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NAME OF AUTHOR / NOM DE L'AUTEUR

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TITLE OF THESIS / TITRE DE LA THÈSE

Organosilyl (π -cyclopentadienyl) dicarbonyl iron and Related Compounds: Synthesis and Spectroscopic Properties

UNIVERSITY / UNIVERSITÉ

University of Alberta

DEGREE FOR WHICH THESIS WAS PRESENTED

GRADE POUR LEQUEL CETTE THÈSE FUT PRÉSENTÉE

Ph.D.

YEAR THIS DEGREE CONFERRED / ANNÉE D'OBTENTION DE CE DEGRÉ

1974

NAME OF SUPERVISOR / NOM DU DIRECTEUR DE THÈSE

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ORGANOSILYL(π -CYCLOPENTADIENYL)DICARBONYLIRON
AND RELATED COMPOUNDS: SYNTHESIS AND
SPECTROSCOPIC PROPERTIES

BY ERIC WOOD

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

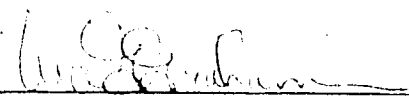
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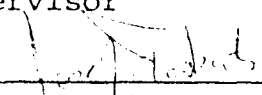
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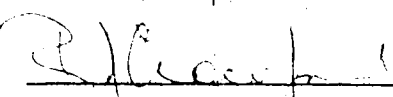
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled ORGANOSILYL(η -CYCLO-PENTADIENYL)DICARBONYLIRON AND RELATED COMPOUNDS: SYNTHESIS AND SPECTROSCOPIC PROPERTIES submitted by ERIC WOOD in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.




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ABSTRACT

The preparation of an extensive series of organosilyl(π -cyclopentadienyl)dicarbonyliron compounds by various reaction pathways is described. Of particular interest were compounds of formula $\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ ($\text{X} \neq \text{R}$), whose solution infrared spectra in the carbonyl region showed the presence of two rotamers and enabled their relative proportions to be determined. Groups X and R were varied in a systematic manner to determine how rotamer populations were affected. Also, related iron-carbon, iron-tin, ruthenium-silicon, and ruthenium-tin compounds were prepared and investigated. The nuclear magnetic resonance results for these compounds were consistent with a low barrier to rotation about the metal-Group IV element bond. It is suggested that the deciding factor controlling which rotamer is favored is an attractive interaction between the π -cyclopentadienyl moiety and substituents X or R. Structural evidence supports this hypothesis.

Reaction of selected organosilyl(π -cyclopentadienyl)dicarbonyliron compounds with PMe_2Ph yielded mono- and bisphosphine substituted complexes. The bisphosphine compounds were of interest since the phosphorus-methyl resonance showed temperature dependent proton magnetic resonance behavior in some cases.

The preparation of hydridobisorganosilyl(π -cyclopentadienyl)monocarbonyliron complexes by the oxidative elimination reaction involving $\text{CpFe}(\text{CO})_2\text{SiR}_3$ and HSiR_3 was investigated with various silanes, and the compounds were studied spectroscopically. In addition, the kinetics of the reductive elimination reaction involving $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ with PMe_2Ph was studied, and activation parameters were derived.

ACKNOWLEDGEMENTS

The author extends deep gratitude to Dr. W. A. G. Graham for his patient and able assistance throughout, and for providing an open arena of discussion among the members of the group, past and present, whose suggestions aided immensely in the development and enlargement of facets of the current work. In particular, thanks are extended to R. P. Stewart, Jr., for assistance with force constant work and to A. C. Sarapu for assistance in computational work.

The technical staff of the University of Alberta Chemistry department are acknowledged for their professional competence in running nuclear magnetic resonance spectra, mass spectra, and chemical analysis.

Special thanks to R. K. Pomeroy, for proofreading.

Finally, the cheerful enthusiasm and encouragement of Eunice Elizabeth should be appreciated by all.

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CHAPTER I

INTRODUCTION

The chemistry of Group IVb to transition metal complexes has become well established over the past ten years. General reviews on this subject have discussed synthesis and characteristics of these compounds.^{1,2,3} Two more recent reviews are concerned solely with silicon transition metal compounds^{4,5} and these coupled with the Ph.D. work of Jetz⁶ have served as an invaluable reference source to synthetic aspects of organosilyl-(π -cyclopentadienyl)dicarbonyliron complexes.

In this introduction an attempt to review comprehensively the field of Group IVb to transition metal complexes would be of little use in view of the above; however, an attempt to convey some of the interests in this area of organometallic chemistry will be made. Since in the present work Group IVb = silicon, a more detailed discussion on silicon transition metal complexes will be presented.

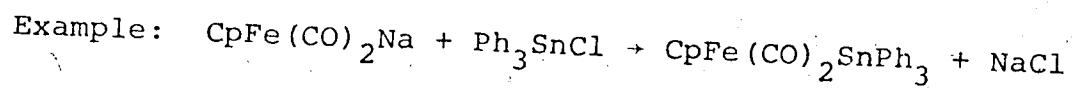
A. Transition Metal - Group IVb Complexes

Transition metal complexes of formula $R_3M'-ML_n$ ^a ($M' = \text{Si, Ge, Sn, Pb}$; $M = \text{transition metal}$) are known for all the Group IVb elements. The environment about M' is the expected tetrahedral configuration. Structural^{7,8,9} and infrared^{10,11,12} evidence has been interpreted as indicating (d+d) π -bonding between M' and M .

i) Preparative Methods

There are six principal methods of synthesizing $R_3M'-ML_n$ compounds. No single method is completely general, but each suits a particular need. These will now be presented along with an example to illustrate the method.

a. Metathetical Reactions with Transition Metal Anions



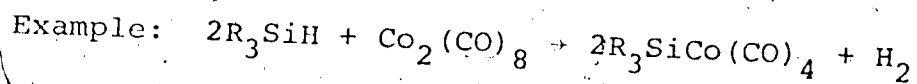
This is perhaps the most widely applied method of forming a transition metal to Group IVb element bond. This method also allows one to place more than one tran-

^aThroughout this thesis R_3M' will be used to denote a general set of substituents attached to the Group IVb element. Also, L_n represents a general set of n ligands on the transition metal. Cyclopentadienyl anion will be abbreviated Cp.

sition metal group upon the Group IVb atom; however, such complexes have not been obtained for silicon.

Normally one employs THF as solvent in this reaction; however, halosilanes react in an anomalous manner¹³ unlike the other Group IVb compounds.¹⁴ Desired silyl complexes may be synthesized by carrying the reaction out in the absence of solvent or by using ether as solvent. Further discussion concerning the anomalous reaction of halosilanes with transition metal anions in THF will be presented in Chapter II.

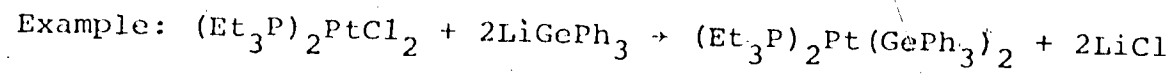
b. Cleavage of Metal-Metal Bonds by Group IVb Hydrides



The above method represents a clean and efficient synthetic route to $R_3M'-ML_n$ compounds. Unfortunately the commercial unavailability of Group IVb hydrides severely limits the generality of the method. However, hydrides of silicon are readily available; therefore this is a particularly useful synthetic route to silicon transition metal complexes.

Chalk and Harrod¹⁵ found that $Co_2(CO)_8$ and R_3SiH reacted rapidly at room temperature. This contrasts with the elevated temperatures required for the reaction of silanes with $M_2(CO)_{10}$ ($M = Mn, Re$)¹¹ and $[CpFe(CO)_2]_2$.⁶ Silanes also react photolytically with $CpRh(CO)_2$ ¹⁶ and $Re_2(CO)_{10}$.¹⁷

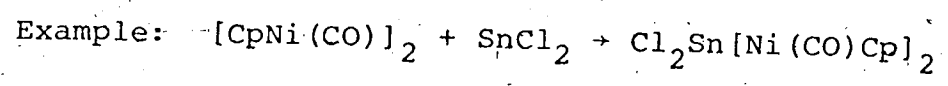
c. Reaction of Transition Metal Halides with Alkali Derivatives of Group IVb Elements



Method (c) is limited by the availability of the Group IVb derivatives³ and also by the reactivity of the solvents in which they sometimes must be prepared. A further complication arises due to a competing side reaction involving halogen - metal exchange.¹⁸

Mercury derivatives of formula $Hg(M'R_3)_2$ have also been reacted with halo-transition metal complexes to afford metal-metal bonded compounds.^{18,19} The compound $Hg(SiMe_3)_2$ was utilized for the preparation of the elusive complex, $(Me_3Si)_2Fe(CO)_4$.²⁰ Again, the limited availability of $Hg(M'R_3)_2$ compounds is a problem.

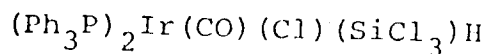
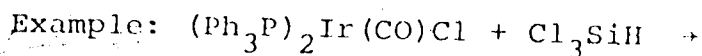
d. Insertion of Divalent Group IVb Halides into Metal-Metal Bonds



This reaction is limited by the availability of the divalent Group IVb halides under standard laboratory conditions. This eliminates silicon and leaves GeI_2 , $GeBr_2$ and the divalent halides of tin and lead. Dioxane complexed $GeCl_2$ has also been used to insert into the iron-methyl bond of $CpFe(CO)_2Me$.²¹ Insertion of tin(II) halides into transition metal-alkyl bonds also

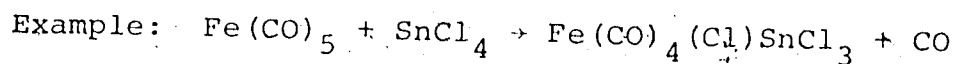
has been applied.²²

e. Oxidative Addition to a Transition Metal Complex



This method is quite restricted in its scope since the transition metal is required to increase its oxidation and coordination number by two. Square planar d^8 complexes are the most common compounds which undergo this reversible reaction. A useful account of oxidative addition reactions has appeared in the literature.²³

f. Oxidative Elimination Reactions



Method (f) differs from (e) in that a neutral ligand such as CO is expelled from the coordination sphere of the transition metal.²⁴ This sometimes results in complexes for which the transition metal possesses an unusual coordination number.²⁵ It also allows one to introduce two univalent ligands onto a transition metal complex outside of the limited scope of the oxidative addition reaction.²⁶

Of the six methods just discussed for the formation of $\text{R}_3\text{M}'\text{-ML}_n$ compounds, the first two were applied in the present work to prepare $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds.

Also, the latter method was employed in the synthesis of $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ complexes. These reactions will be fully discussed in Chapter II.

ii) Bonding Considerations of $\text{R}_3\text{M}'\text{-ML}_n$ Compounds

Organotransition metal complexes usually conform to an empirical principle first devised for classical transition metal carbonyl complexes known as the effective atomic number (EAN) rule. This rule implies that low oxidation state organotransition metal compounds usually will possess a valence shell of 18 electrons. Presumably this represents a configurationally stable situation in analogy with the closed octet of first row elements. That this is the case for most organometallic transition metal compounds isolable under normal circumstances is very useful in elucidating the structures of many of these complexes.

The procedure which is followed in utilizing the EAN rule involves determination of the formal oxidation state of the metal which allows one to determine the number of electrons within the valence shell. To this number is added the electrons donated by the ligands to the metal, the total amounting to 18. This procedure together with examples and exceptions has been discussed.²⁷

In the case of $\text{R}_3\text{M}'\text{-ML}_n$ complexes, $\text{R}_3\text{M}'$ is normally a one electron donating ligand. However, a growing

series of compounds are being investigated where the Group IVb element may be considered a two electron donor.^{28,29,30} Recent structural work³¹ and Mossbauer studies³² indicate that the above compounds are best described as possessing an ylide type structure in which the Group IVb element contributes the usual one electron to the metal-metal bond. An authentic stannylene compound apparently has been prepared,³³ wherein the metal-metal bond necessarily involves donation of two electrons from tin. No doubt interests in this area will continue in view of the close similarity with the well established carbene compounds.³⁴

Since all of the Group IVb elements possess low lying vacant d-orbitals, the possibility of back donation of d_{π} electron density exists. Such back donation has been invoked to account for the greater thermal stability of $R_3M'-ML_n$ complexes as compared to analogous R_3C-ML_n compounds. However, the above interpretation is misleading since it neglects low energy degradation pathways open to transition metal alkyls but not to transition metal Group IVb compounds.³⁵

X-ray structures on Group IVb transition metal compounds^{7,8,9,36,37} have been interpreted as indicating either little or no π -bonding or significant π -bonding between the metals. Differing interpretations arise due to the problems of assigning accurate covalent radii

to the metals involved.³⁸ Also, observed metal-metal bond shortening has been suggested to arise from a weak bonding interaction between equatorial groups such as CO with the Group IVb element.³⁹

Another approach to the question of metal-metal π -bonding makes use of carbonyl stretching force constants and trends observed within a series of compounds. Again, varying interpretations have been made by a number of workers.^{10,11,12,40,41} In order to understand how arguments based on force constants are made, it is necessary to consider the bonding between CO and a transition metal.

The transition metal-CO bond consists of two dative orbital overlaps, as follows: the lone pair on carbon donates electron density into an empty metal orbital, thus forming a σ -bond. A filled metal π -orbital then donates electron density into the CO antibonding orbital, providing some degree of double bond character within the metal-carbon bond. Such a bond is described as synergic since the electron density drifts from CO to metal via the σ -bond and from metal to CO via the π -bond. Since the π -bond involves antibonding orbitals on CO, increasing occupation of this molecular orbital will weaken the carbon-oxygen bond. On the other hand, since the lone pair on carbon is somewhat antibonding, a stronger metal-carbon σ -bond

results in a stronger carbon-oxygen bond.⁴² Since the carbon-oxygen bond strength is related to its stretching force constant, variations in force constants should reflect changes in the metal-carbon bond. This in turn will be related to the demand for metal electron density from other ligands such as R_3M' within the complex. However, often the effect that R_3M' exerts upon the transition metal-carbon σ -bond is overlooked when trends within a series are considered.⁴³ Neglect of the above effect results in an overestimation of the π -bonding effect within these compounds. A further source of confusion arises out of differing approximations applied by various workers^{10,11,12,40,41,43} to the solution of the force constant problem for related systems.

iii) The Transition Metal-Silicon Bond

Studies upon the thermal and chemical properties of silicon-transition metal bonds show it to be highly dependent upon the transition metal.⁴⁴ Generally, the silicon-transition metal bond is thermally stable^{45,46,47,48} in comparison to the alkyl-transition metal bond.⁴⁴

Anhydrous hydrogen halides readily cleave the iron-silicon^{47,49} bond but not the cobalt⁴⁸ or manganese⁴⁶ - silicon bonds. In contrast to the above, the iron-silicon bond resists hydrolysis, methanolysis, and attack by

base such as Et_3N .⁴⁷ In each case the cobalt-^{44,48} and manganese⁵⁰-silicon bonds are readily cleaved.

Recent work on the difficult to prepare silicon-M (M = Mo, W) compounds suggests that these complexes are the least chemically stable of the transition metal-silicon compounds.^{51,52} The above results suggest the following rough order of thermal and chemical stability for M-Si; $\text{Fe} - \text{Si} > \text{Mn} - \text{Si} > \text{Co} - \text{Si} > \text{W} - \text{Si} \approx \text{Mo} - \text{Si}$.

The silicon-transition metal bond shows no tendency to undergo insertion of CO or SO_2 ^{44,50} even though these molecules readily insert into transition metal-alkyl bonds. However, an interesting thermal rearrangement of $\text{CpFe}(\text{CO})_2\text{SiMe}_{2-n}\text{Cl}_n(\text{CH}_2\text{Cl})$ to $\text{CpFe}(\text{CO})_2\text{CH}_2\text{SiMe}_{2-n}\text{Cl}_{n+1}$ ($n = 0, 1, 2$) has been observed,⁵³ indicating that the iron-silicon and iron-carbon bond strengths in these compounds are comparable.

