C$. Its IR spectrum (H_2CCl_2) agreed well with that reported[75] for the authentic material. The IR spectrum of the filtrate was devoid of metal-carbonyl absorption.

Reaction of (η^2-Vinyldimethylethoxysilane)tetracarbonyliron (VIIId) with Antimony Pentachloride

Procedure analogous to that used in the chloride complex reaction above was followed. The ethoxy complex (0.5 g, 1.68 mmol) and antimony pentachloride (0.2 ml, 157 mmol) yielded 89 mg (25%) of dichlorotetracarbonyliron, identical in all respects to that obtrained in the chloride complex reaction.

BIBLIOGRAPHY

1. Zeise, W. Z. Pogg. Ann. 1831, 21, 497.
2. Deganello, G, Uguagliati, P. Inorg. Chim. Acta. 1975, 13, 247.
3. Dewar, M. J. S. Bull. Soc. Chim. Fr. 1951, C71. Chatt, J.: Duncanson, L. A. J. Chem. Soc. 1953, 2939.
4. Emerson, G. F., Pettit, R. J. Amer. Chem. Soc. 1962, 82, 4591.
5. Emerson, G. F., Mahler, J. E., Pettit, R. Chem. Ind. 1964, 836.
6. Margulis, T. N., Schiff, L., Rosenblum, M. J. Amer. Chem. Soc. 1965, 87, 3269.
7. Desent, W. E., Ed., "Non-existent Compounds", Marcel Dekker, NY, 1965.
8. Attridge, C. T. Organometal. Chem. Rev. 1967, 2, 161.
9. Gattermann, L. Ber. 1889, 22, 194.
10. Schlenk, W., Renning, J. Justus Liebigs Ann. Chem. 1912, 394, 221.
11. Kipping, F. S. J. Chem. Soc. 1927, 104.
12. Andrianov, K. A., Sokolov, N. N. Dokl. Akad. Nauk. SSSR. 1952, 82, 909.
13. Gusel 'Nikov, L. E., Nametkin, N. S. Chem. Rev. 1979, 79, 529.
14. Golino, C. M., Bush, R. D., Sommer, L. H. J. Amer. Chem. Soc. 1975, 97, 7371.
15. Gaidis, J. M., Briggs, P. R., Shannon, T. W. J. Phy. Chem. 1971, 75, 974.
16. Sakurai, H. Kira, M., Sato, T. J. Organomental. Chem. 1972, 42, C24.
17. Weber, W. P., Willard, A. K. J. Org. Chem. 1971, 36, 1620.
18. Thomas, A. B., Rochow, E. G. J. Inorg. Nucl. Chem. 1957, 4, 205.
19. Litchin, N., Bartlett, P. D. J. Amer. Chem. Soc. 1951, 73, 5530.

20. Harmon, K. M., Harmon, A. B. J. Amer. Chem. Soc. 1961, 83, 865.

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

22. Corey, J. Y., West, R. J. Amer. Chem. Soc. 1963, 85, 2430.

23. Swain, C. G., Esteve, Jr., R. M., Jones, R. H. J. Amer. Chem. Soc. 1949, 71, 965.

24. Austin, J. D., Esborn, C. J. Chem. Soc. 1964, 2279. Sommer, L. H., Bauman, D. L. J. Amer. Chem. Soc. 1969, 91, 7076.

25. Corriu, R. J. R., Lannea, G. F. Tetrahedron Lett. 1970, 165.
Corriu, R. J. R., Lannea, G. F. Tetrahedron Lett. 1971, 2771.
Corriu, R. J. R., Lannea, G. F. Royo, G. L. J. Organometal. Chem. 1972, 35, 35.
Corriu, R. J. R., Lannea, G. F., Leard, M. J. Chem. Soc. Chem. Commun. 1971, 1365.

26. Corey, J. Y. J. Amer. Chem. Soc. 1975, 97, 3237. Corey, J. Y., Gust, D., Mislow, K. J. Organometal. Chem. 1975, 101, C7.

27. Barton, T. J., Hovland, A. K., Tully, C. R. J. Amer. Chem. Soc. 1976, 98, 5695.

28. Eaborn, C., Happer, D. A. R., Hopper, S. P., Safa, K. D. J. Organometal. Chem. 1979, 170, C9. ibid. 1980, 188, 179.

29. Curtis, M. D. J. Amer. Chem. Soc. 1969, 91, 6011.

30. Hallam, B. F., Pauson, P. C. J. Amer. Chem. Soc. 1956, 3030.

31. Fitch, J. W., Herbold, H. E. Inorg. Chem. 1970, 9, 1926.

32. Fitch, J. W., Flores, D. P., George, J. E. J. Organometal. Chem. 1971, 29, 263.

33. Green, M. L. H., Nagy, P. L. I. Advan. Organometal. Chem. 1964, 2, 325.

34. Malish, W., Panster, P. J. Organometal. Chem. 1974, 64, C5.

35. Emeleus, H. J., Onyszchuk, M. J. Chem. Soc. 1958, 604.

36. Bulkowski, J. E., Miro, N. D., Sepelak, D., Van Dyke, C. H. J. Organometal. Chem. 1975, 101, 267.

37. Sakurai, H., Kamiyama, Y., Nakadaira, Y. J. Amer. Chem. Soc. 1976, 98, 7453.

38. Impastato, F. J., Ihrman, K. G. J. Amer. Chem. Soc. 1961, 83, 3726. Green, M. L. H., Nagy, P. L. J. Chem. Soc. 1963, 189. Heck, R. F., Boss, C. R. J. Amer. Chem. Soc. 1964, 86, 2580. Chaudhari, F. M., Knox, G. R., Pauson, P. L. J. Chem. Soc. C. 1967, 2255. Gibson, D. H., Erwin, D. K. J. Organometal. Chem. 1975, 86, C31.

39. Green, M. L. H., Ed., "Organometallic Compounds", Metheun, London 1968, Vol. 2, Chapter 2.

40. Barton, T. J., McIntosh, C. L. J. Chem. Soc. Chem. Commun. 1972, 861.

41. Radnia, P., McKennis, J. S. J. Amer. Chem. Soc. 1980, 102, 6349.

42. Pauling, L. Ed., "Nature of the Chemical Bond", Cornell Press. NY, 1960.

43. Hunter, B. K., Reeves, L. W. Can. J. Chem. 1968, 46, 1399.

44. Ernst, C. R., Spailter, L., Buell, G. R., Wilhite, D. L. J. Amer. Chem. Soc. 1974, 96, 5375.

45. Schmidbaur, H., Schmidt, M. J. Amer. Chem. Soc. 1962, 84, 1069.

46. Schmidbaur, H., Schmidt, M. Agnew. Chem. Intern. Ed. 1962, 1, 327.

47. Brown, M. P., Webster, D. E. J. Phys. Chem. 1960, 64, 698.

48. Schmidbaur, H. J. Amer. Chem. Soc. 1963, 85, 2336.

49. Ebsworth, E. A. V., Frankiss, S. G. J. Amer. Chem. Soc. 1963, 85, 3516.

50. Bothner By, A. A., Naar Colin, N. C. J. Amer. Chem. Soc. 1958, 80, 1728. Cavanaugh, J. R., Dailey, B. P. J. Chem. Phys. 1961, 34, 1099.

51. Neikam, W. C., Dailey, B. P. ibid. 1963, 38, 445.

52. Winstein, S., Lucas, H. J. J. Amer. Chem. Soc. 1938, 60, 836. Denning, R. G., Harley, F. R., Venanzi, L. M. J. Chem. Soc. A 1967, 324.

53. Coates, G. E., Green, M. L. H., Wade, K. Eds., "Organometallic Compounds", Metheun & Co. LTD, Fetterlane, London, 1968, Vol. 2, P. 16.

54. Maddox, M. L., Stafford, S. L., Kaesz, H. D. Advan. Organometal. Chem. 1965, 3, 47.

55. Kettle, S. F. A., Orgel, L. E. *Chem. Ind.* 1960. 49. Gustorf, E. K., Jun, M. J., Schenck, G. O. *Z. Naturforsch. 1963, 18b*, 503. Schenck, G. O., Gustorf, E. K., Jun, M. J. *Tetrahedron Lett. 1962*, 10591. Stark, K., Lancaster, J. E., Murdoch, H. D., Weiss, E. *Z. Naturforsch. 1964, 19b*, 284.

56. Murdoch, H. D., Weiss, E. *Helv. Chim. Acta. 1963, 46*, 1588.

57. Fitch, J. W., Chan, K. C., Forelich, *J. Organometal. Chem.* 1978, *160*, 477.

58. Rericha, R., Stokr, J., Jakoubkova, M., Svoboda, P., Chvalovsky, V. *Coll. Czech. Chem. Commun. 1974, 39*, 1303.

59. Andrews, D. C., Davidson, G. *J. Organometal. Chem. 1972, 35*, 162.

60. Shapiro, M. J. *J. Org. Chem. 1976, 41*, 3197.

61. Yuriev, V. P., Panasenko, A. A., Khvostenko, V. I., Khalilov, L. M., Yasman, YA. B., Timoshenko, M. M., Chizhow, Yu. V., Zykov, B. G., Furlei, I. I., Rafikov, S. R. *J. Organometal. Chem. 1979, 166*, 169.

62. Smith Third, W. B. International Meeting on Nuclear Magnetic Resonance Spectroscopy, St. Andrews, Scotland 1975.

63. σ_I: Charton, M. *J. Org. Chem. 1964, 29*, 1222. σ_p, σ_{p+}: Swain, C. G., Lupton, Jr., E. C. *J. Amer. Chem. Soc. 1968, 90*, 4328. F, R: Hansch, C., Leo, A., Unger, S. H., Kim, K. H., Nikaitani, D., Lien, E. J. *J. Med. Chem. 1973, 16*, 1207. σ_R, σ_{R+} were calculated using equations $\sigma_R = \sigma_P - \sigma_I$ and $\sigma_{R+} = \sigma_{P+} - \sigma_I$. For the azide subst., the σ_R value was used for σ_{R+}.

64. Charton, M. *J. Amer. Chem. Soc. 1969, 91*, 615. Kutter, E., Hansch, C. *J. Med. Chem. 1969, 12*, 647.

65. Banwell, N., Sheppard, N. *Mol. Phys.* 1960, 3, 351. Pople, J. A., Schneider, W. G., Bernstein, H. J., Eds., "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., Inc., NY, 1960.

66. Summitt, R., Eisch, J. J., Trainor, J. T., Rogers, M. T. *J. Chem. Phys. 1963, 67*, 2362.

67. Bothner-By, A. A., Naar-Colin, C. *J. Amer. Chem. Soc. 1961, 83*, 231.

68. Bothner-By, A. A., Castellano, S., Gunther, H. *J. Amer. Chem. Soc. 1965, 87*, 2439.

69. Bothner-By, A. A., Castellano, S., Ebersole, S. J., Gunther, H. *J. Amer. Chem. Soc. 1966, 88*, 2466.

70. Bothner-By, A. A., Gunther, H. Frad. Soc. discuss. 1962, 34, 127.

71. Schmidbaur, H. Chem. Ber. 1965, 98, 83. Dyer, J., Lee, J. Spectrochim. Acta. 1970, 26A, 1045.

72. ref. 69. Haszeldine, R. N., Keen, D. W., Tipping, A. E. J. Chem. Soc. C. 1970, 414.