B. Organosilyl(π -cyclopentadienyl)dicarbonyliron and Related Compounds

This class of compounds have been studied in the present work and an indication of the interest in these compounds will now be presented.

i) $\text{CpFe}(\text{CO})_2\text{SiR}_3$ Compounds

Interest in these compounds arises from the observation of conformers in the carbonyl infrared spectra of

$\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ compounds. This phenomenon was first observed for the compound $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Me}$ ⁵⁴ whose infrared spectrum showed four strong carbonyl bands. The observation of double the number of carbonyl bands expected was rationalized on the basis that two conformers were present. These conformers arise because rotation about the silicon-iron bond gives rise to two non-equivalent staggered rotamers as shown in Figure I-I. Other types of rotational isomerism have been observed and are exemplified by $\text{CpMo}(\text{CO})_2$ allyl⁵⁵ and $\pi\text{-C}_3\text{H}_4\text{XCo}(\text{CO})_2\text{PY}_3$.⁵⁶

In order to study trends affecting rotamer populations observed by the CO infrared spectra of these compounds, it is necessary to assign the bands to the conformers shown in Figure I-I. A method of assignment has appeared in the literature⁵⁷ and was adopted in this work. After assignment is made, rotamer populations may be determined, assuming that each conformer possesses the same molar extinction coefficient. It is felt that this is a reasonable assumption in view of the nearly identical structure of the molecules. The results of this study will be presented in Chapter IV.

ii) $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ Compounds

Up to the present work, the only known compound of the above formula was the SiCl_3 derivative. This compound

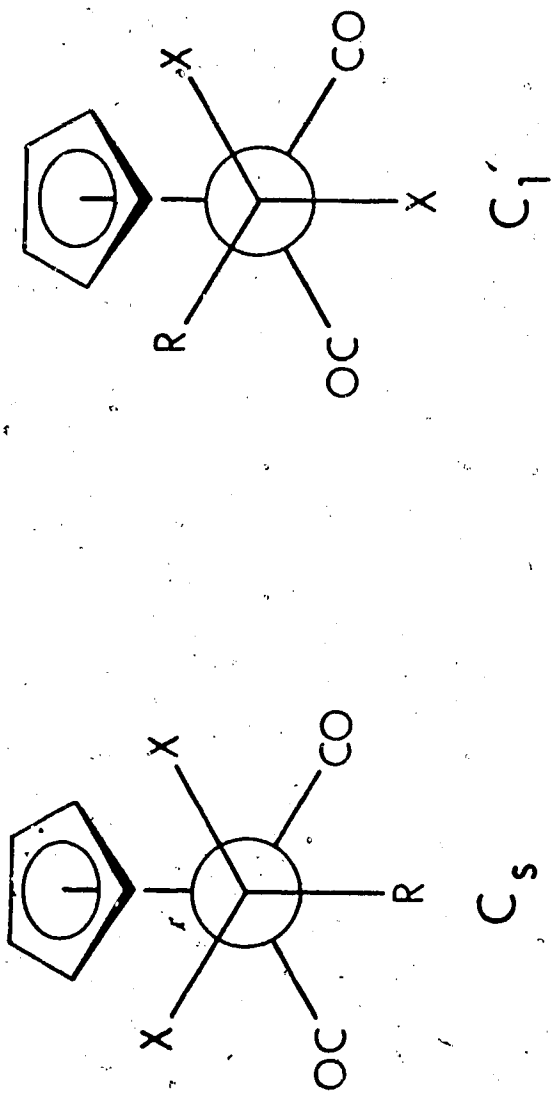


Figure I-I: The two staggered conformers of CpFe(CO)₂SiX₂R viewed down the silicon-iron bond.

possesses strong acidic properties,⁵⁸ an unusual result since organotransition complexes containing a transition metal-hydrogen bond are referred to as hydrido complexes.⁵⁹ (Reference 59 is a useful review on transition metal hydrido compounds.) Other trichlorosilyl transition metal hydrido compounds have been prepared and characterized.^{58,60} Also, the compound $\text{CpMn}(\text{CO})_2\text{H}(\text{SiPh}_3)$ has been reported⁶¹ and the experimental details regarding its preparation are available.⁶²

Further interest in organotransition metal hydrido silyl compounds arises from X-ray results^{62,63,64} where the stereochemical role of the hydrogen atom is important. The above results indicate some degree of transition metal-hydrogen-silicon bridging in these complexes, especially where steric crowding is observed.⁶⁴ Two of the $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ compounds prepared in the present work were investigated by X-ray crystallography⁶⁵ and these results will be discussed in Chapter VI.

Further interest in $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ compounds arose from mass spectra, infrared spectra, and NMR results. These will be discussed in Chapters III, IV, and V respectively.

iii) $\text{CpFe}(\text{CO})_{2-n}(\text{PMe}_2\text{Ph})_n(\text{SiR}_3)_2$ ($n = 1, 2$) Compounds

Compounds of the above general formula have been prepared yielding monocarbonyl derivatives of SiMe_3 and

SnMe_3 with PPh_3 and P(OPh)_3 .⁶⁶ Also, the carbonyl free compounds of SiMe_3 and SnMe_3 with the bidentate phosphine ligands $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ and $\text{cis-Ph}_2\text{PCH=CHPPh}_2$ were prepared.⁶⁶ The above results suggested that bisphosphine derivatives of formula $\text{CpFeL}_2\text{SiR}_3$ ($\text{L} = \text{PMe}_2\text{Ph}$) should be accessible. These compounds would be of interest since an intramolecular rearrangement of a tetrahedral complex through a planar intermediate has been proposed.⁶⁷ NMR results presented in Chapter V on $\text{CpFe(PMePh)}_2\text{SiR}_3$ complexes support the above suggestion.

CHAPTER II
SYNTHETIC ASPECTS

The preparation of compounds of formula $\text{CpFe}(\text{CO})_2\text{SiR}_3$ will now be discussed along with reactions of these complexes. The synthetic methods which have been applied will be recognized to fall into some of the categories presented in Chapter I describing the formation of $\text{R}_3\text{M}'\text{-ML}_n$ compounds.

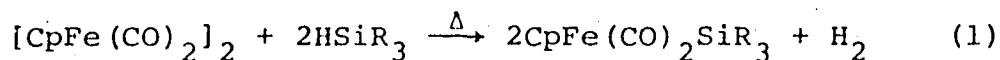
A. Formation of $\text{CpFe}(\text{CO})_2\text{SiR}_3$ Compounds

Complexes of the above general formula are accessible via three reaction pathways in which formation of the iron-silicon bond is accomplished. The first two methods are of general application and have been used in the present work. The third method has been utilized in the preparation of $\text{CpFe}(\text{CO})_2\text{SiH}_3$ ⁶⁸ and is severely limited in its scope as will become evident later.

i) Thermal Reaction: Cleavage of the Iron-Iron Bond by Si-H

Reaction (1) illustrates this preparative method which is analogous to the procedure used by Chalk and Harrod¹⁵ for the synthesis of $\text{Co}(\text{CO})_4\text{SiR}_3$ compounds. In the case of the reaction of $\text{Co}_2(\text{CO})_8$ with HSiR_3 , the reaction proceeds at room temperature. Reaction (1)

on the other hand, requires temperatures of 130°-175°.

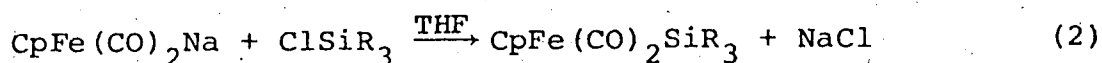


Due to the volatility of most of the silanes employed, reaction (1) is carried out in a Carius tube in the absence of solvent. The time and reaction temperature required are dependent upon the substituents attached to silicon. Generally, it is found that electron withdrawing substituents promote reaction. Thus, Cl_3SiH reacts in 30 minutes at 130° while Me_3SiH requires a reaction time of two days at a temperature of 165°.

Jetz⁶ has employed reaction (1) in the preparation of $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds where $\text{SiR}_3 = \text{SiCl}_3, \text{SiCl}_2\text{Me}, \text{SiMe}_2\text{Cl}, \text{SiMe}_3, \text{SiPh}_3, \text{SiPh}_2\text{H}, \text{SiH}_2\text{Ph}, \text{SiCl}_2\text{Ph}, \text{Si}(\text{OEt})_2\text{Me}$ and $\text{SiPh}(\text{Me})\text{Cl}$. In the present work a wide variety of compounds have been prepared according to reaction (1), and it appears the only limitation on the compounds accessible would be the availability of a particular silane and the thermal stability of the silicon-substituent bond. For example, the silicon-sulfur or silicon-nitrogen⁶⁹ bonds will not survive the necessary reaction temperatures. Therefore, compounds with these linkages are not accessible in this manner.

ii). Metathetical Reaction: Reaction of $\text{CpFe}(\text{CO})_2\text{Na}$ with Si-Cl

Of all the metal carbonyl anions, $[\text{CpFe}(\text{CO})_2]^-$ is the strongest nucleophile,⁷⁰ and it is the only one which reacts normally in THF with a halosilane according to reaction (2).



Reaction (2) has been applied to the synthesis of $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds where $\text{SiR}_3 = \text{SiCl}_{3-x}\text{Ph}_x$ ($x = 0, 1, 2$),⁷¹ $\text{Me}_3\text{Si}(\text{SiMe}_2)_n$ ($n = 1, 2, 3$),⁷² SiMe_2H ,⁷² $\text{SiPh}_{3-x}\text{Me}_x$ ($x = 0, 1, 2$),⁷³ $\text{SiPh}_2(\text{CH}=\text{CH}_2)$,⁷³ $\text{SiPh}(\text{Me})(1-\text{Np})$,⁷³ and $\text{SiCH}_2\text{CH}_2\text{CH}_2(\text{Me})$.⁷⁴ The basic utility of reaction (2) is in obtaining compounds in which a silicon-hydrogen bond is preserved as in $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{H}$.⁷² Where the thermal method (Ai) is feasible, it should be applied because of higher yields obtained for comparable silanes.

In view of the unique behavior of the $\text{CpFe}(\text{CO})_2^-$ anion, it is of interest to inquire why other transition metal carbonyl anions do not react according to reaction (2).¹⁴

The following facts are known:

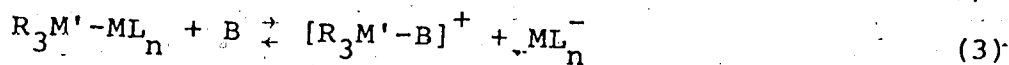
(a) Metal carbonyl anions such as $\text{Mn}(\text{CO})_5^-$, $\text{Co}(\text{CO})_4^-$, $\text{CpFe}(\text{CO})_2^-$, etc. all react in THF with $\text{XM}'\text{R}_3$ ($\text{X} = \text{halogen}$;

M' = Ge, Sn, Pb; R = alkyl or aryl) to produce normal metal-metal bonded compounds.¹⁴

(b) Metal carbonyl anions other than $\text{CpFe}(\text{CO})_2^-$ do not react with halosilanes in THF to form the expected metal-silicon bonded compounds.^{13,75,76}

(c) Metal carbonyl anions will react with halosilanes in the absence of THF to produce the expected compound.^{50,76}

(d) Evidence for a reversible dissociation of the type given in reaction (3) is accumulating.^{77,78}



Curtis⁷⁵ has suggested that the anomolous reaction of halosilanes with transition metal carbonyl anions likely involves nucleophilic attack of a carbonyl oxygen upon the halosilane. This would explain the observed formation of disiloxanes and highly unstable carbonyl compounds later shown to be polynuclear metal carbonyl anions.¹³ However, Curtis' suggestion does not account for the fact that normal reactions occur in the absence of THF.

A possibility not considered by Curtis, but which seems reasonable in view of point (c) above, is that a silicon-transition metal bond is formed which then dissociates according to reaction (3). The $[\text{R}_3\text{Si}+\text{THF}]^+$ cation formed may then attack a nucleophilic centre such as carbonyl oxygen or THF oxygen. This would drive

reaction (3) completely to the right and ultimately result in the production of the observed anomalous products.

This would explain the observed decomposition products formed when $\text{Me}_3\text{SiCo}(\text{CO})_4$ is exposed to THF.⁷⁹ A recent communication also presents convincing evidence for electrophilic attack at carbonyl oxygen on the basis of products obtained when $\text{Co}_2(\text{CO})_8$ or $\text{NaCo}(\text{CO})_4$ react with $\text{Me}_{4-x}\text{SiCl}_x$ ($x = 4, 3$) in ethereal solvent.⁸⁰

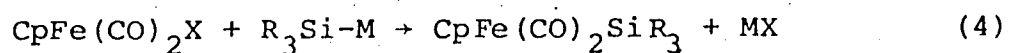
The above evidence and the four points presented seem more consistent with the following interpretation for the anomalous reactions of halosilanes with transition metal carbonyl anions. The weak nucleophile THF could displace SiR_3^+ from R_3SiML_n in the manner described under point (d). Normally this would be a reversible displacement which explains point (a). However, the intermediate $[\text{R}_3\text{Si}\cdots\text{THF}]^+$ could be highly reactive, and would then attack the carbonyl oxygen or the THF oxygen resulting in the production of either disiloxanes, cis- and trans- $\text{R}_3\text{SiOCH=CHEt}$, or metal carbonyl compounds such as anions or neutral species containing the " R_3SiOC " moiety.^{79, 80}

In connection with the above, it was found that $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Ph}$ survived refluxing in THF for one day in overall 75% yield. Thus, the normal reaction of $\text{CpFe}(\text{CO})_2^-$ with halosilanes is "normal" in the sense that the iron-silicon bond in these complexes is highly

resistant to THF attack. The latter would result from the fact that equilibrium (3) lies far to the left when ML_n^- is $CpFe(CO)_2^-$.

iii) Reaction of $CpFe(CO)_2$ Halides with R_3SiLi

It was pointed out earlier that this method is of limited utility, and it is only included for completeness. Reaction (4) illustrates the method which to date has only been applied to the formation of $CpFe(CO)_2SiH_3$.⁶⁸



(X = halogen, M = Li, K)

The method is analogous to reactions carried out in platinum chemistry^{81,82} and is severely limited by the availability of R_3Si-M .³ This obvious limitation and the wide scope of preparations offered by Methods (Ai) and (Aii) render this route of little interest for the formation of $CpFe(CO)_2SiR_3$ compounds.

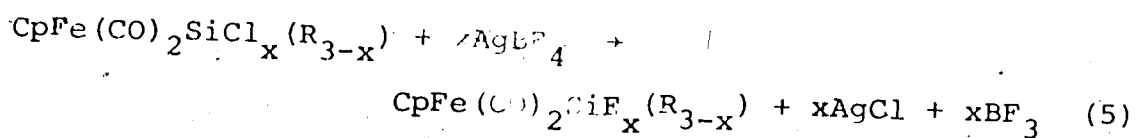
B. Reactions of $CpFe(CO)_2SiR_3$ at Silicon

In Chapter I an indication of the chemical stability of the transition metal-silicon bond was presented. The results suggested that the iron-silicon linkage was chemically the most inert. This allows one to perform reactions at silicon, exploiting the reactivity of the

silicon-chlorine bond. Thus, the following two synthetic methods have been applied to the synthesis of $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds.

i) Formation of $\text{CpFe}(\text{CO})_2\text{SiF}_x(\text{R}_{3-x})$ ($x = 3, 2, 1$)

The reaction of chlorosilanes with AgBF_4 has been described by Marks and Yam.⁸³ Reaction (5) illustrates



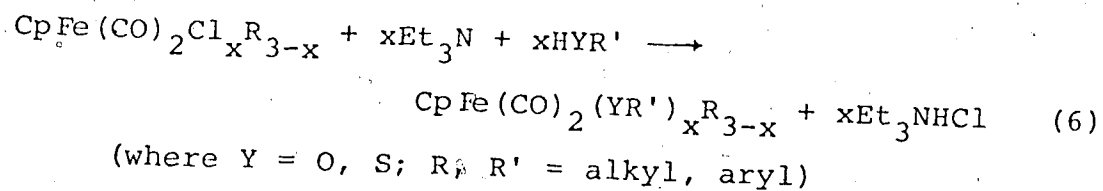
this preparative method. The reaction proceeds rapidly in polar solvents such as acetonitrile or acetone; however, in the present work it was found that significantly higher yields could be obtained by employing benzene as solvent. In this case, a reaction time of two hours is required with vigorous stirring.

The limited availability of fluorosilanes makes this method an attractive route to fluorosilyl-iron carbonyl compounds. Also, the one fluorosilane which is available, HSiF_3 , does not react cleanly with $[\text{CpFe}(\text{CO})_2]_2$ by the thermal method. Large amounts of ferrocene⁸⁴ are formed making work up difficult since $\text{CpFe}(\text{CO})_2\text{SiF}_3$ is very volatile, like ferrocene. To avoid this problem, a clean synthesis of $\text{CpFe}(\text{CO})_2\text{SiF}_3$ can be accomplished by reaction of AgBF_4 with $\text{CpFe}(\text{CO})_2\text{SiCl}_3$.⁸³

ii) Formation of $\text{CpFe}(\text{CO})_2\text{Si}(\text{YR})_x(\text{R}')_{3-x}$ ($\text{Y} = \text{O, S; } x = 1, 2$)

The synthesis of silicon alkoxy and silicon thiol compounds is well established in main group silicon chemistry.⁸⁵ However, analogous transition metal-silicon compounds have not been thoroughly investigated. A recent article has appeared⁸⁶ dealing with the reaction of $\text{CpFe}(\text{CO})_2\text{SiCl}_3$ with alcoholates.

The method given by reaction (6) was applied in the present work and it is considered that this is a superior synthetic route to these compounds. This method has the advantage of the milder chemical conditions, since excess Et_3N will not attack the iron-silicon bond, whereas excess alcoholate readily cleaves this linkage.⁸⁶



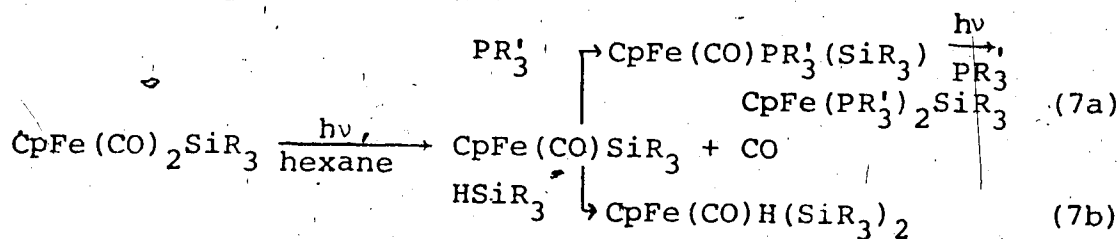
Thus, an excess of Et_3N can be used and the reaction can be carried out in the alcohol or thiol, acting as solvent and reactant. Where the alcohol or thiol are not volatile, the reaction can be conveniently carried out in ether with stoichiometric amounts of RYH ($\text{Y} = \text{O, S}$).

Reaction(6) proceeds rapidly for primary and secondary alkyl groups and requires heat for tertiary alkyl

and for aryl groups. Thiols react more slowly than alcohols, *t*-butyl mercaptan reacting incompletely even after ten days. The thermal instability of the silicon-sulfur bond dictates that reaction temperatures involving thiols must be kept below 100°.

C. Carbonyl Substitution in $\text{CpFe}(\text{CO})_2\text{SiR}_3$

Two examples of reactions in which silicon-chlorine^o bonds have been utilized in the synthesis of further $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds have just been discussed. It is also possible to prepare further organosilane iron compounds by replacement of one or both carbonyl groups. Such a substitution is best accomplished through ultraviolet irradiation which produces a coordinatively unsaturated intermediate by expulsion of a carbonyl group. The intermediate may then add a two-electron donating ligand such as a phosphine or two one-electron donating fragments of a neutral molecule such as H-SiR_3 . This is indicated by reactions (7).



i) Substitution of Carbonyl by Phosphine

This is a well established reaction of transition

metal carbonyl chemistry, and has already been applied to some $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds.^{66,74,87} Reaction (7a) illustrates the stoichiometry, which can involve the expulsion of both carbonyls depending upon the amount of phosphine involved and also upon the phosphine. Only monosubstitution is accomplished if $\text{PR}'_3 = \text{PPh}_3$, even if a large excess of phosphine is employed. For other phosphines, some degree of disubstitution is observed, but often a mixture of mono- and disubstitution results, independent of the stoichiometry of reaction (7a).

Separation of such a product mixture is best accomplished by column chromatography. This method cannot be applied when silicon-halogen bonds are present. The reactivity of these bonds results in decomposition of the desired compounds upon the column. Purification must be accomplished by solvent extraction and recrystallization, a sometimes difficult task with excess phosphine present.

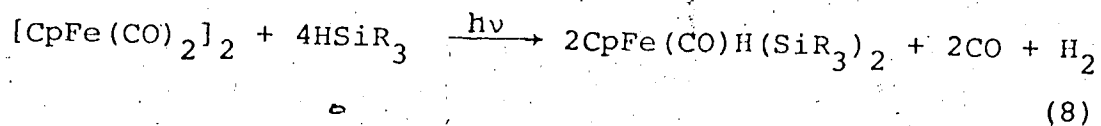
ii) Substitution of Carbonyl by H-SiR_3

The replacement of a carbonyl by H-SiR_3 represents a well known reaction of organotransition metal chemistry, namely oxidative elimination.²⁵ Such a replacement has only been observed for the silanes HSiCl_3 ⁶⁰ and HSiPh_3 .²⁶ It was found in this work that

various silanes would react in the manner given by equation (7b).

The compound $\text{CpFe}(\text{CO})\text{H}(\text{SiCl}_3)_2$ was found to possess strong acidic properties.⁵⁸ Also, this hydrido complex is formed during the thermal reaction of HSiCl_3 with $[\text{CpFe}(\text{CO})_2]_2$.⁵⁸ The trichlorosilyl derivative, however, is apparently unique, since none of the $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ compounds synthesized in the present work showed acidic properties,^a nor were these compounds formed in thermal reactions between $[\text{CpFe}(\text{CO})_2]_2$ and HSiR_3 .

A more convenient preparation of these hydrido compounds is illustrated by reaction (8). This reaction

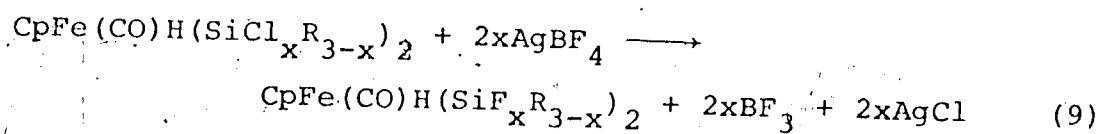


is carried out in a sealed quartz Carius tube in the absence of solvent. Reaction is usually complete in five days; however, HSiPh_3 failed to produce the desired product. This method seems to be more general than that given by reaction (7b) although silanes with electron releasing substituents are slow to react.

It is possible to substitute fluorine for chlorine in the chlorosilyl compounds obtained above, by the action

^aFor example, $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_{3-x}\text{Ph}_x)_2$ ($x = 1, 2$) compounds would not react with an excess of Et_3N in *n*-hexane.

of AgBF_4 . In this case benzene is preferred as solvent, since other more polar solvents result in complete decomposition. This is not surprising since one would expect the iron-hydrogen bond to be susceptible to attack by AgBF_4 . Fortunately, the low solubility of AgBF_4 in benzene probably suppresses this degradation pathway allowing fluorination to occur at silicon. The method is otherwise identical with that given under Section (Bi) and the stoichiometry is given by reaction (9).

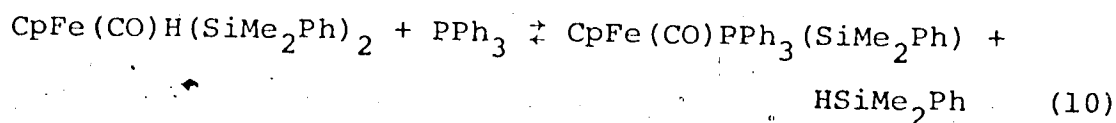


D. Reductive Elimination of $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ with PPh_3

It was found in the present work that $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ compounds would react with phosphines to produce phosphine compounds of the type already described. The reaction thus results in the liberation of HSiR_3 and therefore falls into a reaction class known as reductive elimination.⁶¹ The compound $\text{CpMn}(\text{CO})_2\text{H}(\text{SiPh}_3)$ was also observed to react in this manner and this reaction was studied kinetically.⁶¹ By following the kinetics of the reaction of $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ with excess PPh_3 in the carbonyl infrared region,⁸⁸ a similar study was undertaken. The complete details of this study are presented under the

experimental section of this chapter.

In order to study the kinetics of reaction (10), it was necessary to verify that phosphine concentration would not affect the pseudo-first order rate constant (PPh_3 being in excess in the reaction). It was found that a 5 - 25 fold excess of PPh_3 did not affect k_{obs}



at $69.9^\circ \pm 0.2^\circ$ for the above reaction. The results obtained are presented in Table II-1.

Table II-2 presents the observed rate constants as a function of reaction temperature. A typical plot for an experimental run is given in Figure II-II. Good first order correlation is obtained for the disappearance of reactant well past one half life. However, the product is observed to appear in a nonlinear fashion. A possible explanation of this may be either decomposition of product or further reaction of product occurring as it is produced. No products other than $\text{CpFe(CO)PPh}_3(\text{SiMe}_2\text{Ph)}$ and HSiMe_2Ph could be identified after the kinetic run was completed. Product data were not utilized in this kinetic study because of this complication.

From the seven rate constants obtained as a function of temperature, the activation parameters were obtained, the

TABLE II-1

k_{obs} as a Function of PPh_3 Concentration at $69.9 \pm 0.2^\circ\text{C}$
for the Reaction of $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ with PPh_3

$[\text{PPh}_3]$ mM	Excess of PPh_3 ^a (n-fold)	$10^4 \times k_{\text{obs}}$ sec^{-1}
15	5	1.39
20	6.7	1.34
30	10	1.42
40	13.3	1.42
50 ^b	16.7	1.40
75 ^b	25	1.33

^aThe concentration of $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ was initially 3.0 mM for each kinetic run.

^bA weak absorption at 1955 cm^{-1} begins to appear in the infrared spectrum when $[\text{PPh}_3] \geq 50 \text{ mM}$. This is due to overtones of the phenyl groups in PPh_3 . To avoid this complication, $[\text{PPh}_3]$ was chosen at $\sim 30 \text{ mM}$ for the kinetic work.

TABLE II-2

Measured Rate Constants^a for the Reaction of
 $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ with PPh_3
as a Function of Temperature

Reaction Temp. °C \pm 0.2°	$10^4 \times k_{\text{obs}}$ sec ⁻¹
54.9	0.124 \pm 0.005
59.8	0.310 \pm 0.005
65.1	0.633 \pm 0.006
69.9	1.38 \pm 0.04
74.0	1.85 \pm 0.04
79.7	5.91 \pm 0.07
84.6	8.12 \pm 0.08

^aThe results reported are the average of two
matched runs.

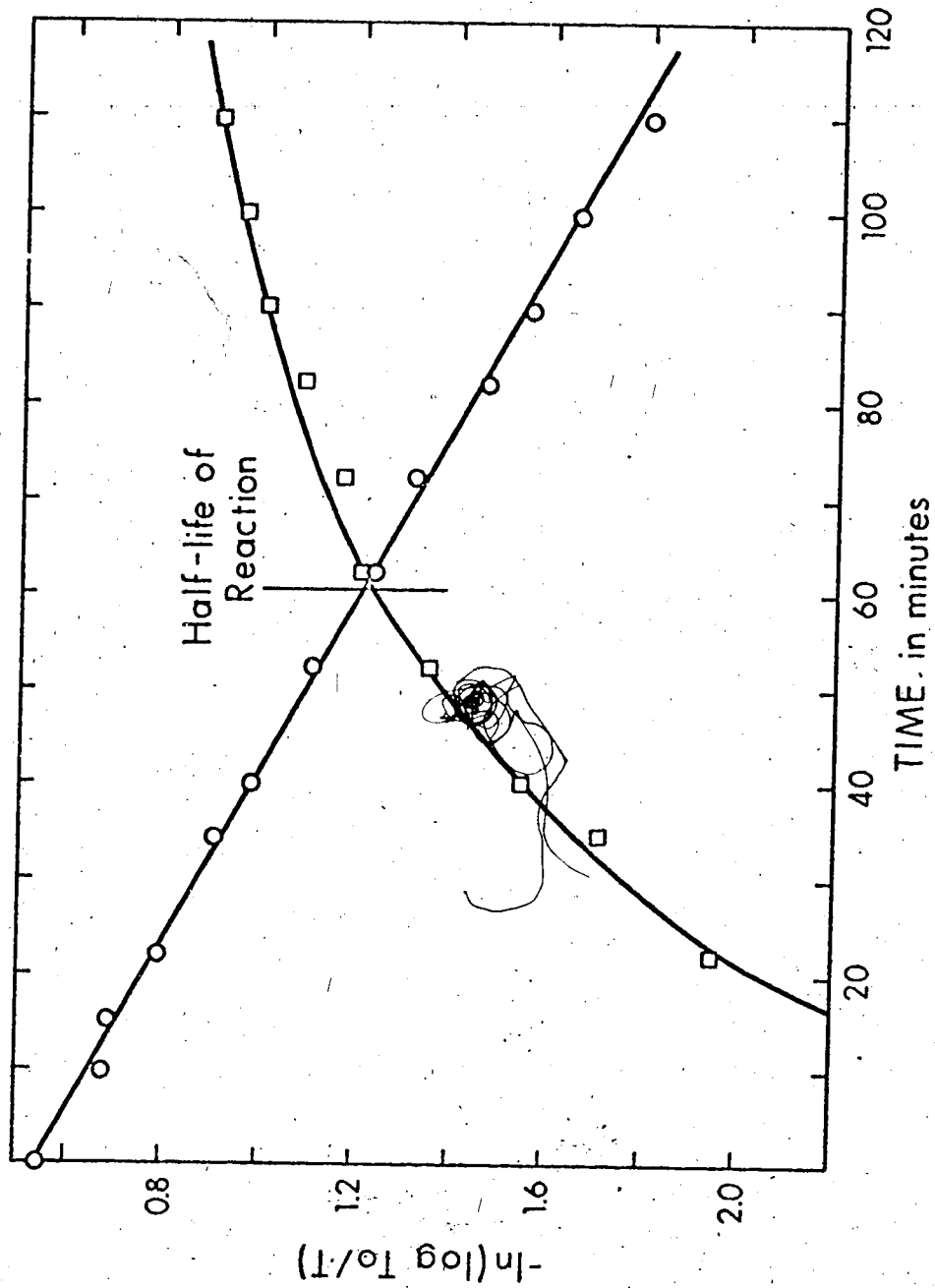


Figure II-II. Observed disappearance and appearance of $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ \odot and $\text{CpFe}(\text{CO})\text{PPh}_3\text{SiMe}_2\text{Ph}$ \square with time. Reaction was monitored by carbonyl infrared as described in the experimental section. This study was carried out at $74.0 \pm 0.2^\circ$.

values being: $\Delta H^\ddagger = 32.4 \pm 1.4$ kcal/mole and $\Delta S^\ddagger = 18 \pm 4$ eu. These results may be compared with those obtained for $\text{CpMn}(\text{CO})_2\text{H}(\text{SiPh}_3)$; ⁶¹ $\Delta H^\ddagger = 29.2 \pm 0.3$ kcal/mole and $\Delta S^\ddagger = 16.3 \pm 1.0$ eu. The observation of a moderately large positive ΔS^\ddagger in each case is strong evidence for a dissociative mechanism.

The close similarity in ΔH^\ddagger indicates that the energy gap between ground and transition states must in each case be similar. This suggests that comparable transition states are involved in these reductive elimination reactions.

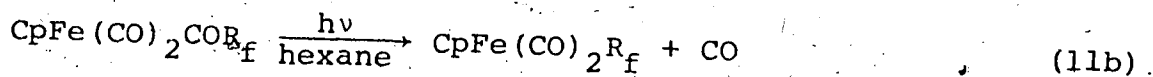
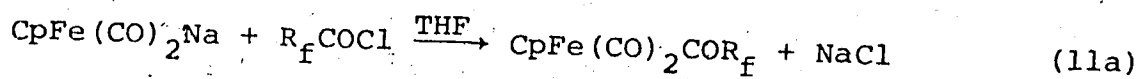
E. Preparation of Compounds Related to $\text{CpFe}(\text{CO})_2\text{SiR}_3$

The compounds $\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ are of interest from the point of view of their carbonyl infrared spectra. They show four strong carbonyl bands which indicates the presence of rotamers in solution. These compounds and this phenomenon will be discussed in Chapter IV. With respect to the study of factors influencing rotamer populations, related compounds such as $\text{CpM}(\text{CO})_2\text{M}'\text{X}_2\text{R}$ ($\text{M} = \text{Fe}, \text{Ru}; \text{M}' = \text{C}, \text{Si}, \text{Sn}$) were prepared. Many of these compounds have been prepared previously but have not been studied in detail from the point of view of their infrared and NMR spectra. These will be elaborated upon in Chapters IV and V. An outline of the

preparation of these compounds is presented here.

i) Compounds of Type $\text{CpFe}(\text{CO})_2\text{R}$ ($\text{R} = \text{C}_2\text{F}_5, \text{C}_3\text{F}_7, \text{CH}_2\text{C}_6\text{F}_5$)

The synthetic route to these compounds is well established⁸⁹ and given by equations (11).



Reaction (11a) is best accomplished by addition of $\text{CpFe}(\text{CO})_2\text{Na}$ solution to an excess of the acyl chloride. The decarbonylation step must be done photolytically, since it does not take place thermally.

The compound $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_5$ is reported in the literature.⁹⁰ It was obtained along with the side product, $\text{CpFe}(\text{CO})_2\text{CH}_2(p\text{-C}_6\text{F}_4\text{Fe}(\text{CO})_2\text{Cp})$ by addition of $\text{C}_6\text{F}_5\text{CH}_2\text{Br}$ to $\text{CpFe}(\text{CO})_2\text{Na}$. In the present work it was found that formation of side product could be suppressed by addition of a solution of the anion to the pentafluorobenzyl halide. In this way, $\text{C}_6\text{F}_5\text{CH}_2\text{Br}$ is always in excess. Thus, the anion will preferentially react with the carbon-bromine bond rather than attack the para-fluoro position.

ii) Compounds of Type $\text{CpFe}(\text{CO})_2\text{SnX}_2\text{R}$

These compounds were available from Dr. J. K. Hoyano who prepared them as part of his Ph.D. work. The method of preparation is described in Chapter 6 of his thesis⁶² and is similar to that employed in this work for the preparation of analogous ruthenium compounds.

iii) Compounds of Type $\text{CpRu}(\text{CO})_2\text{SiX}_2\text{R}$

These compounds are accessible via the thermal reaction method discussed for the $\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ compounds. However, $[\text{CpRu}(\text{CO})_2]_2$ must first be prepared. A reasonably convenient preparation from RuCl_3 is described in the literature.⁹¹ Also, the compound $\text{CpRu}(\text{CO})_2\text{SiCl}_3$ ⁹² has been prepared.