73. Cundy, C. S., Lappert, M. F. J. Chem. Soc. Chem. Commun. 1972, 445.

74. Plouman, R. A., Stone, F. G. A. Z. Naturforsch. 1962, 17b, 575.

75. Hieber, W., Wirsching, A. Z. Anorg. Allgem. Chem. 1940, 245, 35.

76. Svoboda, P., Vaisarova, V., Chvalovsky, V. Coll. Czech. Chem. Commun. 1972, 37, 2258.

77. Kumada, M., Yamaguchi, M., Yamamoto, Y., Nakajima, J., Shiina, K. J. Org. Chem. 1956, 21, 1264.

78. Sakurai, H., Tominaga, K., Kumada, M. J. Org. Chem. 1966, 39, 1279.

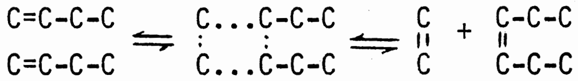
PART II

INSERTION OF TRANSITION METAL SPECIES INTO SUBSTITUTED (CYCLOBUTADIENE)TRICARBONYLIRON COMPLEXES

CHAPTER I

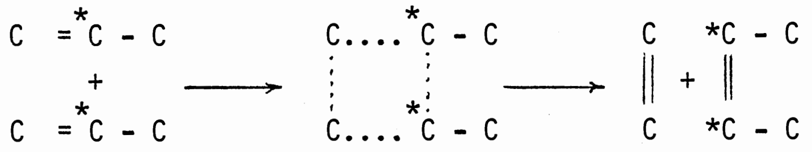
INTRODUCTION

Catalysic conversion of olefins into the analogues of lower and higher carbon number (dismutation also called disproportionation) and olefin metathesis (the term metathesis is used in chemistry to describe reactions in which groups are transferred or exchanged: in organic chemistry the term has been used for the "scrambling" of olefins and acetylenes or the radical abstraction of an atom to produce another radical.) are the most interesting olefin reactions. Olefin disproportionation was first discovered by Banks and co-workers.[1] In the presence of molybdenum or tungsten oxides on alumina, or of the corresponding hexacarbonyls on alumina, the *n*-butenes dismutate to olefins ranging from C_2 to C_8, with ethylene, propylene, pentenes, and hexenes as the main products. Further study done by Bradshaw and co-workers[2] led to the conclusion that dismutation occurs via a "quasi-cyclobutane" intermediate formed by the correct alignment of the carbon atoms at the double bonds of two reacting olefins; for example:



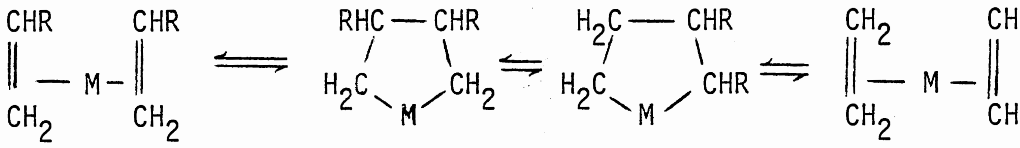
$$\begin{array}{c}C{=}C{-}C{-}C\\ C{=}C{-}C{-}C\end{array} \rightleftharpoons \begin{array}{l}C\cdots C{-}C{-}C\\ \vdots\quad\;\vdots\\ C\cdots C{-}C{-}C\end{array} \rightleftharpoons \begin{array}{c}C\\ \|\\ C\end{array} + \begin{array}{l}C{-}C{-}C\\ \|\\ C{-}C{-}C\end{array} \qquad (1)$$

Using ^{14}C-labelled propene, Mol and co-workers[3] supported the formation of "quasi-cyclobutane" as an intermediate in the disproportionation of propenes. They reported that the ethylene formed from disproportionation of ^{14}C-labelled propene showed no radioactivity, in contrast with the butene which showed a specific radioactivity twice as much as that of the starting material.



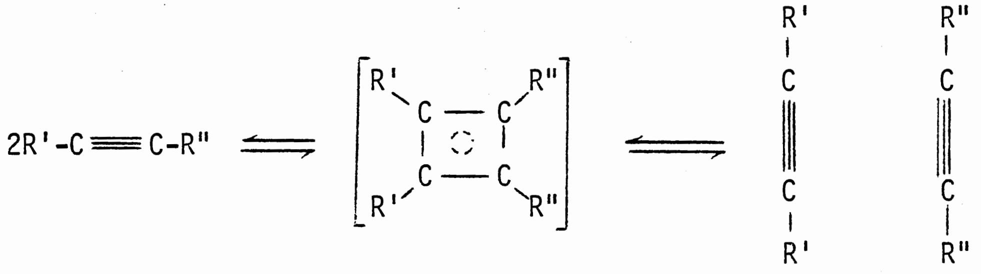
(2)

The mechanism for the olefin metathesis has also been reported to involve "quasi-cyclobutane"; however, Grubbs and Brunck[4] provided evidence that these reactions involve a metallocyclic (a metal-carbon σ-bonded) intermediate instead of a direct metal-catalyzed electrocyclic rearrangement (Eq. 3). Other mechanisms have also been suggested. All of the suggested mechanisms have been accumulated in a review by Haines and Leigh.[5]



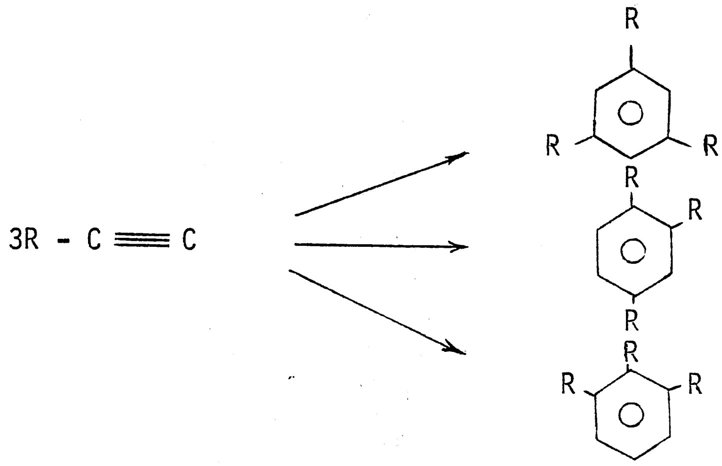
(3)

In 1968 Pennella and co-workers[6] discovered that the disproportionation reaction is not limited to alkenes, and alkynes also undergo dismutation using tungsten oxide as a catalyst. They proposed that the reaction mechanism involves the formation of a four membered intermediate from the two interacting acetylenic structures. The over-all process according to this mechanism involves the cleavage of two triple bonds and the formation of two new triple bonds.

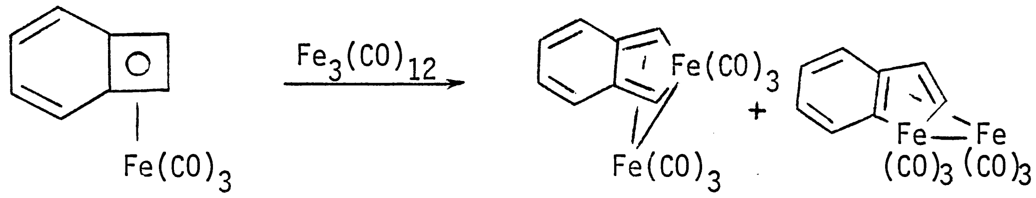


(4)

Further study of alkynes disproportionation was done by Moulijn and co-workers.[7] They found that disproportionation is not limited to β-alkynes; α-alkynes also yield disproportionation products when the proper reaction conditions are chosen. Additionally, a quantitatively more important reaction appeared to be cyclotrimerization of the alkynes (Eq. 5). Greco and co-workers[8] prepared and studied a number of acetylene complexes of tungsten and molybdenum halides. They proposed a decomposition scheme which contained a metallocyclic intermediate to explain the formation of both metathesis and cyclotrimerization products. In 1974 Pettit and co-workers[9] observed the formation of the benzoferroles (IIa, and IIIa), metallocyclic complexes, by the insertion of the tricarbonyliron moiety into (benzocyclobutadiene)tricarbonyliron I. They suggested that cyclobutadiene metal complexes could conceivably be involved in alkyne metathesis. Fritch and Vollhardt[10] studied the pyrolysis of substituted η^4-cyclobutadiene-η^5-cyclopentadienylcobalt complexes, which led to the formation of the corresponding acetylene components, and concluded that cyclobutadiene-metal complexes are potential intermediates in alkyne metathesis.

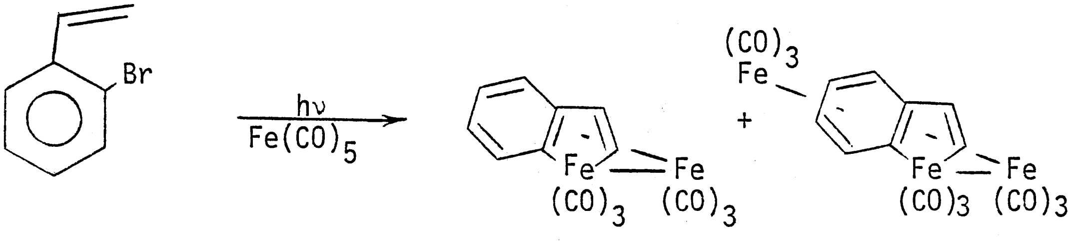


(5)



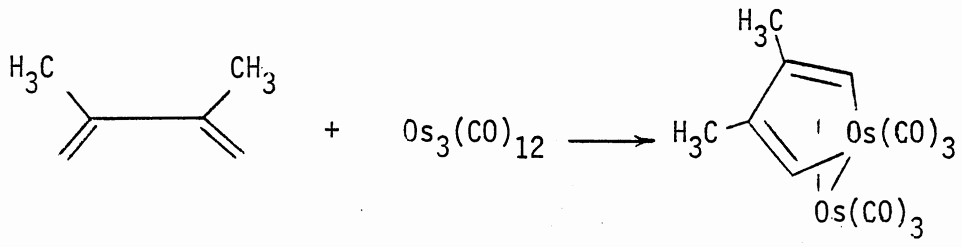
I IIa IIIa (6)

The controversy in the mechanism of the disproportionation (metathesis) of alkenes and alkynes encouraged the investigation on the synthesis and chemistry of metallocyclic complexes and a variety of metallocyclic complexes have now been synthesized. Three routes have been used to synthesize the metallocyclic complexes: 1) the reaction of acetylenes with metal carbonyls, 2) the displacement reaction of either the hetero or metallocyclopentadienes, and 3) the insertion of the metal carbonyls into cyclobutadiene-metal complexes. Other reactions have also been reported to afford metallocyclic complexes. For example, irradiation of o-bromostyrene in the presence of $Fe(CO)_5$ led to the formation of benzoferrole IIIa and the (benzoferrole)tricarbonyliron complex IV via dehydrobromination (Eq. 7).[11] Also reaction of $Os_3(CO)_{12}$



IIIa IV (7)

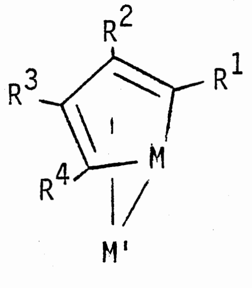
with 2,3-dimethylbutadiene afforded the binuclear complex analogous to ferrole.[12]



(8)

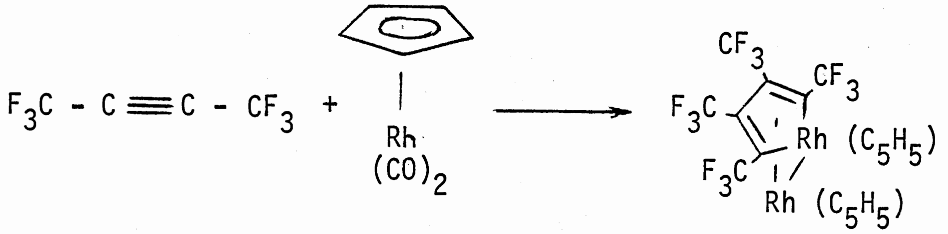
Reaction of Acetylene with Metal Carbonyl Complexes

In 1953 Reppe and Vetter[13] reported the isolation of a binuclear complex with the empirical formula $C_{10}H_4O_8Fe_2$ from the catalytic reaction of alkaline solutions of pentacarbonyliron and acetylene. However, the structure of this complex was a matter of controversy until 1961, when an X-ray crystallographic analysis by Hock and Mills[14] determined that the binuclear complex isolated from the reaction of 2-butyne and pentacarbonyliron under similar conditions employed by Reppe has the structure V, M = M' = $Fe(CO)_3$; $R^1 = R^4 = OH$; $R^2 = R^3 = CH_3$. Further investigation of the latter reaction by Hübel[15] led to the conclusion that the reaction of iron carbonyl derivatives with substituted acetylenes in chemically inert organic solvents to form binuclear species was general. Metallocyclopentadiene complexes of type V have