It was found that $[\text{CpRu}(\text{CO})_2]_2$ reacted less cleanly with silanes than does $[\text{CpFe}(\text{CO})_2]_2$. For example, HSiCl_2Me reacts to form a mixture of compounds of formula $\text{CpRu}(\text{CO})_2\text{SiCl}_x\text{Me}_{3-x}$ ($x = 3, 2, 1$). Such a mixture proved to be almost inseparable and details are presented under the experimental section. As a result of this handicap, coupled with the limited amount of $[\text{CpRu}(\text{CO})_2]_2$ available, the studies on the ruthenium system were much more restricted than those on iron.

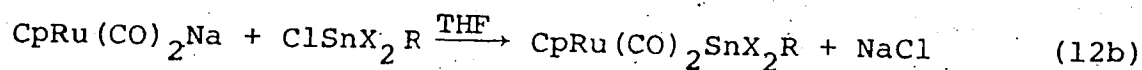
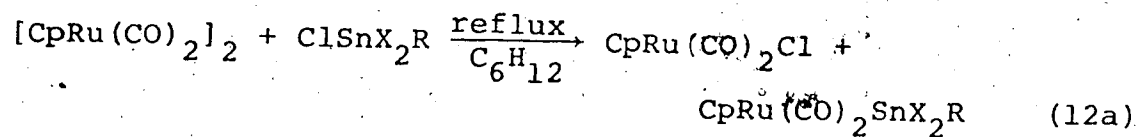
These compounds are less volatile than their iron counterparts and are white when pure. This makes

purification by sublimation or chromatography very difficult. They appear to be more air sensitive than their iron analogs, although the oily nature of the crude reaction products may mean that some reactive impurity is responsible for this.

The reaction of HSiCl_3 with $[\text{CpRu}(\text{CO})_2]_2$ was reported to yield only $\text{CpRu}(\text{CO})_2\text{SiCl}_3$ and no other ruthenium complex.⁹² When a similar reaction was undertaken in this work, small amounts of $\text{CpRu}(\text{CO})\text{H}(\text{SiCl}_3)_2$ were detected in the infrared. This hydrido compound was also prepared in good yield by the photolytic method described in reaction (8). This compound will be discussed more fully in Chapter V since NMR studies show it to be strongly acidic in acetonitrile solution.

iv) Compounds of Type $\text{CpRu}(\text{CO})_2\text{SnX}_2\text{R}$

There are two possible reaction pathways to these compounds. Each has been utilized in the preparation of the iron analogs.⁶² Reactions (12) indicate these pathways.

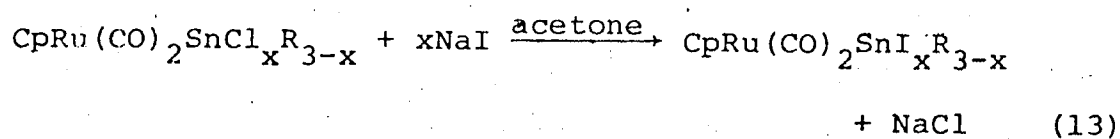


Method (a) was found to result in the production of large amounts of $\text{CpRu}(\text{CO})_2\text{Cl}$ but little of the desired

product. The small quantity of $\text{CpRu}(\text{CO})_2\text{SnX}_2\text{R}$ produced was not separable from $\text{CpRu}(\text{CO})_2\text{Cl}$.

Method (b) was applied in the preparation of the incompletely characterized compounds $\text{CpRu}(\text{CO})_2\text{SnMe}_{3-x}\text{Cl}_x$ ($x = 0, 1$).⁹² This method was used in the present work but because of limitations in the amount of $[\text{CpRu}(\text{CO})_2]_2$ available, only the compound $\text{CpRu}(\text{CO})_2\text{SnI}_2\text{Me}$ was prepared in sufficient quantity to be characterized by analysis. Other ruthenium-tin compounds were prepared, and their infrared carbonyl spectra were recorded and found to be consistent with the electronic influence of the substituents in the tin.

Reaction (13) was applied to the preparation of iodotin compounds from the chloro compounds obtained as described above.



Experimental

All reactions and manipulations were carried out under a nitrogen atmosphere. The compounds prepared in this work were generally air sensitive but could be handled for brief periods in the air. The hydrido compounds tended to be light sensitive, particularly those possessing silicon-fluorine bonds. Yields of new compounds prepared were generally better than 50% unless otherwise indicated.

Solvents were used immediately after being distilled from the following drying agents: *n*-pentane, *n*-hexane, *n*-heptane, and benzene from CaH_2 ; THF from CaH_2 and then from potassium-benzophenone; CH_3CN from Drierite and then from CaH_2 ; decalin from sodium wire onto sodium wire by vacuum distillation at 0.4 - 0.2 mm Hg; anhydrous ether was used as obtained from Mallinckrodt Chemical Works; CH_2Cl_2 was used as obtained from Terochem Laboratories Ltd.

The chemicals used in this work are presented in Table II-3 along with their source. The following were further purified in the indicated manner: $[\text{CpFe}(\text{CO})_2]_2$ by soxhlet extraction with CH_2Cl_2 . The solution was then filtered while hot and a small amount of *n*-heptane added. Slow removal of CH_2Cl_2 on a rotary evaporator results in formation of microcrystals of pure $[\text{CpFe}(\text{CO})_2]_2$. Chlorosilanes were degassed before use to remove HCl. All other chemicals were used as obtained.

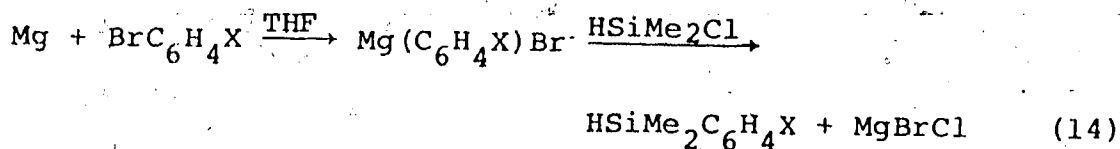
TABLE II-3

Chemicals Used in this Work and their Sources

Compound	Source
$[\text{CpFe}(\text{CO})_2]_2$	Strem Chemicals Inc.
Silanes and Stannanes	Pierce Chemical Company
Pentafluorophenyls	Imperial Smelting Corporation (N.S.C.) Ltd.
Thiols	Aldrich Chemical Company
Fluoro-alcohols and acyls and $\text{BrCH}_2\text{C}_6\text{F}_5$	Pierce Chemical Company
AgBF_4	Ozark-Mahoning Company
Phenol	Matheson, Coleman, and Bell
Iso-propanol and Tert- butanol	Fisher Scientific Company
Magnesium turnings	British Drug Houses Ltd.
$\text{RuCl}_3 \cdot \text{Hydrate}$	Engelhard Industries
Triethylamine	J. T. Baker Chemical Company
Phosphines	Pierce Chemical Company
<i>p</i> -Bromo- <i>N,N'</i> -dimethyl- aniline	Eastman Organic Chemicals
<i>p</i> -Bromo-methoxybenzene	K & K Laboratories, d.
<i>p</i> -Dibromobenzene and <i>p</i> -Bromo and <i>o</i> -Bromotoluene	Aldrich Chemical Company
<i>p</i> -Fluoro-bromobenzene	Pierce Chemical Company
Bromoethane	J. T. Baker Chemical Company

Preparation of Some Silanes not Commercially Available

It was found desirable to prepare some silanes according to the method given by reaction (14). Typically, the Grignard reaction was carried out on a



0.1 mole scale and silane was added to the prepared Grignard over a period of 30 minutes with stirring. The solution was stirred for a further hour and then filtered and THF was distilled off until a viscous liquid remained. The silane was then collected by vacuum distillation and its identity confirmed by NMR. In Table II-4 the details of the vacuum distillation conditions for each silane prepared are presented and in Table II-5 pertinent NMR results are given.

The silanes $\text{HSiMe}_2\text{C}_6\text{F}_5$, $\text{HSi}(\text{C}_6\text{F}_5)_2\text{Me}$, and $\text{HSi}(\text{C}_6\text{F}_5)_2\text{Ph}$ were prepared in an analogous manner using the Grignard $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$, and the appropriate chlorosilane. The compound $\text{HSi}(\text{Et})_2\text{Ph}$ was also prepared by the Grignard route from HSiCl_2Ph and $\text{Mg}(\text{Et})\text{Br}$ with ether in place of THF as solvent. The conditions of vacuum distillation for these silanes are also reported in Table II-4.

The silanes $\text{HSi}(\text{OPh})_2\text{Ph}$, $\text{HSi}(\text{Ot-Bu})_2\text{Me}$, and $\text{HSi}(\text{SPh})_2\text{Me}$ were prepared from the appropriate chloro-

TABLE II-4.

Vacuum Distillation Conditions for Silanes

Prepared in this Work

Silane	Pressure	Temperature
	mm Hg	°C
$\text{HSiMe}_2(p\text{-C}_6\text{H}_4\text{OMe})$	1.5	63 - 68
$\text{HSiMe}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$	2.0	92 - 94
$\text{HSiMe}_2(p\text{-C}_6\text{H}_4\text{F})$	0.5	32 - 35
$\text{HSiMe}_2(p\text{-C}_6\text{H}_4\text{Me})$	1.5	42 - 45
$\text{HSiMe}_2(p\text{-C}_6\text{H}_4\text{SiMe}_2\text{H})^a$	0.05	31 - 34
$\text{HSiMe}_2(o\text{-C}_6\text{H}_4\text{Me})$	1.0	28 - 31
$\text{HSiMe}_2\text{C}_6\text{F}_5$	0.5	31 - 35
$\text{HSi}(\text{C}_6\text{F}_5)_2\text{Me}$	0.5	80 - 87
$\text{HSi}(\text{C}_6\text{F}_5)_2\text{Ph}$	0.02	140 - 145
HSiEt_2Ph	0.5	56 - 60

^aThis compound was prepared from $\text{HSiMe}_2(p\text{-C}_6\text{H}_4\text{Br})$ by reaction with magnesium and then treatment of the Grignard with HSiMe_2Cl .

TABLE II-5

NMR Results^a for Silanes Prepared in the Present Work

Silane	Si-H (τ)	Si-Me (τ)	³ J _{H-Me} (Hz)
HSiMe ₂ (<i>p</i> -C ₆ H ₄ NMe ₂)	5.36	9.69	4.0
HSiMe ₂ (<i>p</i> -C ₆ H ₄ OMe)	5.29	9.63	3.7
HSiMe ₂ (<i>p</i> -C ₆ H ₄ F)	5.35	9.55	3.6
HSiMe ₂ (<i>p</i> -C ₆ H ₄ Br)	5.35	9.57	3.5
HSiMe ₂ (<i>p</i> -C ₆ H ₄ Me)	5.43	9.73	3.5
<i>p</i> - ² (HSiMe ₂) ₂ C ₆ H ₄	5.30	9.66	3.8
HSiMe ₂ (<i>o</i> -C ₆ H ₄ Me)	5.36	9.71	4.0
HSiMe ₂ C ₆ F ₅	5.29	9.46	4.2
HSi(C ₆ F ₅) ₂ Me	4.62	9.01	4.2
HSi(C ₆ F ₅) ₂ Ph	4.60	----	----
HSi(<i>o</i> t-Bu) ₂ Me	4.99	8.94	1.4
HSi(OPh) ₂ Ph	4.84	----	----
HSiEt ₂ Ph	5.51	----	4.1 ^b

^aAll spectra were measured neat with TMS internal reference. Phenyl resonances and resonances of substituents attached to the phenyl group were observed in the expected positions and exhibited the expected couplings.

^bThis represents the measured coupling of Si-H to the methylene resonance.

silane and alcohol or thiophenol. The reactions were carried out on a 0.1 mole scale at 0° with ether solvent. The alcohol and silane were stirred in ether and an ethereal solution of excess Et₃N was slowly added resulting in a vigorous reaction with precipitation of Et₃NHCl. The addition was allowed to take place over one hour and then the solution was allowed to warm to room temperature with continued stirring. The solution was filtered, ether removed, and the residual silane was then used without further purification.

A. Preparation of CpFe(CO)₂SiR₃ Compounds

i) Thermal Reaction Method

Preparation of CpFe(CO)₂SiPh₂Me: A sample of [CpFe(CO)₂]₂ (1.77 g) was placed in a 75 ml Carius tube equipped with a side arm and TF6/13 Rotoflo seal. To this was added 2.0 ml of HSiPh₂Me and the tube was evacuated and sealed. The mixture was heated in a silicon oil bath at 170° for 3 days. After cooling, accumulated CO was vented and the tube was attached to a vacuum system overnight to remove small amounts of ferrocene formed during the reaction. Crude product was extracted with *n*-pentane and filtered. The solution was cooled at ca. -20° overnight to remove unreacted [CpFe(CO)₂]₂ by crystallization. The desired compound may be re-

crystallized at -78° from *n*-pentane affording orange crystals.

Alternatively, unreacted $[\text{CpFe}(\text{CO})_2]_2$ may be removed from the crude product mixture by chromatography. This is accomplished on a Florisil column with 1:1 benzene-pentane elutant. A yellow band (product) separates well ahead of $[\text{CpFe}(\text{CO})_2]_2$ (purple band) and this was collected. Removal of solvent and extraction with *n*-pentane followed by cooling to -78° yields yellow crystals as above.

The above procedure was applied to the preparation of the compounds listed in Table II-6 with the noted modifications. *Analytical data and melting points* for the compounds prepared are listed in Table II-7.

ii) Anion Reaction Method

Preparation of $\text{CpFe}(\text{CO})_2\text{SiPh}(\text{Me})\text{H}$: A sample of $[\text{CpFe}(\text{CO})_2]_2$ (1.77 g) was dissolved in 100 ml of THF and added to a prepared Na/Hg amalgam (0.5 g of Na in 10 ml of Hg). The solution was vigorously stirred for a 25 minute period during which time the initial purple colored solution changed to orange and finally to a dirty green. Excess amalgam was then drained off through a 4 mm bore tap in the bottom of the flask. A 2.0 ml sample of $\text{HSiMe}(\text{Ph})\text{Cl}$ was then dissolved in 25 ml of THF and added over a 10 minute period with stirring

TABLE II-6
Compounds Prepared by the Thermal Reaction Method
with Noted Modifications

Compound	Modification	
	Reaction Time	Reaction Temp. °C
$\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Ph}$	1 day	160°
$\text{CpFe}(\text{CO})_2\text{SiMe}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$	1 day	150°
$\text{CpFe}(\text{CO})_2\text{SiMe}_2(p\text{-C}_6\text{H}_4\text{OMe})$	2 days	160°
$\text{CpFe}(\text{CO})_2\text{SiMe}_2(p\text{-C}_6\text{H}_4\text{Me})$	2 days	165°
$p\text{-di}(\text{CpFe}(\text{CO})_2\text{SiMe}_2)\text{C}_6\text{H}_4^a$	2 days	160°
$\text{CpFe}(\text{CO})_2\text{SiMe}_2(p\text{-C}_6\text{H}_4\text{F})$	2 days	160°
$\text{CpFe}(\text{CO})_2\text{SiMe}_2(o\text{-C}_6\text{H}_4\text{Me})$	1 day	160°
$\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{C}_6\text{F}_5$	1.5 days	165°
$\text{CpFe}(\text{CO})_2\text{Si}(\text{C}_6\text{F}_5)_2\text{Me}$	1 day	170°
$\text{CpFe}(\text{CO})_2\text{Si}(\text{C}_6\text{F}_5)_2\text{Ph}$	3 days	160°
$\text{CpFe}(\text{CO})_2\text{SiEt}_2\text{Ph}$	3 days	160°
$\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Me}^{b,c}$	4 hours	150°
$\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Cl}^{b,c}$	1 day	150°
$\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Ph}^b$	8 hours	160°

^aNo evidence for formation of $\text{CpFe}(\text{CO})_2\text{SiMe}_2(p\text{-C}_6\text{H}_4\text{SiMe}_2\text{H})$.

^bThese compounds prepared initially by W. Jetz, reference 6.

^cA three-fold excess of silane was employed.

TABLE II-7

Analytical Results, Melting Points, ^a and Colors of CpFe(CO)₂SiR₃
Compounds Prepared by the Thermal Method

Compound	Required		Found		M.P. °C	Color
	C%	H%	C%	H%		
-SiR ₃						
-SiPh ₂ Me	64.7	4.8	64.7	5.1	41-43	yellow
-SiMe ₂ Ph	57.8	5.1	57.3	5.2	64.5-66	orange
-SiMe ₂ (<i>p</i> -C ₆ H ₄ NMe ₂) ^b	57.5	5.9	57.3	6.1	134.5-136	yellow
-SiMe ₂ (<i>p</i> -C ₆ H ₄ OMe)	56.1	5.3	55.8	5.4	59.5-60.5	red-brown
-SiMe ₂ (<i>p</i> -C ₆ H ₄ Me)	58.9	5.5	58.5	5.7	85.5-86.5	yellow-brown
-SiMe ₂ [<i>p</i> -(SiMe ₂) ₂ C ₆ H ₄]	52.5	4.7	52.3	4.7	157.5-159	cream
-SiMe ₂ (<i>p</i> -C ₆ H ₄ F)	54.4	4.5	54.4	4.6	85-88	orange-red
-SiMe ₂ (<i>o</i> -C ₆ H ₄ Me)	58.9	5.5	58.5	5.8	54.5-55.5	red-brown
-SiMe ₂ C ₆ F ₅	44.8	2.7	44.8	2.9	95.5-97	pale yellow
-Si(C ₆ F ₅) ₂ Me	43.3	1.4	43.6	1.7	157-159	orange
-Si(C ₆ F ₅) ₂ Ph	48.7	1.6	49.0	1.7	154.5-155	pale yellow
-SiEt ₂ Ph	60.0	5.9	60.2	6.0	38-39.5	yellow

TABLE II-7 (Continued)

^aMelting points were determined on a Kofler Hot Stage #1356 apparatus.