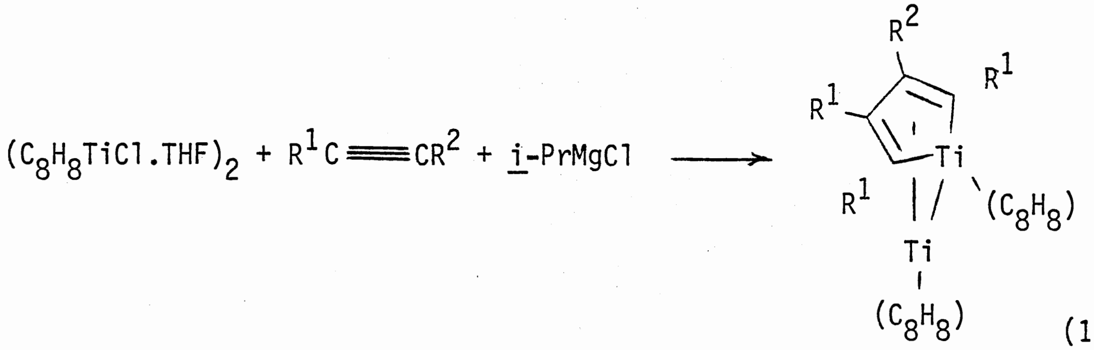


V

also been prepared from intra- and/or intermolecular cyclization reactions of macrocyclic alkadiynes with $Fe_3(CO)_{12}$ or $Fe(CO)_5$.[16, 17] In addition to iron, other transition metals have also been used to generate metallocyclic complexes of type V. For example, the reaction of hexafluorobut-2-yne with $(\eta^5-C_5H_5)_2Rh(CO)_2$ gives the complex $(\eta^5-C_5H_5)_2 Rh_2(C_4F_6)_2$ (Eq. 9).[18] Dimethylacetylenedicarboxylate, $CH_3O_2CC_2CO_2CH_3$, and methylacetylenecarboxylate, $HC_2CO_2CH_3$, react with octakis(trifluorophosphine)dirhodium affording complexes V M = $Rh(PF_3)_3$; M' = $Rh(PF_3)_2$; $R^1 = R^2 = R^3 = R^4 = CO_2CH_3$ and V M = $Rh(PF_3)_3$; M' = $Rh(PF_3)_2$; $R^1 = R^3 = CO_2CH_3$; $R^2 = R^4 = H$, respectively.[19] Reaction of $(C_8H_8TiCl.THF)_2$ with acetylenes RC_2R' (R = R' = Ph; R = R' = p-tolyl; R^1 = Ph, $R^2 = CH_3$) in the presence of i-PrMgCl also led to the formation of binuclear complexes (Eq. 10).[20]



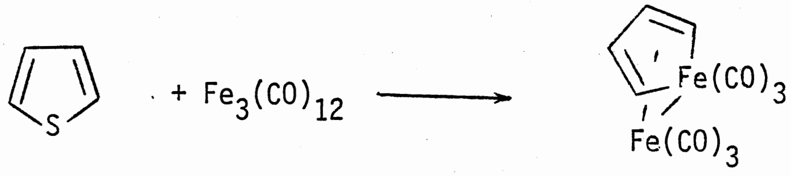
(9)



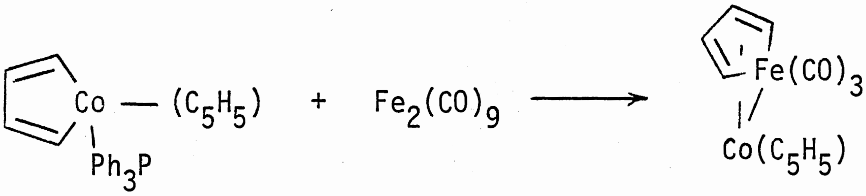
(10)

Displacement of Hetero- or Metallocyclopentadiene by Metal Carbonyls

This method has been used by Dettlaf and Weiss[21] to synthesize the parent ferrole complex, where M = M' = $Fe(CO)_3$; $R^1 = R^2 = R^3 = R^4 = H$. They have reported that the reaction of thiophene with $Fe_3(CO)_{12}$ in n-heptane afford the ferrole complex Va. Most recently, during the course of our investigation the metallocyclic complex Vb, M = $Fe(CO)_3$; M' = (η^5-C_5H_5)Co was prepared from the reaction of (η^5-cyclopentadienyltriphenylphosphine(cobaltacyclopentadiene) complex with enneacarbonyldiron.[22]



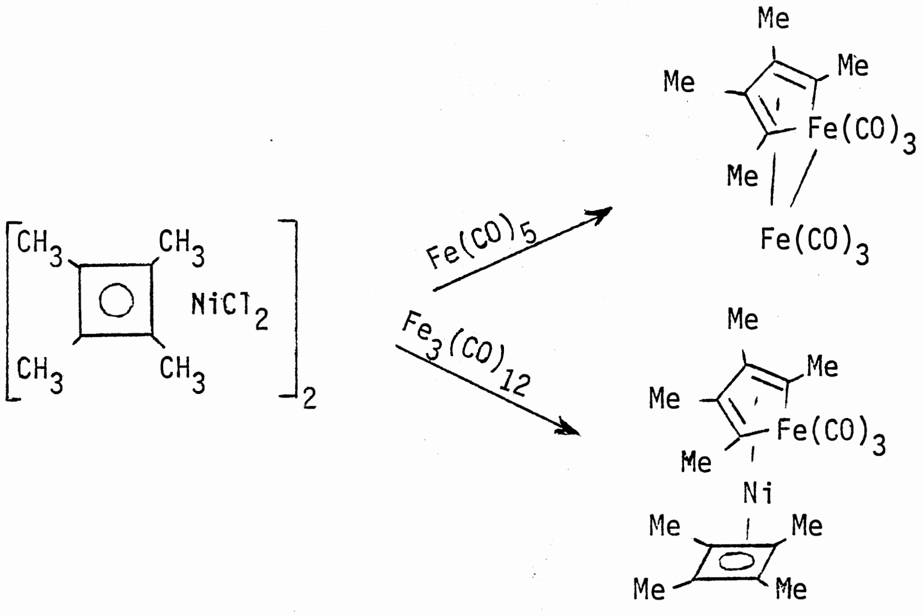
Va (11)



(12)

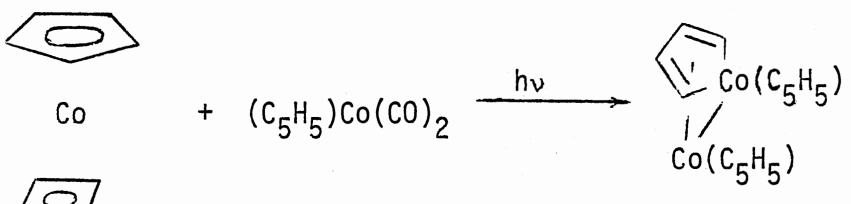
Insertion of Metal carbonyls into Cyclobutadiene-Metal Complexes

The product resulting from the insertion of metal carbonyls into a cyclobutadiene-metal complex was first reported by Bruce and coworkers.[23] They observed that the reaction of (tetramethylcyclobutadiene)nickel chloride dimer with $Fe(CO)_5$ afforded the methyl substituted ferrole V, M = M' = $Fe(CO)_3$; $R^1 = R^2 = R^3 = R^4 = CH_3$. The reaction of (tetramethylcyclobutadiene)nickel chloride with $Fe_3(CO)_{12}$ gave a complex with empirical formula $(CH_3)_8NiFe(CO)_3$, whose structure was latter shown by X-ray crystallographic analysis[24] to be V, M = $Fe(CO)_3$; M' = $(\eta^4\text{-}Me_4C_4)Ni$; and $R^1 = R^2 = R^3 = R^4 = Me$ (Eq. 13). This work represents the only study involving a mixed binuclear metallocyclic complex prior to our investigation. Rosenblum and co-worker[25] prepared a



(13)

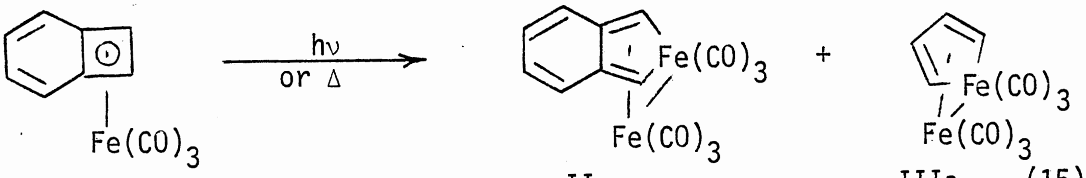
$(\eta^5\text{-}C_5H_5)$ $(\eta^4\text{-}C_4H_4)CO$ complex; photochemical reaction of this complex in the presence of cyclopentadienyldicarbonylcobalt afforded Vc.



Vc

(14)

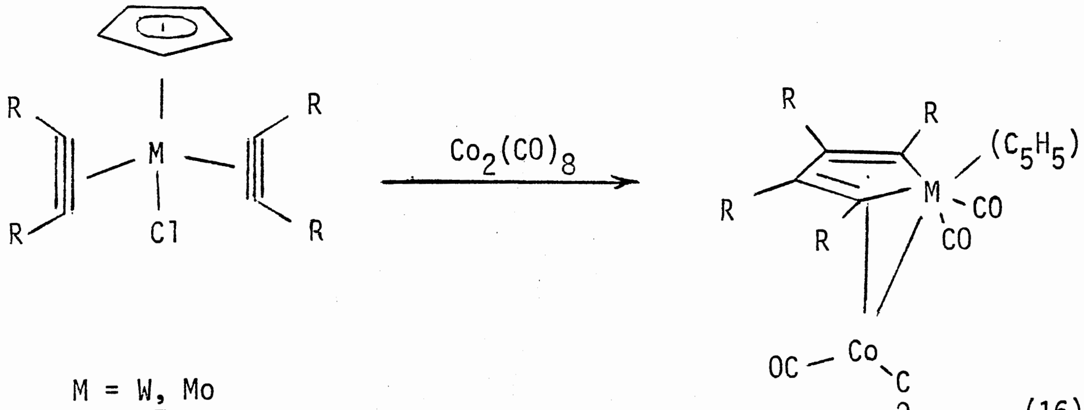
Photochemical reaction of (benzocyclobutadiene)tricarbonyliron with $Fe(CO)_5$[26] or thermal reaction of the same complex with $Fe_3(CO)_{12}$[9] give the sym- and unsym-benzoferroles IIa and IIIa, respectively.



IIa

IIIa (15)

While our work was in progress, Davidson[27] reported that the bis-(hexafluorobut-2-yne) complexes react with $Co_2(CO)_8$ to afford the metallocyclopentadiene complexes (Eq. 16).



M = W, Mo
R = CF_3

(16)

CHAPTER II

STATEMENT OF THE PROBLEM

Although complexes of ferroles and benzoferroles have been known for sometime, and their osmium, rhodium, and cobalt analogues have been discovered during the last decade, very little is known about the physical and chemical properties of these binuclear metallocyclic complexes. For example, the ^{13}C- and ^{1}H-NMR spectral data reported for these complexes are not consistent with each other. The ^{13}C-NMR absorption of the carbons sigma bonded to the metal has been assigned to the most downfield peak, excluding the peaks corresponding to metal carbonyl, whereas the ^{1}H-NMR absorption of the protons attached to these carbon has been reported to appear at higher field than the absorption of the other protons of the metallocyclic ring.

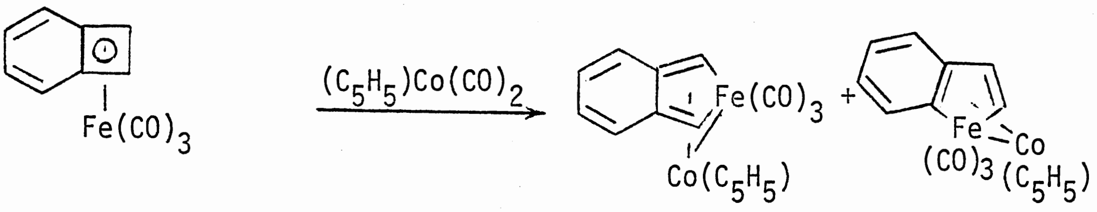
The insertion of transition metal moieties in substituted (cyclobutadiene)tricarbonyliron complexes was to be studied in hopes of developing a novel synthesis of metallocyclic complexes bearing two different transition metals and evaluating their physical and chemical properties. The relative positioning of the metals, which would be ascertained by X-ray crystallographic analysis of the complexes, would be of special theoretical interest. Additionally, the potential interpositioning of the two metal moieties at elevated temperatures was of interest and would be examined.

As mentioned in the Introduction, only one mixed binuclear metal complex, containing a Ni-Fe bond, was known which had been obtained accidently in the study of ligand transformation from the nickel complex to the iron carbonyl complexes.