^bNitrogen analysis; required 3.9%, found 4.7%.

to the anion solution. This addition resulted in heat evolution and the solution turned a yellow-green color. The reaction mixture was stirred for a further hour and then filtered. Solvent was removed and the crude product extracted with *n*-pentane. Cooling of the filtered solution to -78° failed to yield any crystals; therefore, solvent was removed and the compound was purified by vacuum distillation at 0.5 mm Hg, the fraction boiling between 120° - 135° was collected. The product is a golden colored liquid.

The following compounds were prepared according to the above procedure with the noted modifications.

Preparation of $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{H}$: A THF solution of $\text{CpFe}(\text{CO})_2\text{Na}$ was prepared as above and added to an excess of HSiCl_3 cooled to 0° . After addition of all the anion, the solution was stirred for a further hour. Work up was then identical with that described above, the pure product may be collected by sublimation onto a water cooled probe at 0.01 mm Hg.

Preparation of $\text{CpFe}(\text{CO})_2\text{SiPh}_2\text{Cl}$: In the manner described above, $\text{CpFe}(\text{CO})_2\text{Na}$ was added to an excess of Ph_2SiCl_2 . After removal of solvent the crude product was washed with three 10 ml portions of *n*-pentane to remove unreacted Cl_2SiPh_2 and $[\text{CpFe}(\text{CO})_2]_2$. The product was then extracted with hot *n*-heptane and cooled in the

refrigerator yielding yellow microcrystals of product. The compound $\text{CpFe}(\text{CO})_2\text{SiCl}_2(\text{CH}=\text{CH}_2)$ was prepared in a similar manner.

Analytical Results, melting points, and colors for the above compounds are presented in Table II-8.

B. Reaction of the Si-Cl Bond

i) With AgBF_4

Preparation of $\text{CpFe}(\text{CO})_2\text{SiF}_2\text{Me}$: A solution of 1.45 g of $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Me}$ in 50 ml of benzene was placed in a 100 ml round-bottomed flask equipped with side arm for nitrogen inlet. A 3.0 g sample of AgBF_4 was added and the solution was stirred for two hours. During this period evolution of BF_3 gas was evident, it being blown off by the stream of nitrogen. After completion of the reaction, the solution was filtered and solvent removed. The crude product was extracted with *n*-pentane, the solution filtered, and the filtrate was cooled to -78° affording pale yellow crystals of product. These crystals slowly melt at room temperature.

The procedure outlined above was followed in the preparation of $\text{CpFe}(\text{CO})_2\text{SiF}_2\text{Ph}$, $\text{CpFe}(\text{CO})_2\text{SiPh}_2\text{F}$, $\text{CpFe}(\text{CO})_2\text{SiF}_2(\text{CH}=\text{CH}_2)$, $\text{CpFe}(\text{CO})_2\text{SiPh}(\text{Me})\text{F}$, $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{F}$, and $\text{CpFe}(\text{CO})_2\text{SiF}_3$.⁸³ These compounds were prepared from the appropriate chlorosilyl compound

TABLE II-8

Analytical Results, Melting Points, ^a and Colors of CpFe(CO)₂SiR₃
Compounds Prepared by the Anion Method

Compound	Required			Found			M.P. °C	Color
	C%	H%	Cl%	C%	H%	Cl%		
-SiR ₃	56.3	4.7	-----	56.1	4.8	-----	liquid	golden
-SiMe(H)Ph	30.4	2.2	25.4	30.4	2.2	23.3	56.5-58	rose
-SiCl ₂ H	57.8	3.8	9.0	57.8	3.8	9.0	101-102	yellow
-SiPh ₂ Cl	35.6	2.6	23.4	35.0	2.7	22.6	oil	orange

^aMelting points were determined on a Kofler Hot Stage #1356 apparatus.

^bThis compound has been reported very recently in the literature, reference 49.

and an excess of AgBF_4 .

The preparation of $\text{CpFe}(\text{CO})_2\text{SiF}_2\text{H}$ requires a reaction temperature of 0° ; therefore, toluene was employed as solvent. The lower reaction temperature is necessary because of the reactivity of the Si-H bond. Even at 0° a small amount of $\text{CpFe}(\text{CO})_2\text{SiF}_3$ is produced which may be removed by fractional crystallization. The desired product may be sublimed onto a water cooled probe at 0.05 mm Hg affording pure, beige colored crystals of product.

The analytical, melting point, and color data for these compounds are presented in Table II-9.

ii) With Alcohols

Preparation of $\text{CpFe}(\text{CO})_2\text{Si}(\text{OMe})_2\text{Me}$: A 1.45 g sample of $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Me}$ was dissolved in 25 ml of methanol and placed in a 100 ml round bottomed flask equipped with side arm for nitrogen inlet. Dropwise addition of Et_3N (3.5 ml) with stirring resulted in a vigorous reaction. The reaction mixture was stirred for a further 30 minutes and then filtered. Methanol and excess Et_3N were removed and the crude product extracted with *n*-pentane. Filtration and cooling of the solution to -78° afforded cream colored crystals of product. Due to their low melting point, the crystals exist in a sticky form at room temperature.

The following compounds were also prepared by the

TABLE II-9

Analytical Results, Melting Points,^a and Colors of CpFe(CO)₂SiR₃
Compounds Prepared by the Action of AgBF₄ on Chlorosilyl Compounds

Compound	Required		Found		°C	Color
	C%	H%	C%	H%		
-SiR ₃						
-SiF ₂ Me	37.0	2.9	37.2	3.1	liquid	pale yellow
-SiF ₂ Ph	48.7	3.1	48.5	3.3	68.5-70	pale yellow
-SiF(Me)Ph	53.2	4.1	53.0	3.9	41.5-42	beige
-SiF ₂ H	34.4	2.5	34.2	2.7	78-80.5	beige
-SiMe ₂ F	42.5	4.3	42.4	4.2	liquid	pale yellow
-SiPh ₂ F	60.3	4.0	58.8	4.0	87-88	pale yellow
-SiF ₂ (CH=CH ₂) ^b	40.0	3.0	39.4	2.7	liquid	yellow

^aMelting points were determined on a Kofler Hot Stage #1356 apparatus.

^bThis compound has been reported very recently in the literature, reference 49.

above procedure: $\text{CpFe}(\text{CO})_2\text{SiR}_3$, where $\text{SiR}_3 = \text{SiMe}_2(\text{OMe})$, $\text{Si}(\text{OMe})_2\text{Ph}$, $\text{SiMe}_2(\text{OEt})$, $\text{Si}(\text{OEt})_2\text{Me}$,⁶ $\text{Si}(\text{OEt})_2\text{Ph}$, $\text{SiPh}_2(\text{OMe})$, $\text{SiPh}_2(\text{OEt})$, $\text{Si}(\text{O}i\text{-Pr})_2\text{Me}$, $\text{SiMe}_2(\text{O}i\text{-Pr})$, $\text{Si}(\text{O}i\text{-Pr})_2\text{Ph}$, and $\text{SiMe}_2(\text{O}t\text{-Bu})$ from the appropriate chlorosilyl compound and alcohol.

The following compounds were also obtained with the noted modifications.

Preparation of $\text{CpFe}(\text{CO})_2\text{SiMe}_2(\text{OH})$ The reaction was carried out in ether solvent with 0.5 g of $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Cl}$ and 1 ml of H_2O . The addition of 3 ml of Et_3N resulted in rapid reaction. The compound was worked up as for $\text{CpFe}(\text{CO})_2\text{Si}(\text{OMe})_2\text{Me}$ and the product is obtained as yellow crystals which are very air sensitive. Analogous reactions on $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Me}$ and $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Ph}$ failed to yield any ether soluble carbonyl containing product.

Preparation of $\text{CpFe}(\text{CO})_2\text{SiMe}_2(\text{OC}_6\text{F}_5)$: Due to the low volatility of $\text{C}_6\text{F}_5\text{OH}$, stoichiometric amounts of $\text{C}_6\text{F}_5\text{OH}$ and $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Cl}$ were reacted in 20 ml of ether. The reaction was initiated by dropwise addition of Et_3N . The compounds $\text{CpFe}(\text{CO})_2\text{Si}(\text{OC}_6\text{F}_5)_2\text{Me}$ and $\text{CpFe}(\text{CO})_2\text{Si}(\text{OC}_6\text{F}_5)_2\text{Ph}$ were prepared in a similar manner.

Attempts to prepare $\text{CpFe}(\text{CO})_2\text{Si}(\text{O}t\text{-Bu})_2\text{Me}$ by any of the above methods failed. Also, phenoxy compounds are very difficult to prepare by these routes. These

compounds are readily accessible by the thermal method, the silanes being prepared easily from the appropriate chlorosilane and alcohol with Et_3N as reaction initiator as described earlier.

Thus, the thermal reaction of $[\text{CpFe}(\text{CO})_2]_2$ with $\text{HSi}(\text{O}t\text{-Bu})_2\text{Me}$ at 170° for 7 days yields small amounts of product which can be purified by chromatography on a Florisil column with 1:1 benzene-pentane elutant. A yellow band elutes first and this is product. Attempts at recrystallization failed, and only a yellow oil could be isolated.

Preparation of $\text{CpFe}(\text{CO})_2\text{Si}(\text{OPh})_2\text{Ph}$: This compound was obtained via the thermal route as described for the preparation of $\text{CpFe}(\text{CO})_2\text{SiPh}_2\text{Me}$. Reaction time was 4 days at 170° .

The two compounds $\text{CpFe}(\text{CO})_2\text{Si}(\text{OPh})_x\text{Me}_{3-x}$ ($x = 1, 2$) were kindly provided by Dr. C. E. Jones of this group. The method of preparation was similar to the above, with reaction times of 2 and 3 days respectively.

Formation of $[\text{CpFe}(\text{CO})_2\text{SiMe}_2]_2\text{O}$: This unusual compound was obtained from a reaction between $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Cl}$ and $\text{Me}_3\text{SiOH}^{93}$ in ether. It was intended that $\text{CpFe}(\text{CO})_2\text{SiMe}_2(\text{OSiMe}_3)$ would be the product but none of this compound was observed. The procedure was as follows: 1.5 g of $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Cl}$ was dissolved in

25 ml of ether and 2.0 ml of Me_3SiOH was added. Drop-wise addition of 4 ml of Et_3N produced a vigorous reaction and the solution was stirred for 30 minutes. Work-up was similar to that described for $\text{CpFe}(\text{CO})_2\text{Si}(\text{OMe})_2\text{Me}$.

Preparation of $\text{CpFe}(\text{CO})_2\text{Si}(\text{OCH}_2\text{CF}_3)_x\text{Me}_{3-x}$ ($x = 1, 2$):

The two fluoroalkoxy compounds $\text{CpFe}(\text{CO})_2\text{Si}(\text{OCH}_2\text{CF}_3)_x\text{Me}_{3-x}$ ($x = 1, 2$) were prepared according to the procedure for $\text{CpFe}(\text{CO})_2\text{Si}(\text{OMe})_2\text{Me}$. However, it was found necessary to reflux the reaction mixture consisting of 6 ml of Et_3N , 4 ml of HOCH_2CF_3 and 1.0 g of chlorosilyl compound for 3 hours. This was necessary to drive the reaction to completion.

Similar reactions with $\text{HOCH}(\text{CF}_3)_2$, $\text{HOC}(\text{Me})_2\text{CF}_3$, and $\text{HOC}(\text{CF}_3)_2\text{Me}$ gave only ill-defined reaction mixtures consisting of unreacted starting material and various carbonyl containing species (from the infrared). The compound $\text{CpFe}(\text{CO})_2\text{SiMe}(\text{Cl})[\text{OC}(\text{Me})_2\text{CF}_3]$ was isolated from a refluxing mixture of 1.0 g of $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Me}$, 4.0 ml of $\text{HOC}(\text{Me})_2\text{CF}_3$, and 6.0 ml of Et_3N after one day of reaction. No evidence for replacement of the second chloro group was found. It is not understood why $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Cl}$ and $\text{HOC}(\text{Me})_2\text{CF}_3$ would not react to produce $\text{CpFe}(\text{CO})_2\text{SiMe}_2[\text{OC}(\text{Me})_2\text{CF}_3]$ under similar conditions.

Analytical data, melting points, and colors of these compounds are presented in Table II-10.

iii) With Thiols

A direct extension of the alkoxy and phenoxy compounds just described are the thiol compounds. Since the silicon-sulfur bond is insufficiently thermally stable, these compounds are not accessible via the thermal route. This was verified by the reaction of $\text{HSi}(\text{SPh})_2\text{Me}$ and $[\text{CpFe}(\text{CO})_2]_2$ at 130° . After one day of reaction, sulfur was visible at the top of the Carius tube. Extraction of the reaction mixture with *n*-heptane and a subsequent infrared spectrum of the carbonyl region showed only $[\text{CpFe}(\text{CO})_2]_2$ present. No parent ion for the silane was observed in the mass spectrum, indicating complete degradation of $\text{HSi}(\text{SPh})_2\text{Me}$ at the reaction temperatures employed.

Preparation of $\text{CpFe}(\text{CO})_2\text{SiMe}_2(\text{SEt})$: A 1.3 g sample of $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Cl}$ was placed in a 100 ml Carius tube along with 4 ml of ethanethiol. Rapidly 2.5 ml of Et_3N was syringed into the tube which was then quickly sealed. The mixture was heated at 45° for 14 hours during which time Et_3NHCl was observed to precipitate. The tube was vented and the crude product extracted with *n*-pentane. The solution was filtered and afforded

an oil after cooling to -20° .

It is highly recommended that the Carius tube method described above be used for the preparation of these compounds. This is because it is desirable to seal off the volatile thiols, which possess revolting odors difficult to contain even in the fume hood. The following $\text{CpFe}(\text{CO})_2\text{SiR}_3$, where $\text{SiR}_3 = \text{Si}(\text{SEt})_2\text{Me}$, $\text{Si}(\text{SEt})_2\text{Ph}$, $\text{SiMe}_2(\text{SPh})$, $\text{Si}(\text{SPh})_2\text{Me}$, and $\text{Si}(\text{SPh})_2\text{Ph}$ compounds were also prepared from the appropriate thiol and chlorosilyl compound according to the above procedure.

The compounds $\text{CpFe}(\text{CO})_2\text{Si}(\text{SC}_6\text{F}_5)_2\text{Me}_{3-x}$ ($x = 1, 2$) and $\text{CpFe}(\text{CO})_2\text{Si}(\text{SC}_6\text{F}_5)_2\text{Ph}$ were prepared from stoichiometric amounts of $\text{C}_6\text{F}_5\text{SH}$ and chlorosilyl compound. The reactions were carried out in ether solvent and were taken to completion by excess Et_3N .

The compounds $\text{CpFe}(\text{CO})_2\text{Si}(\text{Si-Pr})_x\text{Me}_{3-x}$ ($x = 1, 2$) and $\text{CpFe}(\text{CO})_2\text{Si}(\text{Si-Pr})_2\text{Ph}$ were prepared by refluxing the thiol and excess Et_3N with the chlorosilyl compound for one week. Similar reactions with $t\text{-BuSH}$ were unsuccessful even after 10 days of reaction time.

The analytical, melting point, and color data are presented in Table II-11.

TABLE II-10

Analytical Results, Melting Points, ^a and Colors of CpFe(CO)₂SiR₃ Compounds Prepared by Reaction of Chlorosilyl Compounds with Alcohols

Compound	Required		Found		M.P.	Color
	C%	H%	C%	H%	°C	
-SiR ₃						
-Si(OMe) ₂ Me	42.4	5.0	42.4	5.0	32-32.5	cream
-SiMe ₂ (OMe)	45.1	5.3	45.3	5.6	liquid	orange
-Si(OMe) ₂ Ph	52.3	4.7	51.8	4.7	58.5-59.5	cream
-SiPh ₂ (OMe)	61.5	4.6	60.8	4.6	97-98.5	beige
-SiMe ₂ (OEt)	47.1	5.7	47.1	5.7	liquid	orange
-Si(OEt) ₂ Ph	54.8	5.4	54.0	5.3	34-35.5	cream
-SiPh ₂ (OEt)	62.4	5.0	61.6	5.0	91.5-92.5	orange
-SiMe ₂ (OH)	42.9	4.8	42.9	4.8	45.5-47	yellow
-Si(Oi-Pr) ₂ Me	49.7	6.5	49.2	6.6	liquid	yellow
-SiMe ₂ (Oi-Pr)	48.9	6.1	47.7	7.1	oil	orange
-Si(Oi-Pr) ₂ Ph	57.0	6.0	56.9	6.5	oil	red-brown
-SiMe ₂ (Ot-Bu)	42.9	6.5	42.4	7.0	oil	orange

TABLE II-10 (Continued)

Compound	Required			Found			M.P. °C	Color
	C%	H%		C%	H%			
-SiR ₃								
-Si(Ot-Bu) ₂ Me	52.4	7.1		49.5	7.5		oil	yellow
-SiMe ₂ (OC ₆ F ₅)	43.1	2.6		43.1	2.8		33.5-34.5	beige
-Si(OC ₆ F ₅) ₂ Me	41.0	1.4		41.1	1.5		85-87	beige
-Si(OC ₆ F ₅) ₂ Ph	46.3	1.5		46.1	1.5		98.5-99	yellow
-Si(OPh) ₂ Ph	64.1	4.3		62.6	4.0		125-126.5	beige
-SiMe ₂ (OPh) ^b	54.9	4.9		54.8	4.9		39-40	pale yellow
-Si(OPh) ₂ Me ^b	59.1	4.5		58.6	4.4		56-68	pale yellow
-SiMe ₂ (OCH ₂ CF ₃)	39.5	3.9		41.0	4.1			yellow
-Si(OCH ₂ CF ₃) ₂ Me	34.4	2.9		32.8	3.5		oil	golden
-SiMe(Cl)[OC(Me) ₂ CF ₃]	37.7	3.7		38.2	4.0		oil	orange
-SiMe ₂ OSiMe ₂	44.4	4.5		43.9	4.5		68.5-70	yellow

^aMelting points were determined on a Kofler Hot Stage #1356 Apparatus.

^bThese compounds were characterized by Dr. C. E. Jones, unpublished results at the University of Alberta.

TABLE II-11

Analytical Results, Melting Points,^a and Colors of CpFe(CO)₂SiR₃
Compounds Prepared by Reaction with Thiols

Compound	Required			Found			M.P. °C	Color
	C%	H%	S%	C%	H%	S%		
-SiR ₃								
-SiMe ₂ (SET)	44.6	5.4	10.8	43.4	5.9	8.6	oil	orange
-Si(SET) ₂ Me	42.1	5.3	18.7	41.8	5.0	17.7	oil	orange
-Si(SET) ₂ Ph	50.5	5.0	15.8	51.5	4.9	13.8	oil	orange
-SiMe ₂ (SC ₆ F ₅)	41.5	2.5	7.4	41.5	2.9	7.2	29.5-31	yellow
-Si(SC ₆ F ₅) ₂ Me	38.8	1.3	10.4	39.1	1.4	10.3	79-80	yellow
-Si(SC ₆ F ₅) ₂ Ph	43.1	1.5	9.4	44.9	1.6	9.5	126-128	yellow
-SiMe ₂ (SPH)	52.3	4.7	9.3	52.3	4.9	9.6	oil	yellow
-Si(SPh) ₂ Me	54.8	4.1	14.6	54.7	4.0	14.8	59-60.5	yellow
-Si(SPh) ₂ Ph	60.0	4.0	12.8	59.8	4.1	11.8	104-106	yellow
-SiMe ₂ (Si-Pr)	46.5	5.8	10.3	47.0	5.8	10.1	oil	yellow
-Si(Si-Pr) ₂ Me	45.4	5.8	17.3	44.1	5.8	14.6	52-54	yellow
-Si(Si-Pr) ₂ Ph	52.8	5.6	14.8	51.8	4.8	13.4	104-106	beige

^aMelting points were determined on a Kofler Hot Stage #1356 apparatus.

C. Replacement of Carbonyl in $\text{CpFe}(\text{CO})_2\text{SiR}_3$

i) Substitution by Phosphines

Preparation of $\text{CpFe}(\text{CO})\text{PPh}_3(\text{SiMe}_2\text{Ph})$: A 1.05 g sample of $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Ph}$ was dissolved in 200 ml of *n*-hexane and placed in a 250 ml quartz reaction vessel equipped with a water cooled cold finger. A sample of PPh_3 (2.5 g) was added to the stirred solution and this was irradiated for 20 hr with a 140 watt Hanovia ultra-violet source. This irradiation resulted in precipitation of a large amount of material since the product is only sparingly soluble in *n*-hexane. Solution and precipitated product were collected and the solvent removed. The crude product was dissolved in a minimum quantity of 1:1 benzene-pentane and chromatographed on Florisil. A pale yellow band was eluted first which was found to contain PPh_3 and $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Ph}$. An orange band was eluted next and was determined to be the desired product. Removal of solvent and extraction with hot *n*-heptane followed by cooling afforded orange crystals. The product appears to be indefinitely air stable. Even though a greater than two-fold excess of PPh_3 was employed, there was no evidence for the formation of any disubstituted phosphine product.

Preparation of $\text{CpFe}(\text{CO})_{2-x}(\text{PMe}_2\text{Ph})_x\text{SiMe}_2\text{Ph}$ ($x = 1, 2$):

A 1.05 g sample of $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{Ph}$ was reacted in the

manner described above with 2.2 ml of PMe_2Ph . This resulted in the formation of a mixture of both mono- and disubstituted phosphine compounds. These two products can be separated by column chromatography using the procedure outlined above. The first band eluted was dark orange, identified as $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{SiMe}_2\text{Ph}$ by its single carbonyl stretching peak in the infrared. Trailing that band was a narrow red one which showed no carbonyl infrared absorption. Removal of solvent and extraction of each residue with *n*-pentane followed by cooling, produced crystals of each compound. The monosubstituted product was found to be contaminated to some extent with the disubstituted phosphine compound. Since $\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiMe}_2\text{Ph}$ is less soluble in *n*-pentane, slow cooling of the mixture in *n*-pentane caused precipitation of large orange crystals of the disubstituted product. Further cooling of the remaining yellow solution yields yellow microcrystals of $\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})\text{SiMe}_2\text{Ph}$.

This reaction method was applied to the following organosilyl compounds: $\text{CpFe}(\text{CO})_2\text{SiMe}_3$, $\text{CpFe}(\text{CO})_2\text{SiPh}_2\text{Me}$, $\text{CpFe}(\text{CO})_2\text{SiPh}_3$, $\text{CpFe}(\text{CO})_2\text{SiCl}_3$, and $\text{CpFe}(\text{CO})_2\text{SiF}_2\text{Me}$.

In some cases only the bisphosphine compound was obtained. For the silanes possessing halogen groups, chromatography could not be applied due to the reactivity of the silicon-halogen bond with the column material. In each case,

the bisphosphine compound was isolated in crystalline form from CH_2Cl_2 -*n*-heptane at -20° .

Analytical, melting point, and color data are presented in Table II-12.

ii) Oxidative Elimination with H-SiR_3

Preparation of $\text{CpFe}(\text{CO})\text{H}(\text{SiPh}_2\text{Me})_2$: Using the ultraviolet apparatus described in the preparation of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SiMe}_2\text{Ph}$, 2.0 g of $\text{CpFe}(\text{CO})_2\text{SiPh}_2\text{Me}$ and 1.5 ml of HSiPh_2Me were dissolved in 200 ml of *n*-hexane and irradiated for 18 hr. The solution was then filtered and solvent removed. Crude product was extracted with *n*-pentane, filtered, and cooled to -20° . This afforded beige colored crystals of the desired product which are quite air stable.

The above method was applied to the preparation of $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ compounds where $\text{SiR}_3 = \text{SiCl}_2\text{Ph}$, SiMe_2Ph , SiCl_2Me , and $\text{SiMe}_2\text{C}_6\text{F}_5$. An attempt to prepare $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Cl})_2$ by this method was unsuccessful, but the compound was obtained by the following method.

Preparation of $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Cl})_2$: A 2.0 g sample of $[\text{CpFe}(\text{CO})_2]_2$ was placed in a 50 ml quartz Carius tube equipped with a ball joint connector to a side arm. The tube could be sealed by means of a Fischer and Porter valve and the ball joint connection was made secure by sealing it with Apiezon wax. The HSiMe_2Cl

TABLE II-12

Analytical Results, Melting Points,^a and Colors of CpFe(CO)L(SiR₃)
and CpFe(L)₂SiR₃ (L = PPh₃ and PMe₂Ph) Compounds

Compound	Required		Found		M.P. °C	Color
	C%	H%	C%	H%		
CpFe(CO)(PPh ₃)SiMe ₂ Ph	70.4	5.7	69.1	6.2	151-153	orange
CpFe(CO)(PMe ₂ Ph)SiMe ₂ Ph	62.6	6.4	62.3	6.6	140-141	yellow
CpFe(PMe ₂ Ph) ₂ SiMe ₂ Ph	65.4	7.1	64.9	7.2	163-165	orange
CpFe(PMe ₂ Ph) ₂ SiMe ₃	61.1	7.7	60.3	7.6	132-134	red
CpFe(PMe ₂ Ph) ₂ SiPh ₂ Me	68.4	6.7	67.4	6.7	160-161	orange
CpFe(CO)(PMe ₂ Ph)SiPh ₂ Me	67.2	6.0	66.6	6.1	137-138	yellow
CpFe(PMe ₂ Ph) ₂ SiPh ₃	71.3	6.4	69.9	6.5	188-190	orange
CpFe(PMe ₂ Ph) ₂ SiCl ₃	48.5	5.1	47.6	5.2	164-165	yellow
CpFe(PMe ₂ Ph) ₂ SiF ₂ Me	55.3	6.3	54.1	6.3	127-128	orange

^aMelting points were determined on a Joffler Hot Stage #1356 apparatus.

(4.0 ml) was distilled into the tube which was then sealed off by means of the valve. The tube and contents were irradiated for 5 days and then the tube was vented. Crude product was extracted with *n*-pentane, filtered, and cooled to -78° affording red-brown crystals of product.

From the appropriate chlorosilyl compounds prepared according to the above methods, the fluorosilyl compounds were obtained by the AgBF_4 method of reaction (9):

The reaction is performed in benzene solution over a 2 hr period and it was desirable to use an excess of AgBF_4 .

When the reaction was attempted with $\text{CpFe}(\text{CO})\text{H}(\text{SiCl}_2\text{Ph})_2$ only traces of the desired product were obtained together with a mixture of $\text{CpFe}(\text{CO})_2\text{SiF}_3$ and $\text{CpFe}(\text{CO})_2\text{SiF}_2\text{Ph}$.

This reaction is not understood since the compound $\text{CpFe}(\text{CO})\text{H}(\text{SiCl}_2\text{Ph})_2$ is quite stable and does not differ from the other hydrido compounds in its properties.

Analytical, melting point and color data for the above class of compounds are presented in Table II-13.

D. Kinetic Study on the Reductive Elimination Reaction of $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ with PPh_3

The experimental procedure reported here closely parallels that of Hart-Davis and Graham.^{61,88} Disappearance of starting material with reaction time was monitored

TABLE II-13

Analytical Results, Melting Points,^a and Colors
of CpFe(CO)H(SiR₃)₂ Compounds

Compound	Required			Found			M.P.		Color
	C%	H%	Cl%	C%	H%	Cl%	°C		
-SiR ₃									
-SiPh ₂ Me	70.3	5.9	----	69.5	5.6	----	124-125		beige
-SiCl ₂ Ph	43.2	3.2	27.2	43.6	3.3	26.0	131-132		pale yellow
-SiMe ₂ Ph	62.9	6.4	----	62.1	6.4	----	91-91.5		pale yellow
-SiCl ₂ Me	25.5	3.2	37.8	25.7	3.3	38.2	66-66.5		yellow
-SiF ₂ Me	30.8	3.9	----	30.2	3.9	----	82-83		pale yellow
-SiF ₃	22.5	1.9	----	22.7	2.0	----	85-85.5		bright yellow
-SiMe ₂ Cl	35.7	5.4	21.1	35.1	5.4	20.6	58-58.5		red-brown
-SiMe ₂ F	39.5	5.9	----	38.5	5.9	----	63.5-64		pale yellow
-SiMe ₂ (C ₆ F ₅)	44.0	3.0	----	44.0	3.1	----	93.5-95		pale yellow

^aMelting points were determined on a Kofler Hot Stage #1356 apparatus.

by carbonyl infrared (ν_{CO} for $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ at 1946 cm^{-1} in decalin). Also, the appearance of product band at 1914 cm^{-1} was followed; however, it was observed to grow in a nonlinear manner (see Figure II-II) and was not utilized in this analysis. Both reactant and product were demonstrated to obey Beer's Law up to the 6 mM concentration range. Thus, a plot of concentration versus $\log T_0/T$ (where T_0 = baseline transmittance, T = peak height transmittance) produced a satisfactory straight line over 1- to 6 mM range. On this basis, the initial concentration of $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ was chosen as 3 mM for all kinetic runs.

Pseudo first order reaction conditions were verified at $69.9 \pm 0.2^\circ$ by determining k_{obs} for varying PPh_3 . These results have been presented in Table II-1. The method used to measure k_{obs} at a particular temperature will now be described and differed only for the above verification in that varying weights of PPh_3 were introduced into the reaction flask according to the concentrations listed in Table II-1.

The initial reaction flask was made up in the following manner: a 12.7 mg (3.0 mM) sample of $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ was weighed into a 10 ml volumetric flask and 75 mg (28.6 mM) PPh_3 was then introduced and decalin was added up to the mark. The solution was thoroughly mixed and then sealed under a nitrogen atmos-

phere with a serum cap. The flask was wrapped with aluminum foil to exclude light and placed in a constant temperature bath preset to the desired reaction temperature. Typically, two matched flasks were run at the same time with $t = 0$ taken as the time when the flasks were introduced into the bath. A sample (0.3 ml) was syringed out of each flask and placed in a solution infrared cell. The region between $1980 - 1880 \text{ cm}^{-1}$ was monitored and 12 - 20 readings were normally taken for each kinetic run. The readings were spread out over two half lives and a final t_{∞} reading was taken, corresponding to the time of the order of ten half lives. A typical run taken at 74.0°C is shown in Figure II-II. Note that the calculated half life of the reaction corresponds closely to the point where reactant and product intersect, despite the nonlinear behavior of the appearance of $\text{CpFe}(\text{CO})\text{PPh}_3(\text{SiMe}_2\text{Ph})$.

Values of k_{obs} at seven temperatures (see Table II-2) were used to evaluate the activation parameters for the reaction. The Wynn-Jones and Eyring equation (15) was used to evaluate ΔH^{\ddagger} and h the aid of

$$k_{\text{obs}} = (kT/h) \exp(-\Delta G^{\ddagger}/RT) \quad (15)$$

a computer program ACTIVE. This program plots $\ln(k_{\text{obs}}/T)$ against $1/T$ and fits the data to the best straight line by a least squares procedure. From such a plot, ΔH^{\ddagger} may

be evaluated from the slope and ΔS^\ddagger from the intercept. ACTIVE also evaluates ΔG^\ddagger for each k_{obs} . These values should be equivalent to ΔG^\ddagger values evaluated from $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. This then provides a means of testing each experimental point. All seven k_{obs} used in this work were within 0.6% of the calculated ΔG^\ddagger values; therefore none was rejected.

E. Other Related Compounds

- i) $\text{CpFe}(\text{CO})_2\text{R}$ (R = C_2F_5 , C_3F_7 , and $\text{CH}_2\text{C}_6\text{F}_5$)

Preparation of $\text{CpFe}(\text{CO})_2\text{C}_3\text{F}_7$: The method of King and Bisnette⁸⁹ was followed in the preparation of this compound. In our hands, the following modification resulted in a cleaner reaction.

A 5 mmole sample of $\text{CpFe}(\text{CO})_2\text{R}$ prepared in 150 ml of THF and this solution was added under strict anaerobic conditions to a 10 mmole solution of $\text{C}_3\text{F}_7\text{COCl}$ in 50 ml of THF cooled to -78° . The solution was stirred throughout the addition and then allowed to slowly warm to room temperature with continued stirring. The solution was filtered, solvent removed, and the crude product extracted with benzene and filtered. The solution was concentrated to 10 ml and an equal portion of n -pentane was added. Chromatography on a Florisil column allowed separation of a yellow band from

$[\text{CpFe}(\text{CO})_2]_2$. Solvent was removed and the acyl product was photolyzed in *n*-hexane to give $\text{CpFe}(\text{CO})_2\text{C}_3\text{F}_7$. This compound was purified by sublimation onto a Dry Ice-acetone probe at 0.01 mm Hg. This procedure was also followed in the preparation of $\text{CpFe}(\text{CO})_2\text{C}_2\text{F}_5$.