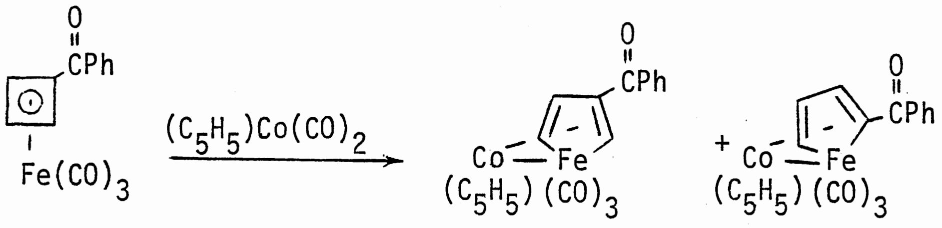
CHAPTER III

RESULTS AND DISCUSSION

Sym- and *unsym*-[tricarbonyl(benzoferracyclopentadiene)]-η^5-cyclopentadienylcobalt and [tricarbonyl(benzoylferracyclopentadiene)]-η^5-cyclopentadienylcobalt were prepared from the insertion of (cyclopentadienyl)dicarbonylcobalt into (benzo- and benzocylcyclobutadiene)tricarbonyliron, *I* and *VI*, respectively. These complexes were prepared to evaluate the physical and chemical properties of the metallocyclic complexes. In addition, the relative positioning of the metals and the fluxional behavior of the resulting metallocyclic complexes were investigated.

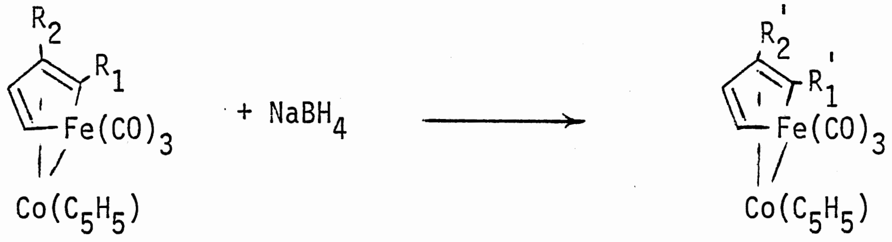


I IIb IIIb (17)



VI Vd Ve (18)

The [tricarbonyl(α-hydroxybenzylferracyclopentadiene)]-η^5-cyclopentadienylcobalt complexes, Vf and Vg, were prepared from the reduction of corresponding ketone complexes, Vd and Ve (Eq. 19), to investigate the stability of a positive charge positioned α to the metallocyclic ring.

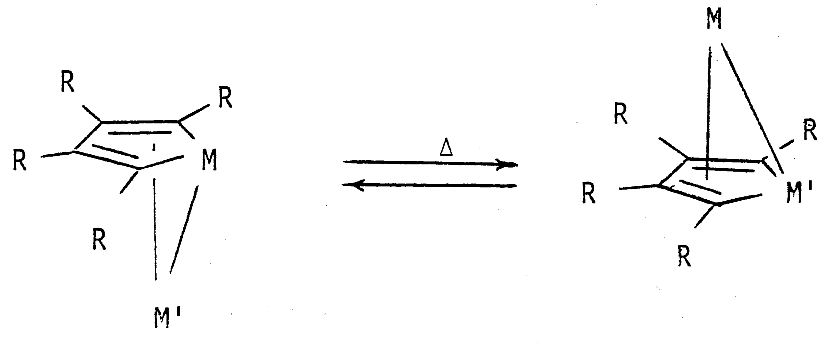


Vd: $R_1 = H$; $R_2 = \overset{O}{\overset{\|}{C}}Ph$ Vf: $R_1' = H$; $R_2' = CHOHPh$

Ve: $R_1 = \overset{O}{\overset{\|}{C}}Ph$; $R_2 = H$ Vg: $R_1' = CHOHPh$; $R_2' = H$ (19)

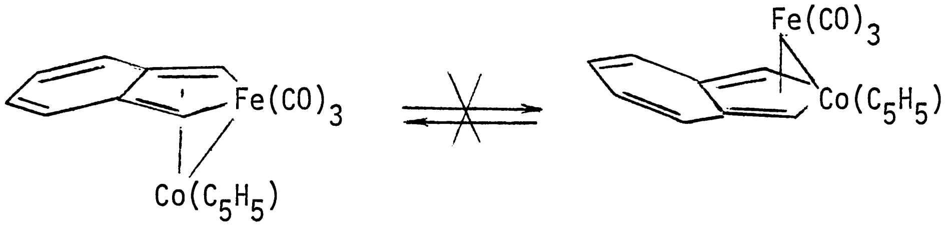
The structure of complex IIb was determined by X-ray crystallographic analysis; the structures of the rest of the complexes prepared are believed to be similar to that of IIb based upon spectroscopic data.

The metallocyclic complexes prepared were usually red solids, the color changing from light-red to dark black-red depending on the substituent on the metallocyclic ring. Crystals suitable for X-ray crystallographic analysis were usually obtained from a mixture of acetone and water. Complexes Vf and Vg could only be obtained as viscous oils; attempts to crystallize these complexes were unsuccessful. In contrast to [cyclopentadienyl(cobaltacyclopentadiene)]-η^5-cyclopentadienylcobalt (Vc), but similar to ferroles and benzoferroles, all the complexes prepared were conspicuously stable toward air and moisture. The insertion of (cyclopentadienyl)dicarbonylcobalt into (benzo- and (benzoylcyclobutadiene)tricarbonyliron (I and VI) led to the formation of complexes IIb and IIIb in a ratio of 5:1, and complexes Vd and Ve in a ratio of 3:1, respectively, which suggests that the insertion occurred mainly from the sterically less hindered side. The symmetry of the complex IIb causes the presence of a better conjugation in that complex than complex IIIb. Complex Vd could also have a higher degree of conjugation because of the possible deviation of the benzoyl group in complex Ve from coplanarity with the metallocyclic ring due to steric interaction with one of the metal-carbonyl groups. Thus, in addition to steric effects, thermodynamic considerations might also explain the observed ratio of the isomers. Although ferroles and complex Vc were reported to exhibit fluxional behavior (Eq. 20), examination of the variable temperature ^{1}H-NMR spectra of complexes IIb and Vb did not reveal any evidence for fluxional behavior in these complexes (Eq. 21 and 22).

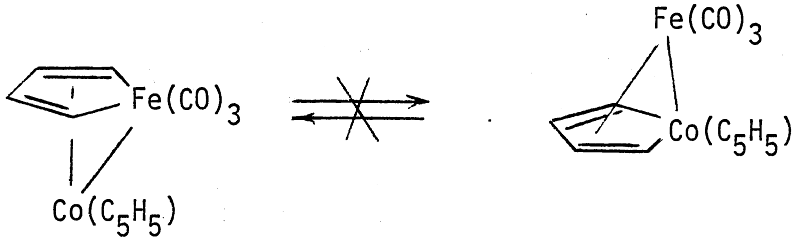


$M = M' = Fe(CO)_3$, R = Ph

$M = M' = (C_5H_5)Co$, R = H (20)



(21)



(22)

X-Ray Crystallographic Data

The X-ray crystallographic data has been tabulated in Tables I-IV. The structure of complex <u>IIb</u> (Figure 1) shows the cobalt to be sandwiched between the cyclopentadienyl and the metallocyclopentadiene five membered rings in a cobaltocene type complex with average Co-cyclopentadienyl carbon distance 2.048(4) Å and average Co-metallocyclopentadiene ring carbon distance 2.035(3) Å. The iron-cobalt distance is 2.482(1) Å. The two five membered rings are eclipsed and not skewed (Fig. 1). The iron retains its coordination to three carbonyl groups (average Fe-carbonyl carbon distance 1.784(4) Å). The carbonyls show Fe-C-O angles 176.9(3)°-178.7(4)° and the carbonyl groups are nonbridging. The ferracyclopentadiene ring is approximately planar, but examination of distances in the ring gives evidence of bond fixation

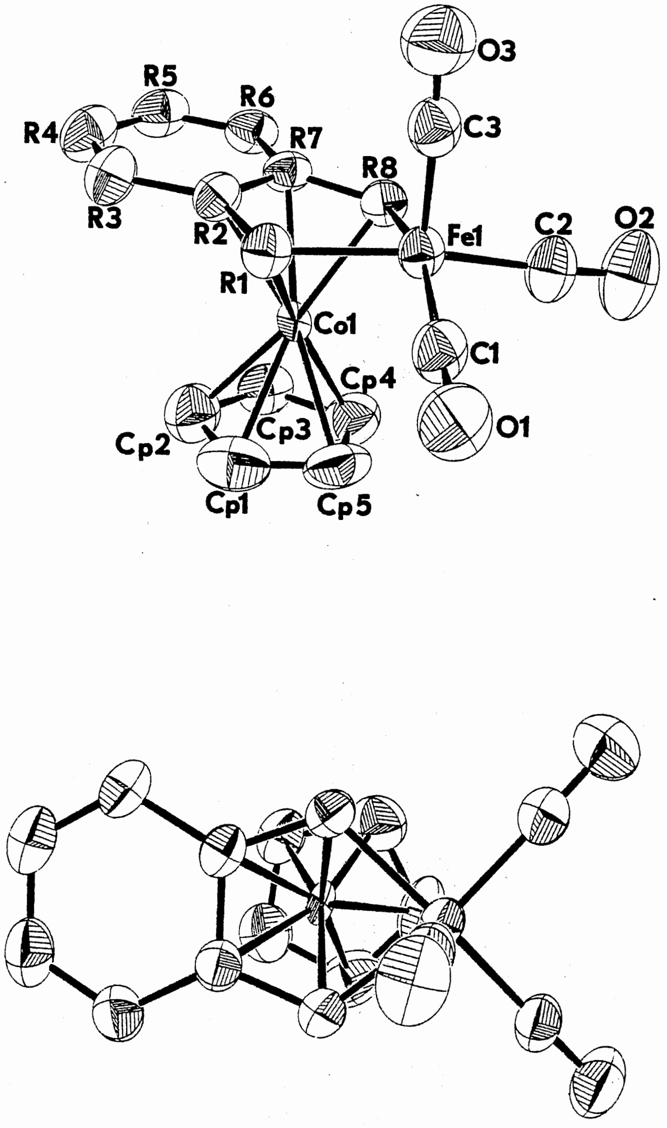


Figure 1. The molecular geometry of $C_{16}H_{11}O_3CoFe$.

TABLE I

CRYSTAL DATA*

Formula	$C_{16}H_{11}O_3CoFe$
Mol. wt.	366.052
	λ = 0.71069 Å
	a = 13.772 (4)
	b = 6.449 (3)
	c = 17.004 (6)
	β = 110.52 (2)°
	v = 1414.45
	transmission factors .14 → .20
	4652 independent observations
	R = 4.8%
	$P2_1/m$
	Z = 4, D_{cal} = 1.718 g cm^{-3}

*)Error in parentheses are deviations in the last significant figure.

[R3-R4 1.352(5), R4-R5 1.415(6), and R5-R6 1.352(5) Å]. Normal carbon-carbon bond length in benzene is 1.40 Å; carbon-carbon double bond length is 1.33 Å; and carbon-carbon single bond length is equal to 1.53 Å. Thus bond fixation is manifested by increased double bond character of two of the bonds in the six membered ring and increased the single bond character of the other carbon-carbon bonds of that ring.

TABLE II

POSITIONAL PARAMETERS FOR $C_{16}H_{11}O_3$CoFe*

	x(σ(x))	y(σ(y))	z(σ(z))	U equiv x 10^4
Co(1)	0.28934(4)	0.81171(6)	0.79594(2)	334(1)
Fe(1)	0.27063(3)	0.79894(7)	0.93582(2)	376(1)
CP1	0.4278(3)	0.7250(7)	0.7870(3)	701(18)
CP2	0.3567(3)	0.7608(7)	0.7069(2)	615(15)
CP3	0.3242(3)	0.9671(6)	0.7026(2)	544(13)
CP4	0.3750(3)	0.0578(6)	0.7814(3)	615(15)
CP5	0.4384(2)	0.9068(8)	0.8338(2)	679(16)
R1	0.2558(2)	0.5734(5)	0.8565(2)	406(10)
R2	0.1745(2)	0.5925(5)	0.7768(2)	397(10)
R3	0.1400(3)	0.4457(6)	0.7093(2)	514(12)
R4	0.0646(3)	0.4900(7)	0.6366(2)	605(14)
R5	0.0198(3)	0.7002(6)	0.6246(2)	567(13)
R6	0.0515(2)	0.8469(6)	0.6851(2)	488(11)
R7	0.1297(2)	0.7966(5)	0.7649(2)	384(10)
R8	0.1778(2)	0.9286(5)	0.8343(2)	387(9)
C1	0.3886(3)	0.6920(7)	0.0092(2)	488(14)
C2	0.2893(3)	0.0460(6)	0.9879(2)	557(3)
C3	0.1794(3)	0.6875(6)	0.9736(2)	481(11)
O1	0.4628(2)	0.6284(6)	0.0560(2)	781(12)
O2	0.2970(3)	0.2004(5)	0.0207(2)	931(17)
O3	0.1192(2)	0.6082(6)	0.9954(2)	759(13)

TABLE II (Continued)

	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$	U equiv x 10^4
HP1	0.4629(3)	0.5964(7)	0.8069(3)	
HP2	0.3343(3)	0.6619(7)	0.6619(2)	
HP3	0.2755(3)	0.0346(6)	0.6547(2)	
HP4	0.3677(3)	0.1987(6)	0.7966(3)	
HP5	0.4816(2)	0.9258(8)	0.8914(2)	
H1	0.3007(2)	0.4547(5)	0.8703(2)	
H3	0.1701(3)	0.3096(6)	0.7155(2)	
H4	0.0404(3)	0.3997(7)	0.5922(2)	
H5	-0.0340(3)	0.7328(6)	0.5723(2)	
H6	0.0222(2)	0.9837(6)	0.6751(2)	
H8	0.1650(2)	0.0752(5)	0.8313(2)	

*) U equiv = $(U_{11} + U_{22} + U_{33})/3$.