Preparation of $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_5$ This compound has been reported⁹⁰ from the reaction of $\text{CpFe}(\text{CO})_2\text{Na}$ and $\text{C}_6\text{F}_5\text{CH}_2\text{Br}$. However, significant amounts of $\text{CpFe}(\text{CO})_2\text{CH}_2\text{p-C}_6\text{F}_4\text{Fe}(\text{CO})_2\text{Cp}$ formed in that preparation. It was found that formation of the latter compound could be suppressed by adding a solution of the anion to $\text{C}_6\text{F}_5\text{CH}_2\text{Br}$ cooled to -78°C .

ii) Thermal Reaction of $[\text{CpRu}(\text{CO})_2]_2$ with HSiR_3

Preparation of $\text{CpRu}(\text{CO})_2\text{SiCl}_2\text{Me}$ A 0.75 g sample of $[\text{CpRu}(\text{CO})_2]_2$ and 3.0 ml of HSiCl_2Me were combined in a Carius tube and heated to 145° for one day. The tube was cooled and vented, and crude product was extracted with *n*-pentane and filtered. An infrared spectrum showed several carbonyl bands which were determined to arise from a mixture of $\text{CpRu}(\text{CO})_2\text{SiCl}_x\text{Me}_{3-x}$ ($x = 3, 2, \text{ and } 1$). While $\text{CpRu}(\text{CO})_2\text{SiCl}_2\text{Me}$ is the major reaction component, the other compounds are virtually inseparable from it.

A reasonably pure sample, that is, one which showed

only traces of the above impurities in the infrared was obtained from *n*-pentane at -78° . The compound is obtained as a pale yellow oil after several extractions with *n*-pentane. This procedure results in loss of much compound, but represents the only satisfactory way of removing contaminants.

The above procedure was also applied to the synthesis of $\text{CpRu}(\text{CO})_2\text{SiMe}_2\text{Cl}$ and $\text{CpRu}(\text{CO})_2\text{SiCl}_2\text{Ph}$ using the appropriate silane.

Preparation of $\text{CpRu}(\text{CO})_2\text{SiPh}_x\text{Me}_{3-x}$: A 0.5 g sample of $[\text{CpRu}(\text{CO})_2]_2$ and 1.0 g of H_2 were reacted at 180° for 2 days. Extraction of crude product with *n*-pentane followed by filtration and cooling to -20° afforded a white powder. The compounds $\text{CpRu}(\text{CO})_2\text{SiPh}_x\text{Me}_{3-x}$ ($x = 1, 2$) were prepared similarly with reaction times of 8 hr and 1 day, respectively.

Preparation of $\text{CpRu}(\text{CO})_2\text{SiCl}_2\text{H}$: This compound was prepared by the anion route from $\text{CpRu}(\text{CO})_2\text{Na}$ and HSiCl_3 . The reaction would not proceed in THF, reflecting the weaker nucleophilicity of $\text{CpRu}(\text{CO})_2\text{Na}$, but could be accomplished in the absence of solvent.

The anion $\text{CpRu}(\text{CO})_2^-$ was prepared as the sodium salt in THF by stirring 0.6 g of $[\text{CpRu}(\text{CO})_2]_2$ in 50 ml of THF with 0.5 g of Na in 5 ml of Hg for 2 hr. Solvent was removed and excess HSiCl_3 was distilled into the

reaction flask cooled to -78° . The solution was allowed to warm to 0° and it was stirred for one hour. The excess HSiCl_3 was then removed and the compound extracted with *n*-pentane, filtered, and cooled to -78° . This afforded pale yellow crystals of $\text{CpRu}(\text{CO})_2\text{SiCl}_2\text{H}$.

Preparation of $\text{CpRu}(\text{CO})_2\text{SiF}_x(\text{Me}_{3-x})$ ($x = 3, 2, 1$):

These compounds were prepared from the appropriate chlorosilyl derivatives and AgBF_4 . Reaction and work up were identical with those described for the iron analogs.

However, $\text{CpRu}(\text{CO})_2\text{SiCl}_2\text{Ph}$ reacted to give only $\text{CpRu}(\text{CO})\text{SiF}_3$, a puzzling result reminiscent of the results observed when $\text{CpFe}(\text{CO})\text{H}(\text{SiCl}_2\text{Ph})_2$ was reacted with AgBF_4 .

Preparation of $\text{CpRu}(\text{CO})\text{H}(\text{SiCl}_3)_2$: A 0.5 g sample of $[\text{CpRu}(\text{CO})_2]_2$ and 2.5 ml of HSiCl_3 were placed in a quartz Carius tube which was sealed and irradiated with a 140 watt Hanovia ultraviolet source for 4 days. The tube was vented and crude product was extracted with *n*-pentane. Filtration of solution and cooling to -78° afforded white crystals of $\text{CpRu}(\text{CO})\text{H}(\text{SiCl}_3)_2$.

iii) $\text{CpRu}(\text{CO})_2\text{SnX}_2\text{R}$ Compounds

Due to the limited quantity of $[\text{CpRu}(\text{CO})_2]_2$ and the low yields of reactions producing these ruthenium-tin compounds, only $\text{CpRu}(\text{CO})_2\text{SnI}_2\text{Me}$ was made in sufficient quantity for elemental analysis. The other compounds

prepared were confirmed by their infrared spectra in the carbonyl region which were consistent with the groups attached to tin.

A THF solution of $\text{CpRu}(\text{CO})_2\text{Na}$ was prepared as described for the preparation of $\text{CpRu}(\text{CO})_2\text{SiCl}_2\text{H}$. This solution was added to 1.0 g of Cl_3SnMe in 50 ml of THF with stirring. After one hour of reaction, the solution was filtered and solvent removed. An infrared spectrum of an *n*-heptane extract confirmed the formation of $\text{CpRu}(\text{CO})_2\text{SnCl}_2\text{Me}$. This crude compound was dissolved in acetone and reacted with an excess of NaI by stirring the solution for 20 minutes. Filtration and removal of solvent left behind a pale yellow pasty solid which was extracted with *n*-pentane and filtered. Cooling afforded yellow crystals.

The compounds $\text{CpRu}(\text{CO})_2\text{SnMe}_2\text{X}$ and $\text{CpRu}(\text{CO})_2\text{SnX}_2$ (*n*-Bu) ($\text{X} = \text{Cl}, \text{I}$) were prepared from $\text{CpRu}(\text{CO})_2\text{Na}$ and Me_2SnCl_2 or $\text{Cl}_3\text{Sn}(\text{n-Bu})$ and also by reaction of the chlorotin compounds with NaI in acetone.

Analytical results, melting points, and colors are presented in Table II-14 for all the new compounds prepared in this section.

TABLE II-14

Analytical Results, Melting Points, ^a and Colors of CpRu(CO)₂M'R₃
Compounds and CpRu(CO)H(SiCl₃)₂

Compounds	Required		Found		M.P.	Color
	C%	H%	Cl/I%	H%		
-M'R ₃						
-SiCl ₂ Me	28.6	2.4	21.0	3.0	19.9	oil
-SiPh ₂ Me	57.3	4.3	---	4.6	---	78-80
-SiCl ₂ Ph	39.2	2.5	17.9	2.6	20.6	68-69.5
-SiMe ₂ Ph	50.3	4.5	---	4.2	---	54.5-56
-SiPh ₃	62.4	4.2	---	5.0	---	158-161
-SiF ₃	27.4	1.6	---	1.8	---	88.5-90
-SiCl ₂ H	26.0	1.9	22.0	2.0	19.0	37-38.5
-SnI ₂ Me ^b	15.7	1.3	41.5	1.3	40.9	55-57
CpRu(CO)H(SiCl ₃) ₂						
	15.9	1.3	45.8	1.6	41.3	105-107

^aMelting points were determined on a Kofler Hot Stage #1356 apparatus.

^bExact mass measurement gave 611.6691, calculated for CpRu(CO)₂SnI₂Me, 611.6590.

CHAPTER III

MASS SPECTROSCOPY RESULTS

When one prepares an organometallic compound, a tentative confirmation of expected products immediately after reaction proves invaluable; assuming the product(s) are neutral and volatile, mass spectroscopy suits this purpose. Thus, by running the mass spectrum of a crude reaction product sample, the presence or absence of expected product(s) or contamination by undesirable side product(s) may be inferred. In most metal carbonyl derivatives, the parent molecular ion is observed and therefore species may be identified with particular ease. An exception to the above arises whenever complete fragmentation of the parent molecular ion occurs within the ionization chamber.

In fact, in the present work the compounds of formula $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ show the highest m/e fragment assignable to loss of an R group from the parent molecular ion. Therefore, the possibility that the highest m/e ion observed may correspond to something less than the molecular weight of the compound cannot be overlooked.

The important principle that one never observes m/e ions corresponding to fragments whose masses are greater than that of the molecular weight of the compound has been challenged in the literature.^{94,95} In each case, the authors have claimed to have observed $(P+L)^+$

ions. These results^{94,95} have been carefully studied in this laboratory,⁹⁶ and in each case the principle of the highest observed m/e corresponding to the parent ion and not to $(P + L)$ ions was reaffirmed.

Ions of masses greater than the molecular weight are possible upon rare occasions due to ion-molecule reactions. However, under the normal high vacuum conditions within the mass spectrometer, these events are confined to formation of $(P + H)^+$ ions, and even these ions are rare for inorganic compounds.⁹⁷

A further value of mass spectroscopy arises, in favorable cases, it allows one to infer something about the gross purity of the crude reaction product. This may be illustrated by an example.

The reaction of $[\text{CpFe}(\text{CO})_2]_2$ with HSiF_3 produces $\text{CpFe}(\text{CO})_2\text{SiF}_3$ along with significant amounts of ferrocene. Both compounds are highly volatile and a mass spectrum of crude product shows a typical spectrum for $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds as well as an intense peak at $m/e = 186$ signifying the presence of ferrocene. Such a peak would be absent for a pure sample of $\text{CpFe}(\text{CO})_2\text{SiR}_3$. Obviously, other techniques would show contamination; however, mass spectroscopy allows one to rapidly confirm the presence of a desired product as well as give a qualitative indication of its purity when impurities present are volatile.

In the present work, mass spectra of all the compounds prepared were run. From these spectra, a qualitative inferred fragmentation pattern that the various compounds exhibited, is presented. Only on rare instances were these fragmentation patterns confirmed by observation of metastable ions. It must be pointed out that fragmentation patterns are a sensitive function of conditions within the mass spectrometer, such as probe temperature and electron voltage applied. Results presented here were obtained on a locally modified AEI MS 2 apparatus operating at 70 ev with a source temperature sufficient to produce a parent ion. This temperature varied with the volatility of the compounds, and ranged from 20° to 200°. Since compounds of formula $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ did not exhibit a parent ion over this entire temperature range, chemical ionization was used. This experiment was performed on a AEI MS 12 instrument, the sample being introduced with methane gas. Ionization was accomplished at between 350 - 450 ev.

A. Results for Compounds of Type $\text{CpFe}(\text{CO})_2\text{SiR}_3$

The general inferred fragmentation pattern for these compounds is presented in flow chart format in Figure III-III. In every case, a parent ion was observed, although when one or two thioxy groups were attached to

silicon, the parent ion was very weak.

The dominant feature in the spectra of these compounds is stepwise loss of carbonyl ligands from $[\text{CpFe}(\text{CO})_n\text{SiR}_3]^+$ ($n = 2, 1$), both ions are usually intense peaks within the spectra. That this loss was indeed stepwise was confirmed by the observation of metastable peaks corresponding to $[\text{CpFe}(\text{CO})_n\text{SiR}_3]^+ \rightarrow [\text{CpFe}(\text{CO})_{n-1}\text{SiR}_3]^+$ ($n = 1, 2$). These metastable peaks were observed when one or more of the following R groups, where $\text{R} = \text{Ph}, \text{C}_6\text{F}_5, \text{OPh}, \text{SPh}, \text{OC}_6\text{F}_5, \text{SC}_6\text{F}_5$, was attached to silicon. Their intensity increased with increasing substitution of the above R groups at silicon.

Fragmentation ions corresponding to loss of R from silicon were generally observed, but these were much weaker than fragments arising from CO loss. When R was Ph, $\text{C}_6\text{F}_5, \text{OPh}, \text{SPh}, \text{OC}_6\text{F}_5, \text{SC}_6\text{F}_5$, these substituents were never observed to be lost from silicon.

When $\text{R} = \text{OR}'$ or SR' ($\text{R}' = \text{alkyl}$), loss of R' is observed. Also, elimination of an olefin group from OR' or SR' leaving a rearrangement fragment containing an OH or SH group was observed.

An indication of the stability of the Cp-Fe linkage may be appreciated from the fragmentation of $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds. One never observes loss of Cp or loss of any Cp fragment from any of the molecular ions produced. Generally, the most intense ion observed for these compounds

corresponded to CpFe^+ , and ions such as CpFeSi^+ , CpFeR^+ and CpFeSiR^+ are common.

The mass spectra of $\text{CpM}(\text{CO})_2\text{SiR}_3$ ($\text{M} = \text{Mo}, \text{W}$) compounds have also been studied⁹⁸ and are similar to the spectra observed for $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds.

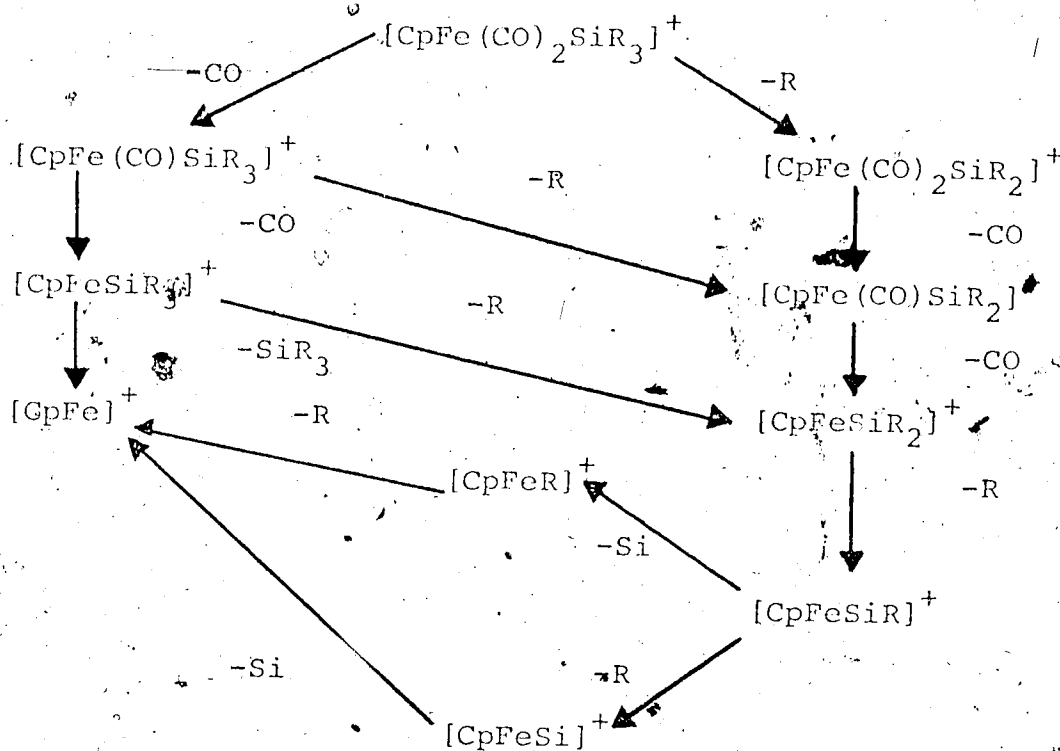


Figure III-III: Flow Chart Representation of the Inferred Fragmentation Pattern of $\text{CpFe}(\text{CO})_2\text{SiR}_3$ Compounds.

Results for Compounds of Type $\text{CpFe}(\text{CO})_{2-n}(\text{PMe}_2\text{Ph})_n\text{SiR}_3$
(n = 1,2)

The general inferred fragmentation pattern for the n = 1 compounds is presented in Figure III-IV.

The spectra are qualitatively similar to those just discussed. Loss of a CO group is observed to be facile, whereas loss of PMe_2Ph is not. Thus the ion $[\text{CpFePMe}_2\text{Ph}]^+$ is observed, but $[\text{CpFe}(\text{CO})]^+$ is never observed. Also, there is no competition between loss of CO and PMe_2Ph from the parent molecular ion, CO being lost preferentially.

The general fragmentation pattern for the n = 2 compounds is presented in Figure III-V.

Evidence for the less facile loss of a phosphine group compared to a CO group again is observed. Thus, the appearance of fragments $[\text{CpFe}(\text{PMe}_2\text{Ph})_n]^+$ (n = 2,1) is a feature of the breakdown pattern of these compounds. Note that no analogous carbonyl containing fragments were observed for $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds.

C. Results for Compounds of Type $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$

This class of compounds exhibits the most interesting mass spectra of all the compounds studied. The general inferred fragmentation pattern is presented in Figure III-VI.

No parent molecular ion was observed for these complexes even under the chemical ionization conditions described earlier. The compound $\text{CpRu}(\text{CO})\text{H}(\text{SiCl}_3)_2$ did exhibit a very weak parent ion, unlike the iron compounds.