σ (U equiv) - $\left[\Sigma\sigma Uii)*Uequiv\right]/\Sigma Uii)*\sqrt{6}$

Errors in parentheses are deviations in the last significant figure.

While few other cobaltocene structures have been examined by single crystal X-ray diffraction techniques, comparisons may be made with cobaltocene,[28] a cobaltocenium salt,[29] and with two other structures containing the metallocyclic ring.[9,21] The carboxycobaltocenium hexafluorophosphate shows an average Co-cyclopentadienyl carbon (Co-Cp) distance of 2.029(9) Å as compared with an average of 2.048(8) Å observed in the X-ray of complex <u>IIb</u>. However, the cobaltocene shows an average Co-Cp distance of 2.096(8) Å which is considerably longer than that in cobaltocenium salt and complex <u>IIb</u>. The lengthening of Co-Cp

TABLE III

BOND ANGLES (°) AND DISTANCES (Å) FOR $C_{16}H_{11}0_{3}CoFe$*

Fe1 - C1	1.803(4)	CP1 - CP2	1.398(5)
Fe1 - C2	1.797(4)	CP2 - CP3	1.397(6)
Fe1 - C3	1.753(4)	CP3 - CP4	1.403(5)
Fe1 - Co1	2.482(1)	CP4 - CP5	1.399(6)
Fe1 - R1	1.945(3)	CP5 - CP1	1.396(7)
Fe1 - R8	1.941(3)		
		R1 Fe1 R8	80.1(1)
Co1 - R1	1.992(3)	R1 Fe1 C2	165.2(2)
Co1 - R2	2.060(3)	R8 Fe1 C1	159.0(2)
Co1 - R7	2.076(3)	C3 Fe1 Co1	133.9(1)
Co1 - R8	2.013(3)	R8 Fe1 C2	89.6(1)
Co1 - CP1	2.043(5)	R1 Fe1 C1	92.5(2)
Co1 - CP2	2.061(5)	C3 Fe1 R8	99.8(1)
Co1 - CP3	2.070(4)	C3 Fe1 R1	91.9(2)
Co1 - CP4	2.044(4)	C3 Fe1 C2	100.4(2)
Co1 - CP5	2.020(4)	C3 Fe1 C1	100.2(2)
		Co1 Fe1 R1	51.8(1)
R1 - R2	1.429(3)	Co1 Fe1 R8	52.4(1)
R7 - R8	1.416(4)		
R2 - R7	1.438(4)	Fe1 C1 01	178.7(4)
R2 - R3	1.435(4)	Fe1 C2 02	177.1(4)
R3 - R4	1.352(4)	Fe1 C3 03	176.9(3)
R4 - R5	1.415(6)	R8 R7 R2	112.4(2)
R5 - R6	1.352(5)	R1 R2 R7	111.6(3)
R6 - R7	1.443(4)	R6 R7 R2	118.7(3)
		R3 R2 R1	129.2(3)
C101	1.130(5)	R2 R1 Fe1	116.7(2)
C202	1.128(5)	R7 R8 Fe1	116.9(2)
C303	1.141(5)		

*) Errors in parentheses are deviations in the last significant figure.

TABLE IV

THERMAL PARAMETERS FOR $C_{16}H_{11}O_3CoFe$*

	U11	U22	U33	U23	U13	U12
Co(1)	308(2)	412(2)	305(2)	15(2)	137(1)	24(2)
Fe(1)	421(2)	428(3)	296(2)	19(2)	147(2)	64(2)
CP1	53(2)	84(3)	91(3)	27(3)	48(2)	24(2)
CP2	70(2)	73(3)	60(2)	-11(2)	46(2)	-9(2)
CP3	54(2)	70(2)	46(2)	17(2)	26(2)	-1(2)
CP4	60(2)	58(2)	81(3)	-6(2)	44(2)	-17(2)
CP5	36(2)	119(4)	48(2)	1(2)	14(1)	-17(2)
R1	47(1)	43(2)	36(1)	4(1)	19(1)	5(1)
R2	42(1)	44(2)	37(1)	0(1)	19(1)	-4(1)
R3	62(2)	50(2)	44(2)	-6(2)	21(2)	-12(2)
R4	62(2)	75(3)	41(2)	-12(2)	14(2)	-27(2)
R5	46(2)	80(3)	39(2)	8(2)	9(1)	-12(2)
R6	35(1)	66(2)	44(2)	14(2)	12(1)	2(1)
R7	31(1)	50(2)	37(1)	7(1)	15(1)	1(1)
R8	39(1)	42(2)	40(1)	4(1)	20(1)	10(1)
C1	54(2)	59(2)	34(2)	-3(2)	16(2)	9(2)
C2	70(2)	53(2)	40(2)	3(2)	15(2)	7(2)
C3	52(2)	57(2)	37(2)	-4(2)	18(1)	4(2)
O1	66(2)	103(2)	52(2)	-1(2)	4(1)	32(2)
O2	133(.3)	55(2)	79(2)	-20(2)	21(2)	2(2)
O3	72(2)	101(2)	67(2)	1(2)	39(2)	-13(2)

*) Anisotropic thermal parameters in the form:

$$\exp\left[-2\pi^{2}\left(U_{11}h^{2}a^{*2} + U_{22}k^{2}b^{*2} + U_{33}l^{2}c^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{13}hla^{*}c^{*} + 2U_{23}klb^{*}c^{*}\right)\right] \times 10^{4}$$ for Co(1) and Fe(1) $\times 10^{3}$ for all other atoms.

Errors in parentheses are deviations in the last significant figure.

in cobaltocene compare with that of cobaltocenium salt has been explained by the presence of an electron in an antibonding orbital of cobaltocene which would decrease the bonding of Co-Cp.[29] Thus, it is resonalbe to suggest that the cobalt in complex IIb is partially positive due to donation of electrons to the iron to satisfy the inert gas configuration of iron. Two other sturctural investigations of the related metallocyclic systems, benzoferrole IIa and ferrole Va, show that the bond angles and distances observed for complex IIb are not atypical. The structure of benzoferrole IIa shows iron-ring carbon distances of 1.95 and 1.96 Å; the same as those of the complex IIb (1.945(3) and 1.941(3) Å) within experimental error. The structure of ferrole also shows distances that are euqivalent to those observed in the complex IIb [(cf. 1.936(6) and 1.953(5) Å]. Bond angles at iron are also similar [80.1(1)° for complex IIb and 79.8(3)° for the ferrole complex]. The ferrole complexes show metal-metal distances of 2.51 Å and the complex IIb shows metal-metal distance of 2.482(1) Å. The structures of benzoferrole and ferrole show semibridging carbonyl groups with one of the three carbonyl groups attached to the iron, bent into bridging configuration with the other metal atom [Fe-C-O angle 167.3(7)°, for ferrole, and 166-167°, for benzoferrole]. The structure of the complex IIb shows no such semibridging carbonyl [Fe-C-O angles 176.9(3)-178.7(4)°].

Benzoferracyclopentadiene Complexes

The appearance of a singlet at 8.19 ppm in the ^{1}H-NMR spectrum of complex IIb, integrating for two protons, was assigned to the protons attached to the carbons adjacent to the metal. Such downfield shift observed for these protons represent the electron withdrawing character of $Fe(CO)_3$ group. Contrary to our observation Victor and co-workers[11] have interpreted the ^{1}H-NMR spectrum of unsym-benzoferrole IIIa based on the electron releasing character of the $Fe(CO)_3$ group. The ^{13}C-NMR chemical shifts of complex IIb were assigned by the consideration of the bond fixation and the electron-withdrawing property of the tricarbonyliron group. The peak at 153.8 ppm was assigned to $C_1 = C_8$ because of its proximity to the iron. The assignment was supported by the ^{13}C-proton coupled spectrum. The peak at 115 ppm was assigned to $C_2 = C_7$ owing to the lack of C-H coupling. The peaks at 129.0 and 130.9 ppm were assigned to $C_4 = C_5$ and $C_3 = C_6$, respectively, using butadiene as a model. This model is consistent with the bond fixation observed by the X-ray crystalographic analysis and the ability of the cyclohexadiene of benzoferroles to form the corresponding dienetricarbonyliron complex.[10, 25]

Although a structure similar to that for unsym-benzoferrole IIIa was tentatively suggested for the other isomer, IIIb, obtained from the insertion of cyclopentadienylcobalt moiety in benzocyclobutadienetricarbonyliron complex I, all the spectroscopic data of this complex and comparison of these data with that in relating benzoferrole supported such an assignment.

The high resolution mass spectrum of complex IIIb gives a parent mass fragment corresponding to $C_{16}H_{11}O_3CoFe$. Investigation of the mass spectra fragmentation of benzoferroles IIa and IIIa, and complexes IIb and IIIb revealed that all of these complexes follow similar fragmentation. The fragmentation pathway is illustrated in Fig. 2 and 3. Attempts to detect metastable peaks were unsuccessful in all cases.

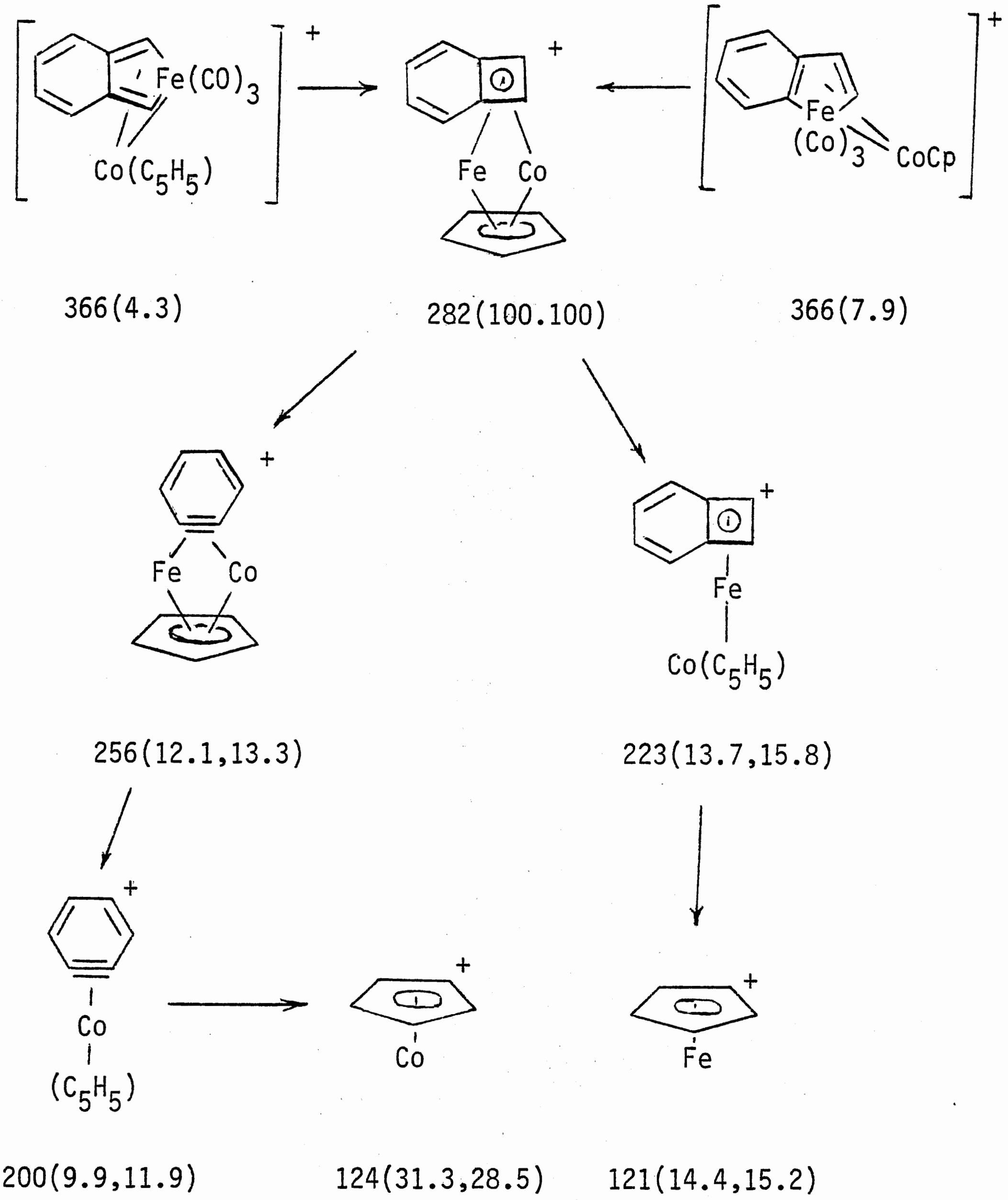


Figure 2. Fragmentation pathways for complexes IIb and IIIb.

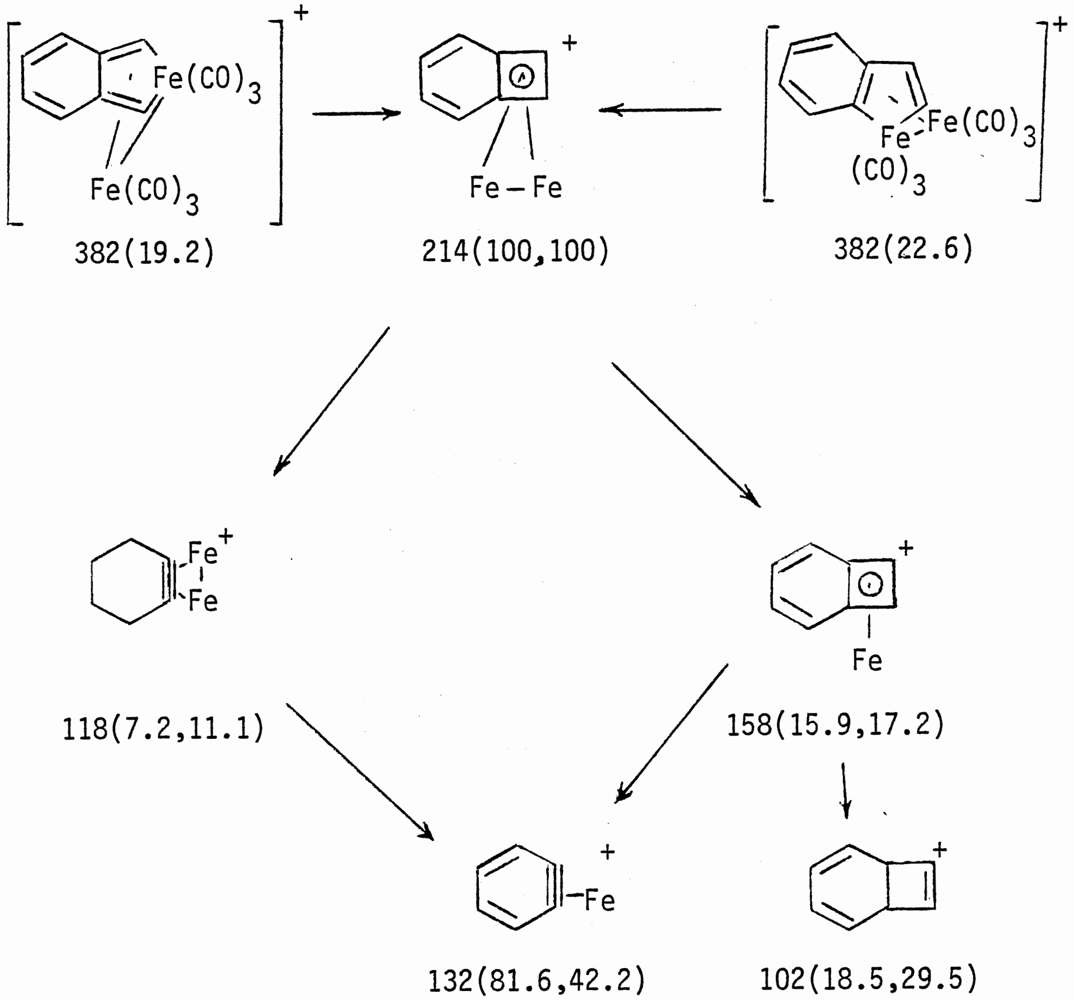
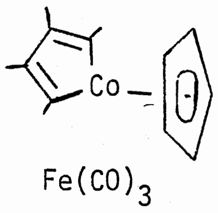


Figure 3. Fragmentation pathways for complexes IIa and IIIa.

The ^{1}H-NMR chemical shifts of complex IIIb are similar to those reported for the unsym-benzoferrole IIIa, if the chemical shift assignment for H_1 and H_2 are reversed.

Benzoylferracyclopentadiene Complexes

The high resolution mass spectra of complexes Vd and Ve give a parent mass fragments corresponding to $C_{19}H_{13}O_3CoFe$. The ^{1}H- and ^{13}C-NMR spectrum of these complexes are comparable with their analogous ferroles (Table V and VI). Thus, a structure similar to ferroles is tentatively suggested for complexes Vd and Ve. Such a structure is related to those reported by Yamazaki and co-workers,[22] as mentioned in Introduction p. 71. An X-ray study of complex indicated that the iron is in the plane of five-membered metallocyclopentadiene ring and the cobalt is π-complexed to the metallocyclopentadiene ring. Although these data might also be consistent with structure VI; comparative bonding study of conical fragments by Hoffmann[30] suggests the preference of the structure Vd and Ve to the corresponding structure VI due to the stronger M-C δ-bonds in Vd and Ve.



VI

The matter as to which one of these complexes is the 2- or 3-substituted benzoyl complexes was determined based on the polarity of these

TABLE V

^{1}H-NMR CHEMICAL SHIFTS DATA^1

Complex	H_1	H_2	H_3	H_4	C_p	Others
Va^2	6.75(dd) (2.4, 5.3)	6.15(dd) (2.3, 5.3)	6.15(dd) (2.3, 5.3)	6.75(dd) (2.4, 5.3)		
Vb	7.39(dd)	5.88(dd)	5.88(dd)	7.39(dd)	4.88(s)	
Vc^3	8.21(5)	4.96(m)	4.96(m)	8.21(t)	4.96, 4.84(ds)	
Vd	2.72(m)	----------	6.28(dd) (2.5, 5.2)	7.72(m)	4.96(s)	Ph: 7.44- 7.72(m)
Ve	----------	5.95(dd) (2.4, 5.0)	5.75(t) (2.4)	7.45(dd) (2.4, 5.0)	5.14(s)	Ph: 7.24- 7.67(m)
Vf_1	7.37(d) (2.5)	----------	5.76(dd) (2.5, 5.0)	7.31(d) (5.0)	4.86(s)	CH: 5.38(s) PH: 7.19(s)
Vf_2	7.37(d) (2.5)	----------	5.94(dd) (2.5, 5.0)	7.31(d) (5.0)	4.9(s)	CH: 5.21(s) PH: 7.17(m)
Vg	----------	5.82(dd) (2.4, 5.2)	5.64(t) (2.4)	7.20(m)	4.94(s)	Ph: 7.2(m) CH: 5.30(s)

1) CS_2 as solvent; values in parentheses are coupling constants in H_z.

2) Reversal of proton-assignment reported, cf. ref. 21.

3) Reversal of proton-assignment reported, cf. ref. 25.

TABLE VI

^{13}C-NMR CHEMICAL SHIFTS DATA[1]

Complex	C_1	C_2	C_3	C_4	C_p	M-$\underline{C}$O	Others
(Va[2])	156.4 (159)	112.1 (169)	112.1 (169)	156.4 (159)			
(Vb)	157.0 (156)	101.4 (167)	101.4 (167)	157.0 (156)	81.1 (180)		
(Vd)	159.8 (156)	114.3	103.2 (169)	155.7 (156)	82.4 (181)	212.7	$\underline{C}$=O:195.9; Ph: 138.4 129.6, 129.1, 133.6
(Ve)	173.7	96.6 (168)	100.9 (168)	156.3 (154)	82.6 (181)	201.5	$\underline{C}$=O:198.8; Ph: 137.4 129.7, 128.8, 132.9
Vf_1	155.66	107.1	100.8	145.13	81.4	213.5	CH=74.0; Ph: 128.7 128.6, 127.9, 127.7
Vf_2	149.59	107.1	100.8	145.22	81.45	213.5	CH=74.3 127.6 127.3, 126.95, 126.8
Vg	154.6	98.5	100.7	147.2	81.4	220.1	CH=83.2

1) acetone-d^6 as solvent; values in parentheses are coupling constants in H$_z$.

2) In agreement with literature values, *cf.*, ref. 31.

complexes. The presence of an electron-withdrawing group such as benzoyl on the carbon adjacent to the iron would presumably make the molecule more polar than were the benzoyl group on the carbon positioned beta to the metal. Thus, the complex which had been collected first from the column as a red band was assigned as the 3-substituted benzoyl complex Vd and the complex which has been collected second from the column as a pink band was assigned as the 2-substituted benzoyl complex Ve. The proposed structural assignment of the two complexes was in agreement with the spectroscopic data and comparison of that data with those of related complexes (Table V and VI).

The ^{1}H-NMR chemical shifts and the corresponding coupling constants of complexes Vd and Ve are similar to that reported for ferroles and [cyclopentadienyl(cobaltacyclopentadiene)]-η^5-cyclopentadienylcobalt (Vc), Table V. However, contrary to our assignments, the ^{1}H-NMR spectra of ferrole Va and its cobalt analogue Vc have been interpreted by Weiss[21] and Rosenblum,[25] respectively, assuming that the metal of the metallocyclic ring shields the proton attached to the carbon adjacent to the metal. Such an assumption is not consistent with the ^{1}H-NMR spectra of benzoferrole (IIa) and complex IIb. The ^{1}H-NMR spectra of both complexes show a singlet, corresponding to the proton attached to the carbon adjacent to the metal, at 7.3 and 8.19 ppm, respectively, which are the most downfield absorption observed in those spectra. The presence of a quartet at 7.72 ppm in the ^{1}H-NMR spectrum of complex Vd which contains two proton on the carbons adjacent to the iron, and the presence of a triplet and a quartet positioned at 5.75 and 5.95 ppm, respectively, in ^{1}H-NMR spectrum of complex Ve which contains one proton attached to the carbon adjacent to the iron, are compatible with the assignment of the structures. All of the chemical shifts of the complexes prepared were solvent dependent, moving downfield by changing the solvent from carbon disulfide to acetone-d^6. The ^{13}C-chemical shifts of the complexes (Tavel VI) have been assigned on the basis of ^{13}C-proton coupled spectra. These chemical shifts and the related C-H coupling constants are in good agreement with those reported for the analogous ferroles. The appearance of the ^{13}C-resonance signals for C_1 and C_4, the carbon atoms adjacent to the iron, downfield relative to the signals for C_2 and C_3 is a reflection of the electron-withdrawing character of the $Fe(CO)_3$ group. Examination of the mass spectral fragmentation of complexes <u>Vb</u>, <u>Vd</u>, <u>Ve</u>, and the rhodium analogue, $C_4H_4(CO)_3Fe(\eta^5\text{-}C_5H_5)Rh$ (<u>Vh</u>) made in our laboratory by King, revealed that all of these complexes appear to follow the same spectral fragmentation pathway as illustrated in figure 4. The metastable peaks corresponding to the $(M^+ - iCO) \longrightarrow [M^+ - (i+1)CO]$ transitions were observed in the low resolution mass spectra of all the complexes. Additionally the metastable peaks at m/e 85.4 and 81.3 which correspond to (180 → 124) and (180 → 121) transitions were observed for complex <u>Vb</u>. For complex <u>Vh</u> metastable peaks at m/e 226.4 and 126 corresponding to (276 → 250) and (224 → 168) were observed.

α-Hydroxybenzylferracyclopentadiene Complexes

Reduction of both complexes <u>Vd</u> and <u>Ve</u> with sodium borohydride afforded the corresponding alcohols <u>Vf</u> and <u>Vg</u>, respectively. The NMR spectra of complex <u>Vf</u> showed that it was a mixture of two diastereomers. Attempts to separate these two diastereoisomers were not successful.

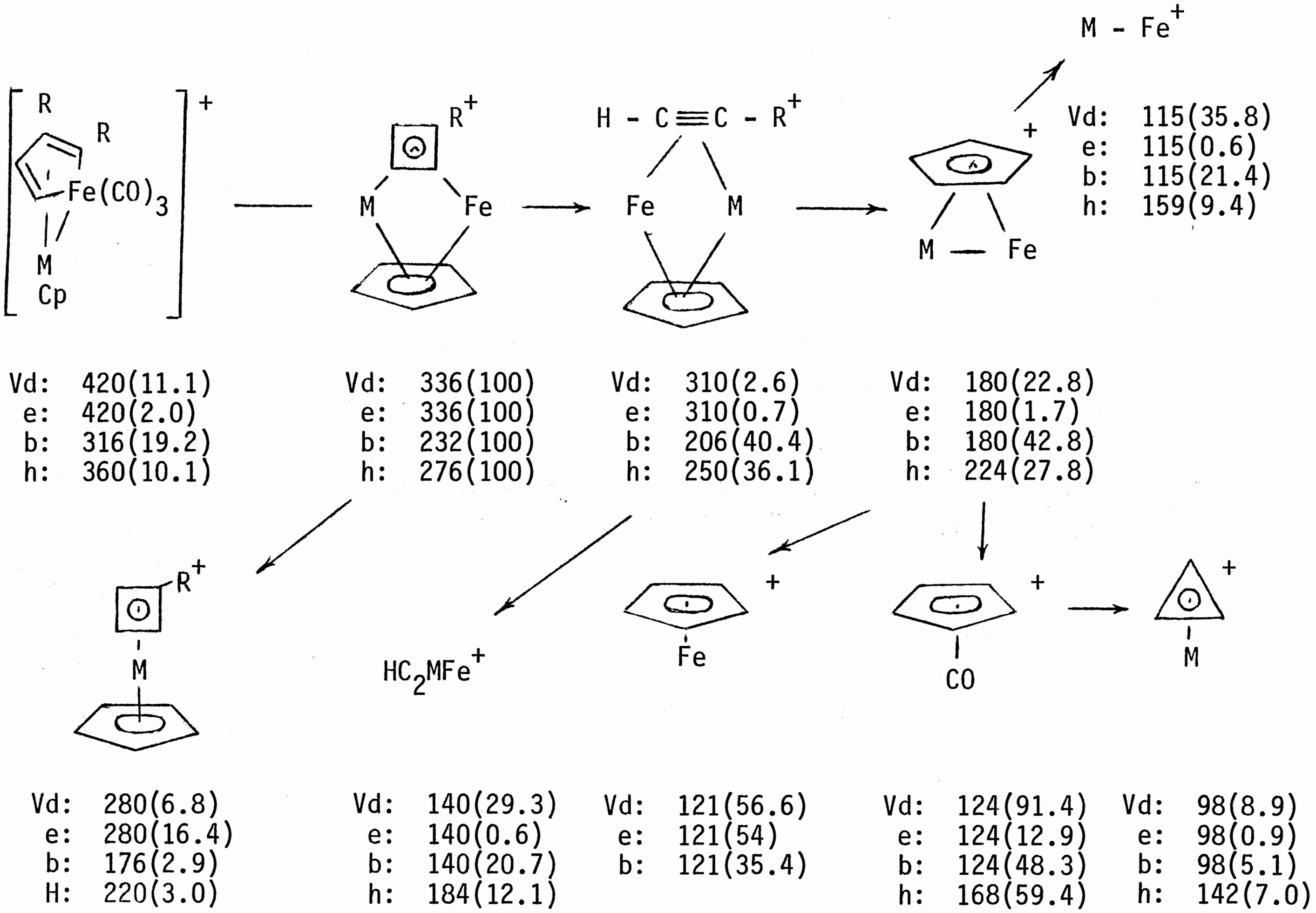
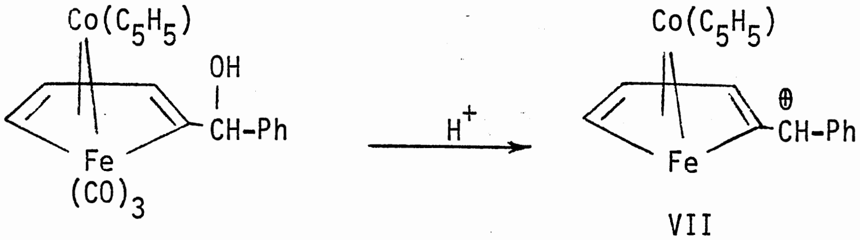


Figure 4. Mass Spectral Fragmentation Pathway for Complexes: Vd, Ve, Vb, and Vh.

In contrast to the reduction of complex <u>Vd</u>, reduction of complex <u>Ve</u> gave apparently only one isomer which could be because of steric or thermodynamic reasons. The ^{1}H- and ^{13}C-NMR spectra of these complexes were similar to those of related complexes, Tables V and VI. The only noteworthy feature about the spectra of these complexes is the change in the magnitude of the coupling constants and a change in the chemical shifts in the ^{1}H-NMR spectrum of complex <u>Vg</u>, with change in solvent. The ^{1}H-NMR spectrum of this complex in carbon disulfide gives a triplet and a quartet at δ 5.64 and 5.82 ppm (Tavle V), respectively. However, changing the solvent from carbon disulfide to acetone-d^6 causes the triplet and the quartet to each become a singlet (each singlet integrated for one proton) positioned at δ 5.98 and 6.1 ppm. No reasonable interaction between solvent and complex which would lead to the disappearance of the coupling constants was found. The mass spectral fragmentation patterns for these complexes were different from those previously described. These complexes prefer to lose a molecule of water (after successive loss of CO's), followed by the loss of the iron and the formation of the cobaltocenium ion.

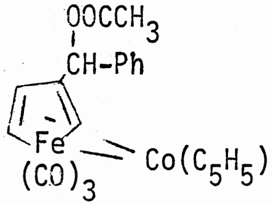
Reactions

Attempts were made to generate carbonium ion positioned alpha to the metallocyclic ring to study the stability of such an ion (Eq. 23).



VII (23)

Treatment of complex Vf with aqueous fluoroboric acid (10 eqv.) at 0°C in acetic anhydride followed by addition of ether did not afford any precipitation. The work-up of the reaction at room temperature afforded a viscous oil. The ^{1}H-NMR of the recovered oil did not provide any information due to high contamination with impurity (or impurities). However, the mass spectra of the oil afforded m/e (rel. intensity): 464(7.1), 436(3.7), and 380(67.4) which correspond to the molecular ion for acylated alcohol (VIII) and the subsequent loss of CO's. Treatment of complex Vf with trifluoroacetic acid (TFA) at



VIII

low temperature was also examined by ^{1}H-NMR. Addition of TFA to this complex at -70°C in sulfur dioxide resulted in the downfield shift of the signal for the benzylic proton and the cyclopentadienyl protons by 0.5 and 0.6 ppm, respectively. Other protons were not detected due to the lack of resolution. The downfield shift of the signal for the benzylic proton need not point to the formation of the desired cation. Such downfield shift is most likely due to the protonation of the hydroxyl group. The ^{1}H-NMR spectrum of the complex Vb in TFA has also been studied in our laboratory by Dr. McKennis and a similar downfield shift for the cyclopentadienyl signal was also observed. Thus, the observed downfield shift for the signal of cyclopentadienyl does not provide any evidence relating to the generation of the desired cation.

Treatment of complex Vg with trityl tetrafluoroborate in dichloromethane resulted in the decomposition of the complex.

CHAPTER IV

EXPERIMENTAL

All reactions were carried out under argon which had been passed through a drying column packed with anhydrous calcium sulfate and sodium hydroxide. The glassware was thoroughly dried under argon using a heat gun. All solvents were reagent grade, anhydrous, and degassed. The process of degassing the solvents and drying sulfur dioxide was identical to that used in part I of this thesis. Also, the same kinds of alumina and silica gel were used for chromatographic purposes. (Cyclopentadienyl)dicarbonylcobalt and (cyclobutadiene)tricarbonyliron were purchased from Strem Chemical, Inc. (Benzocyclobutadiene)tricarbonyliron and (benzoylcyclobutadiene)tricarbonyliron complexes were prepared according to published procedures.[32, 33]

Proton NMR and ^{13}C-NMR spectra were recorded on the same instrument as previously mentioned. All ^{1}H- and ^{13}C-chemical shifts are reported relative to tetramethylsilane using either acetone-d^{6} or carbon disulfide as solvent. Infrared spectra either with pentane as solvent or with a KBr pellet were obtained at ambient temperature using either a Beckman-8A, or a Perkin Elmer 681 infrared spectrophotometer, respectively. Low and high resolution mass spectra were obtained at 70eV with an inlet temperature of ~150^{o}C and an ion-source temperature of ~250^{o}C.

A crystal of [tricarbonyl(ferrabenzocyclopentadiene)] -η^5-cyclopentadienylcobalt complex IIb was mounted on a Syntex P_3 four-circle automated diffractometer. Graphite-monochromated molybdenum Kα radiation (λ= 0.71069 Å) was used. Unit cell dimensions were determined by a least squares fit of the angles of 12 independent reflections; a = 13.772(4), b = 6.449(3), c = 17.004(6) Å, and β = 110.52(2)° during normal allignment. The calculated density (cell volume 1414.4(3) $Å^3$) with four molecules per unit cell (MW = 366.05) is 1.718 $g.Cm^{-3}$. A Θ-2Θ scan mode with variable scan width was used for data collection with $2\Theta_{max} = 110^o$. The intensities of three standards did not decline over the data collection period. 4652 independent reflections were classed as observed $[|F_o|/\sigma|F_o|>3.0$, where F_o is the observed structure amplitude and σF_o is its corresponding estimated standard deviation] after subtraction of background and correction for Lorentz and polarization factors. Solution proceeded by direct methods. Least squares refinement of the scale factor, positional and temperature factors gave an R factor of 4.8% [the agreement factor, $R = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$, where F_c is the calculated structure factor corresponding to F_o, the observed structure factor. The summation is over all the observed reflections.]. Hydrogen positions were calculated and not allowed to vary. Unit weights were used throughout.

Preparations

Sym- and Unsym- [Tricarbonyl(ferrabenzocyclopentadiene)]-η^5-cyclopentadienylcobalt (IIb, and IIIb)

A solution of (benzocyclobutadiene)tricarbonyliron (0.5 g, 2.07

mmol) and (cyclopentadienyl)dicarbonylcobalt (1.3 g, 7.2 mmol) in n-octane (~35 ml) was refluxed for 30 min. At the end of this time the reaction mixture was chromatographed on alumina. The unchanged (cyclopentadienyl)dicarbonylcobalt, observed as a yellow band, was removed by elution with pentane. A red band was then eluted with a mixture of benzene/pentane (1/1). Removal of solvent yielded a mixture of the sym- and unsym-complexes IIb and IIIb; yield 236 mg (31%); ratio sym: unsym = 5:1 based on ^{1}H-NMR. Repetitive chromatography on alumina using a mixture of benzene/pentane (1/4) as eluant effected the separation of the isomers: Sym-Complex: mp 94-96°C; ^{1}H-NMR (CS_2): δ 4.5 (s, C_5H_5), 7.2 (m, H_3 and H_4), and 8.19 (s, H_1); ^{13}C-NMR (acetone-d^6): δ 82.0 (C_5H_5, J_{CH} = 180 Hz), 129.0 (C_4, J_{CH} = 161 Hz), 139.9 (C_3, J_{CH} = 167 Hz), 115.0 (C_2), 153.8 (C_1, J_{CH} = 154 Hz), and 213.6 ppm (CO); IR (pentane): 2035(m), 1985(vw), and 1968(s) cm^{-1}; High resolution MS: 365.9337 (ca.365.9388); MS m/e (rel. intensity) (assignment): 366 (4.3) (M^+), 338 (11.8) (M^+-CO), 310 (20.2)(M^+-2CO), 282(100)(M^+-3CO), 256 (12.1)(M^+-3CO, C_2H_2), 223 (13.7) (M^+-3CO, Co), 200 (9.9) (M^+-3CO, C_2H_2, Fe), 150 (9.6) ($C_7H_7Co^+$), 141 (2.4)($C_2H_2FeCo^+$), 124 (28.5) ($C_5H_5Co^+$), 121 (9.4) ($C_5H_5Fe^+$), and 115 (6.6) ($FeCo^+$). Unsym-complex: ^{1}H-NMR (CS_2): δ 4.56 (s, C_5H_5), 6.69 (d, J = 5.4 Hz, H_2), 6.80-7.16 (m, H_5 and H_6), 7.23 (d, J = 5.4 Hz, H_1), 7.70(d, J = 8.5 Hz, H_7), and 8.1 (d, J = 8.5 Hz, H_5); ^{13}C-NMR (acetone-d^6): δ 4.56 (C_5H_5), 129.8(C_5), 130.8 (C_4), 124.2 (C_3), 100.2 (C_2), and 151.4 ppm (C_1); IR (CS_2); 2025 (vs), 1952 (vs, broad), and 1910 (sh) cm^{-1}; High resolution MS: 365.9397 (ca. 365.9388); MS: identical pattern to that for sym-complex

(Benzoylcyclobutadiene)tricarbonyliron (VI)[33]

Aluminum chloride (1.5 g, 0.01 mol) was placed in a 50-ml, three-neck flask containing 15 ml of carbon disulfide and the solution was cooled by ice-water bath. To this solution freshly distilled benzoyl chloride (0.73 g, 0.005 mol) dissolved in 4 ml of carbon disulfide was added over 5 minutes. The reaction mixture was stirred for 5 more minutes. At the end of this time, a solution of (cyclobutadiene)tricarbonyliron (1.0 g, 0.005 mol), dissolved in 4 ml of carbon disulfide was added over a period of 10 min. The solution was stirred at 0^oC for 45 min and then for additional 30 min at 35^oC. At the end of this time, the reaction mixture was poured onto 15 g of cracked-ice and transferred to a separatory funnel. Fifty milliliters of water was added and the phases were separated. The aqueous layer was extracted three times each with 50 ml of ether. The combined organic layers were washed three times with 50 ml of water and dried over magnesium sulfate. The dried solution was filtered and the solvent was removed *in vacuo*. The crude oil was extracted by pentane and crystalized from pentane, 0.61 g (39.4 %); mp $62\text{-}63^oC$; ^1H-NMR (CS_2): δ 4.4 (s, H_3), 4.52 (s, $H_2 = H_4$), and 7.44 (m, Ph) ppm; ^{13}C-NMR (acetone-d^6): δ 67.9 ($C_2 = C_4$), 70.9 (C_3), 72.4 (C_1), 128.1 ($C_{3'}$), 129.3 ($C_{2'}$), 133.4 ($C_{1'}$), 137.2 ($C_{4'}$), 190.9 ($C{=}O$), and 213.0 (Fe-$\underline{C}$O) ppm; IR (pentane): 2060 (vs), 2000 (vs), 1900 (vs), 1648 (w) cm^{-1}.

[Tricarbonyl(2- and 3-benzoylferracyclopentadiene)]-η^5-cyclopentadienylcobalt (Vd, Ve)

(Benzoylcyclobutadiene)tricarbonyliron (0.165 g, 0.56 mmol) was dissolved in n-octane (15 ml) in a 50-ml three-neck flask and (cyclopentadienyl)dicarbonylcobalt (0.43 g, 2.4 mmol) was added. The reaction mixture was refluxed for 20 hr. At the end of this time the resulting dark-black solution was chromatographed on alumina. Elution with pentane removed the unchanged (cyclopentadienyl)dicarbonylcobalt, as a yellow band. Elution with a mixture of pentane/benzene (1:1) resulted in the appearance and movement of two bands, red and pink in color. They were collected and the solvents were removed. Total weight was 0.136 g (58.1%). The first band, the red band, complex Vd was a dark-black red oil which solidified by sitting in the refrigerator, mp 86-87^{o}C; IR (KBr): 2024(vs), 1955(vs), 1940(vs), 1650(s), and 1597(w) cm^{-1}; High resolution MS: 419.9567 (ca. 419.9494); MS (rel. intensity) (assignment): 420 (11.1) (M^+), 392 (25.4) (M^+-CO), 364 (77.2) (M^+-2CO), 336 (100) (M^+-3CO), 310 (2.6) (M^+-3CO,C_2H_2), 308 (69.8) (M^+-4CO), 280 (6.8) (M^+-3CO,Fe), 252 (34.8) (M^+-4CO,Fe), 249 (86.0) (M^+-4CO,Co), 226 (10.7) ($HC_2PhCoCp^+$), 223 (39.2) ($HC_2PhFeCp^+$), 212 (9.8) ($C_{11}H_8OFe^+$), 200 (24.7) ($C_{10}H_8OFe^+$), 186 (18.4) ($C_9H_6OFe^+$), 180 (22.8) ($CpCoFe^+$), 175 (6.3) ($C_9H_8Co^+$), 150 (10.6) ($C_7H_7Co^+$), 140 (29.3) (HC_2CoFe^+), 124 (91.4) ($CpCo^+$), 121 (56.6) ($CpFe^+$), 115 (35.8) ($FeCo^+$), and 98 (8.9) ($C_3H_3Co^+$). The second band, the pink band, complex Ve was recovered as a red solid and was recrystalized from pentane: mp 130-131^{o}C; IR(KBr): 2031(vs), 2022(vs), 1952(vs), 1933(vs), 1642(s), and 1615(w) cm^{-1}; High resolution MS: 419.9481 (ca. 419.9494); MS: similar pattern to that for the red band.

[(Tricarbonyl(2- and 3-α-hydroxybenzylferracyclopentadiene)]-η^5-cyclopentadienylcobalt (Vg, Vf)

Both isomers of the benzoyl complex were quantitatively reduced to the respective alcohols using the following procedure.

The benzoyl complex (Vd or Ve) was dissolved in 40 ml of methanol in a 50-ml three-neck flask, and the resulting solution was cooled by ice-water bath. Then sodium borohydride (3 eqv.) was added, and the reaction mixture was stirred for 30 min at 0^oC and an additional one hour at room temperature. At the end of this time the reaction mixture was added to Et_2O-H_2O in a separatory funnel. The ether layer was collected and washed four times with 70 ml of water. It was dried with anhydrous sodium sulfate and then filtered. The solvent was removed and the desired complex was obtained as a dark-red oil. A small amount of hydrocarbon was also obtained; however, it was removed by chromatography using silica gel and elution with pentane; 3-hydroxybenzyl complex Vf: IR (CS_2): 2028(vs), 1955(vs, broad), and 1920(sh) cm^{-1}; High resolution MS: 421.9627 (ca. 421.9651); MS: 422(12.2) (M^+), 394(23.4) (M^+-CO), 366(34.7) (M^+-2CO), 339(13.5) (MH^+-3CO), 338(80.5) (M^+-3CO), 320(42.1)(M^+-3CO, H_2O), 294(13.3) (M^+-3CO, H_2O, C_2H_2), 266 (33.3) (M^+ -3CO, OH, Fe), 265(100) (M^+-3CO, H_2O, Fe), 175(10.5) ($C_pCoC_4H_3^+$), 150 (23.2) ($C_pCoC_2H_2^+$), 141(5.9) ($C_2H_2CoFe^+$), 124(53.1) (C_pCo^+), and 115 (5.1) ($CoFe^+$); 2-hydroxybenzyl complex Vg: IR(CS_2): 2030(vs), and 1957(vs) cm^{-1}; High resolution MS: 421.9675(ca. 421.9651); MS: similar pattern to that for the 3-hydroxybenzyl complex Vf was observed except the fragment 189(7.9) ($C_pCoC_p^+$) was also observed.

BIBLIOGRAPHY

1. Banks, R. L., Bailey, G. C. Ind. Eng. Chem. Prod. Res. Develop. 1963, 3, 170.

2. Bradshow, C. P. C., Howman, E. J., Turner, L. J. Catalys. 1967, 7, 269.

3. Mol, J. C., Moulijn, J. A., Boelhouwer, C. J. C. S. Chem. Commun. 1968, 633.

4. Grubbs, R. H., Brunck, T. K. J. Amer. Chem. Soc. 1972, 94, 2538.

5. Haines, R. J., Leigh, G. J. Chem. Soc. Rev. 1975, 4, 155.

6. Pennella, F., Banks, R. L., Bailey, G. C. J. C. S. Chem. Commun. 1968, 1548.

7. Moulijn, J. A., Reitsma, H. J., Boelhouwer, C. J. Catalys. 1972, 25, 434.

8. Greco, A., Pirinoli, F., Dallasta, F. J. Organometal. Chem. 1973, 60, 115.

9. Davis, B. L., Barnett, B. L., Amiet, R. G., Mark, W., McKennis, J. S., Pettit, R. J. Amer. Chem. Soc. 1974, 96, 7108.

10. Fritch, J. R., Vollhardt, K. P. C. Angew. Chem. Int. Ed. Engl. 1979, 18, 409.

11. Victor, R., Ben-Shoshan, R. J. C. S. Chem. Commun. 1971, 1241.

12. Dodge, R. P., Mills, O. S., Schomaker, V. Proc. Chem. Soc. 1963, 380.

13. Reppe, W., Vetter, Ann. Chem. 1953, 582, 133.

14. Hock, A. A., Mills, O. S. Acta Cryst. 1961, 14, 139.

15. Hubel, W., Braye, E. H. J. Inorg. Nuclear. Chem. 1959, 10, 250.

16. Chin, H. B., Bau, R. J. Amer. Chem. Soc. 1973, 95, 5068.

17. King, R. B., Haidue, I., Eavenson, C. W. J. Amer. Chem. Soc. 1973, 95, 2508.

18. Dickson, R. S., Kirsch, H. P. Aust. J. Chem. 1974, 27, 61.

19. Bennett, M. A., Johnson, R. N., Turney, T. W. Inorg. Chem. 1976, 15, 107.

20. Veldman, M. E. E., Van Der Wal, H. R., Veenstra, S. J., De Liefde Meijer, H. J. J. Organometal. Chem. 1980, 197, 59.

21. Dettlaf, G., Weiss, E. J. Organometal. Chem. 1976, 108, 213.

22. Yamazaki, H., Yasufuku, K., Wakatsuki, Y., Symposium on Organometallic Chemistry, Tokyo, Japan, 1980.

23. Bruce, R., Moseley, K., Maitlis, P. M. Can. J. Chem. 1967, 45, 2011.

24. Epstein, E. F., Dahl, L. F. J. Amer. Chem. Soc. 1970, 92. 502.

25. Rosenblum, M., North, B. J. Amer. Chem. Soc. 1968, 90, 1060.
Rosenblum, M., North, B., Wells, D., Giering, W. P. J. Amer. Chem. Soc. 1972, 94, 1239.

26. Victor, R., Ben-Shoshan, R. J. C. S. Chem. Commun. 1974, 93.

27. Davidson, J. L. J. C. S. Chem. Commun. 1980, 749.

28. Bunder, W., Wiess, E. J. Organometal. Chem. 1975, 92, 65.

29. Riley, P. E., Davis, R. E. J. Organometal. Chem. 1978, 152, 209.

30. Todd, L. J., Hickey, J. P., Wilkinson, J. R., Huffman, J. C., Folding, K. J. Organometal. Chem. 1976, 112, 167.

31. Emerson, G. F., Watts, L., Pettit, R. J. Amer. Chem. Soc. 1965, 87, 131.

32. Fitzpatrick, J. D. Diss. Abst. Int. 1966, 27B, 405-B.

VITA2

Parviz Radnia

Candidate for the Degree of

Doctor of Philosophy

Thesis: STUDY IN ORGANOMETALLIC TRANSITION METAL SILICON CHEMISTRY
I. THE QUEST FOR A CATIONIC η^3-SILAPROPENYL METAL COMPLEX PREPARATION OF VINYLSILANE TRANSITION METAL COMPLEXES.
II. INSERTION OF TRANSITION METAL SPECIES INTO SUBSTITUTED (CYCLOBUTADIENE) TRICARBONYLIRON COMPLEXES.

Major Field: Chemistry

Biographical:

Personal Data: Born in Tehran, Iran, August 2, 1953, the son of Mr. Asghar Radnia and Mrs. Ashraf Daruyan.

Education: Graduated from Kamal High School, Tehran, Iran in 1971; obtained Bachelor of Science in Chemistry from Pars College, Tehran, Iran, in 1976; completed the requirements for Doctor of Philosophy degree in Chemistry at Oklahoma State University, Stillwater, Oklahoma, USA, in July, 1981.

Professional Experience: Teaching Assistant, Chemistry Department, Pars College, Tehran, Iran, from February 1975 to August 1975. Graduate Teaching Assistant, Chemistry Department, Oklahoma State University from January 1977 to January 1981.