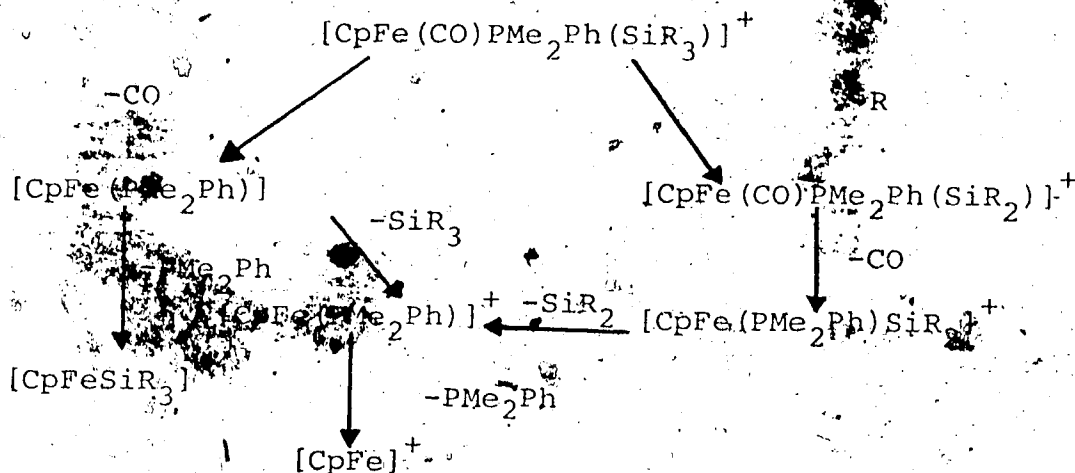


Figure III-IV: Flow Chart Representation of the Inferred Fragmentation Pattern of $\text{CpFe}(\text{CO})\text{PMe}_2\text{Ph}(\text{SiR}_3)$ Compounds.

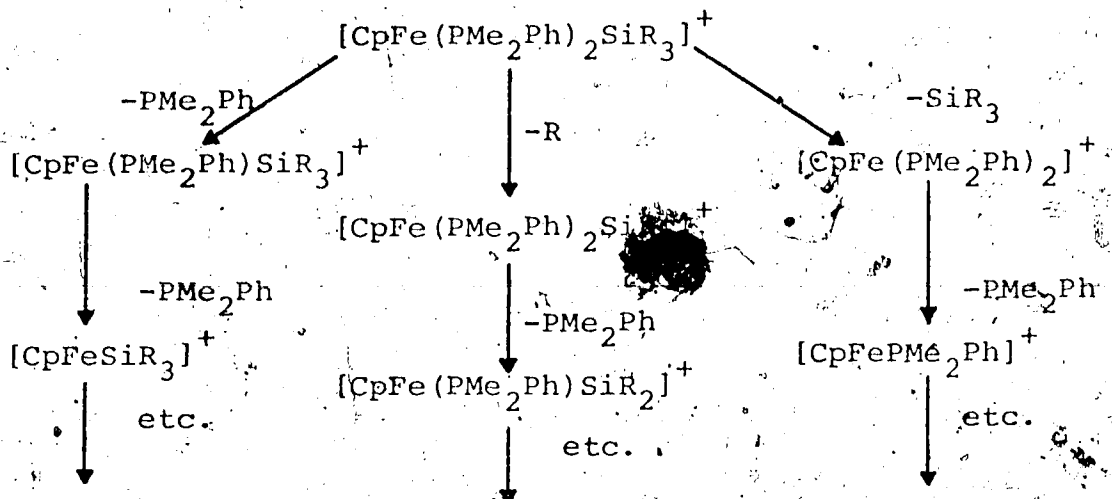


Figure III-V: Flow Chart Representation of the Inferred Fragmentation Pattern of $\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiR}_3$ Compounds.

* * * * *

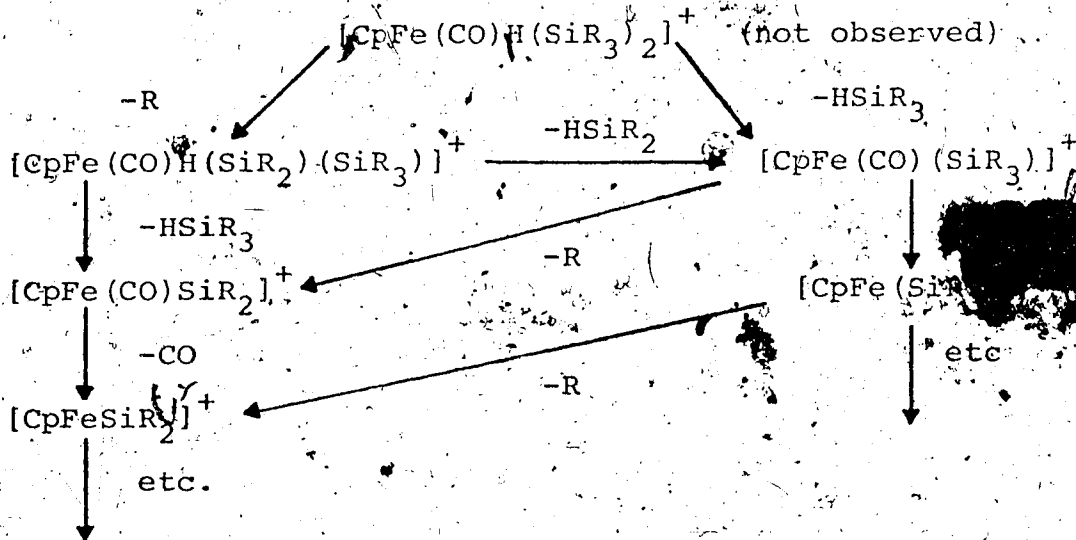


Figure III-VI: Flow Chart Representation of the Inferred Fragmentation Pattern of $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$.

The highest m/e ion observed corresponded to loss of an R substituent from silicon. This facile loss within the spectrometer followed the indicated order of ease: $\text{Cl} \approx \text{F} > \text{Me} \gg \text{Ph} \approx \text{C}_6\text{F}_5$. When two different substituents were present upon silicon, the loss of each possible R group was observed, excepting when $\text{R} = \text{Ph}$ or C_6F_5 . The latter groups were never lost from any of the observed fragments.

The highest m/e ion specifically fragments via loss of HSiR_n ($n = 3, 2$), and only thereafter is CO loss observed. This is quite unusual in view of results observed for the previously discussed compounds, however, this is consistent with results observed for $\text{CpMn}(\text{CO})_2\text{H}(\text{SiPh}_3)$.⁶¹

It is interesting to speculate as to the absence of a parent ion for these compounds. The highest m/e ion observed always corresponded to an ion which might be considered to possess a "silylene" group, that is, an R_2Si moiety analogous to a carbene, and which would donate two electrons to the iron in $[\text{CpFe}(\text{CO})\text{H}(\text{SiR}_2)(\text{SiR}_3)]^+$. That such an ion is favorably formed under the conditions within the mass spectrometer is interesting, but, as yet no chemical routes to these compounds have been found.

CHAPTER IV

INFRARED SPECTROSCOPY RESULTS

Organotransition metal complexes possessing one or more terminally bonded CO ligands characteristically exhibit intense C O stretching modes in the region 2200 - 1800 cm^{-1} . Furthermore, these modes are usually sharp, well resolved bands and provide insight into the structures of many carbonyl containing transition metal complexes.^{99,100,101} (Reference 99 is a useful review on vibrational spectra of metal carbonyl complexes.)

In the present work, the carbonyl infrared region was used as a probe to study the rotamer phenomenon,^{54,57} and effects that various substituents bound to silicon produce on the electron density distribution within these molecules. In order for such studies to be meaningful, it is necessary to obtain spectra of optimum resolution. Thus, all spectra were run on a Perkin-Elmer 337 Grating instrument equipped with a slow scan motor (39 $\text{cm}^{-1}/\text{min}$). This instrument possesses the important feature of not having a grating change at 2000 cm^{-1} . Spectra were recorded on a Hewlett-Packard Model 7127A external recorder and were calibrated with the 2147 cm^{-1} band of carbon monoxide.

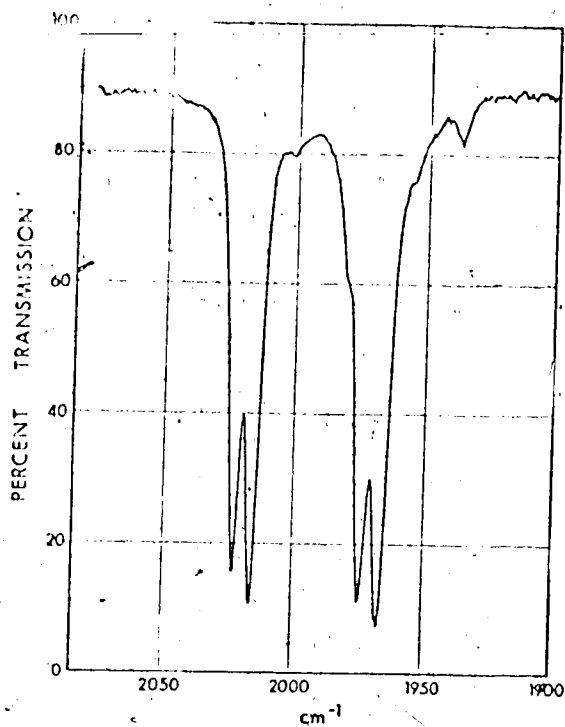
A. Compounds of Type $\text{CpFe}(\text{CO})_2\text{SiR}_3$

i) Assignment of Rotamers in $\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ -Compounds

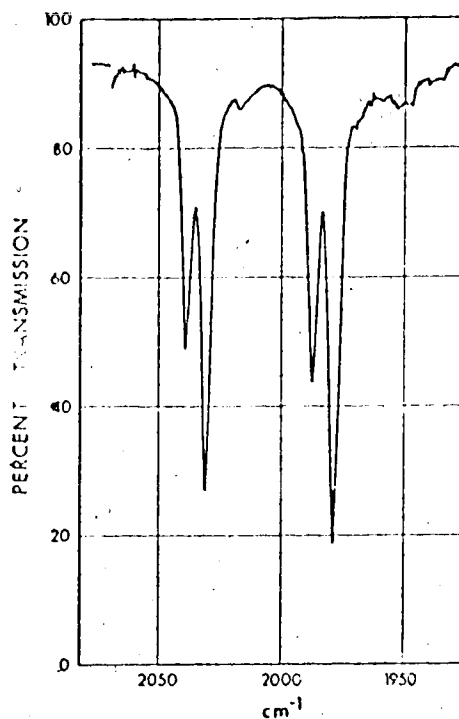
An outline of the rotamer phenomenon observed for $\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ compounds was presented in Chapter I. It will now be instructive to discuss the assignment of the two conformers (see Figure I-1) to the observed carbonyl bands. Representative spectra are displayed in Figure IV-VII.

The procedure adopted has been described in the literature and applied to $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Me}$.⁵⁷ The basis for this method is as follows: One of the rotamers possesses a mirror plane; therefore, both CO ligands are equivalent. Monosubstitution of ^{13}C O into this rotamer produces a satellite band to lower wavenumber of the ^{12}C O stretching mode. The other rotamer possesses no symmetry (see Figure I-1); therefore, ^{13}C O monosubstitution produces two satellite bands below each ^{12}C O mode. Thus, by scanning the ^{13}C O satellite region, a differentiation of the two conformers is possible. Since ^{13}C is 1.1% naturally abundant, nature provides convenient monosubstitution, free of ^{13}C O disubstitution.

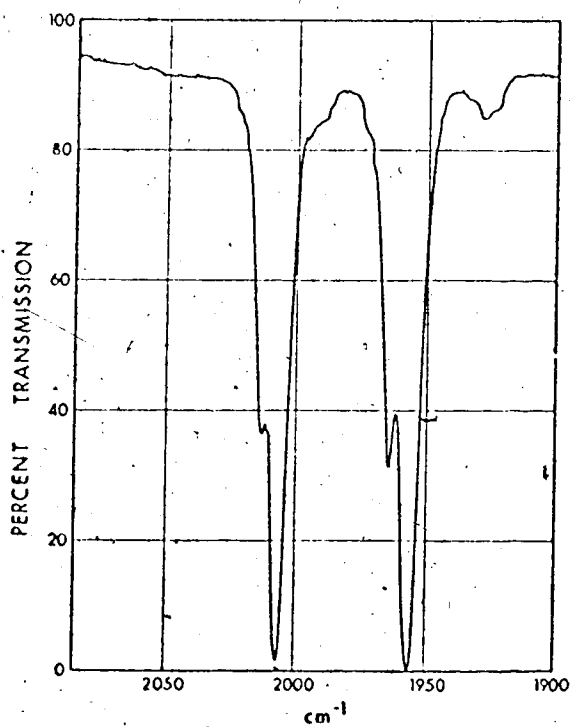
In order to assign unambiguously these satellite bands to the appropriate ^{12}C O stretching modes, the following considerations are necessary. Satellites arising from monosubstituted ^{13}C O molecules are often observed.^{102,103}



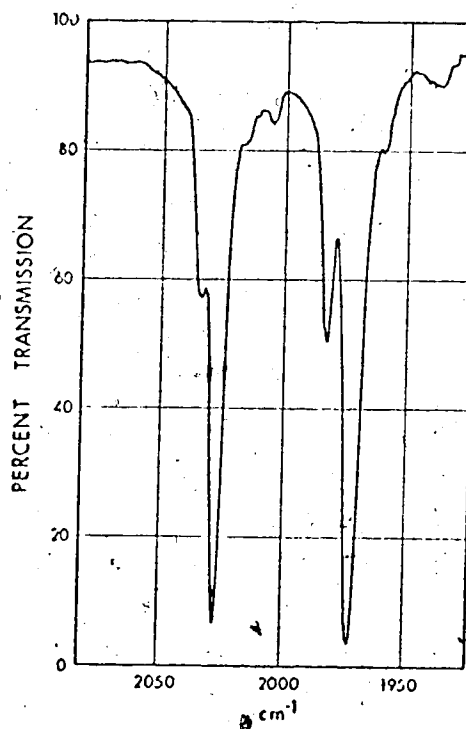
$\text{CpFe}(\text{CO})_2\text{SiF}_2\text{Me}$



$\text{CpRu}(\text{CO})_2\text{SiCl}_2\text{Me}$



$\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{F}$



$\text{CpRu}(\text{CO})_2\text{SiMe}_2\text{Cl}$

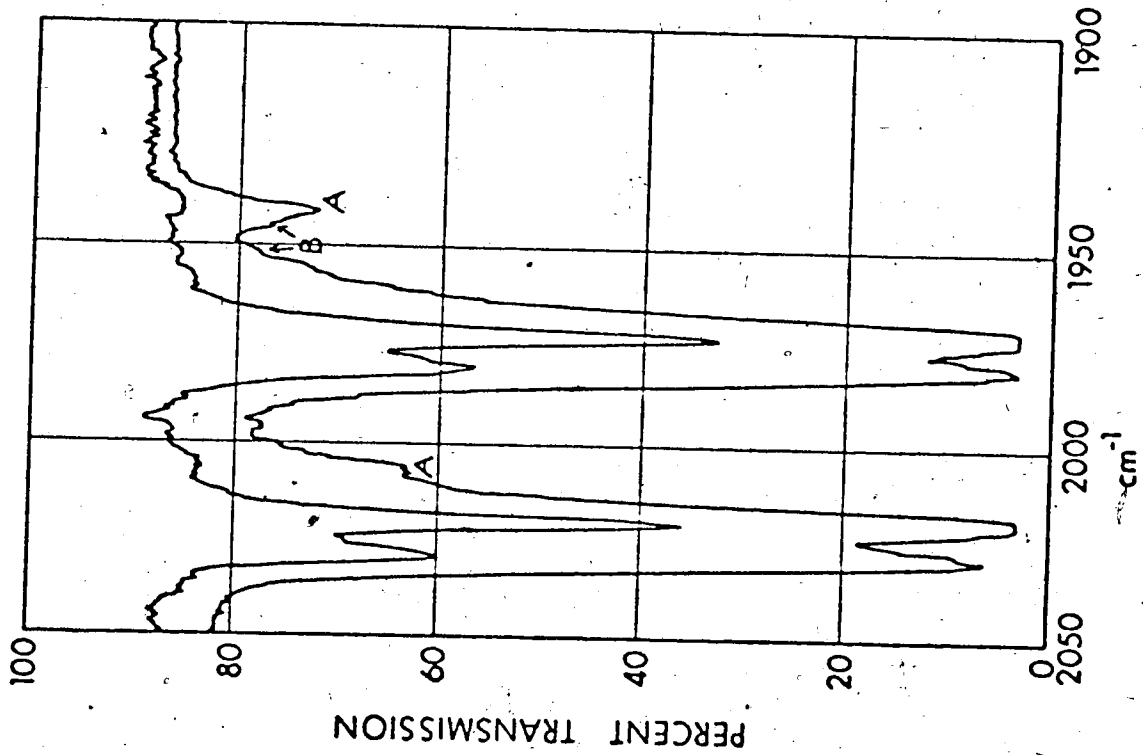
Figure IV-VII: Representative Carbonyl I.R. Spectra of $\text{CpM}(\text{CO})_2\text{M}'\text{R}_3$ Compounds, Exhibiting Rotamers.

They appear to lower wavenumber of the corresponding ^{12}CO bands since frequencies depend upon the square root of the inverse reduced mass of the atoms involved.

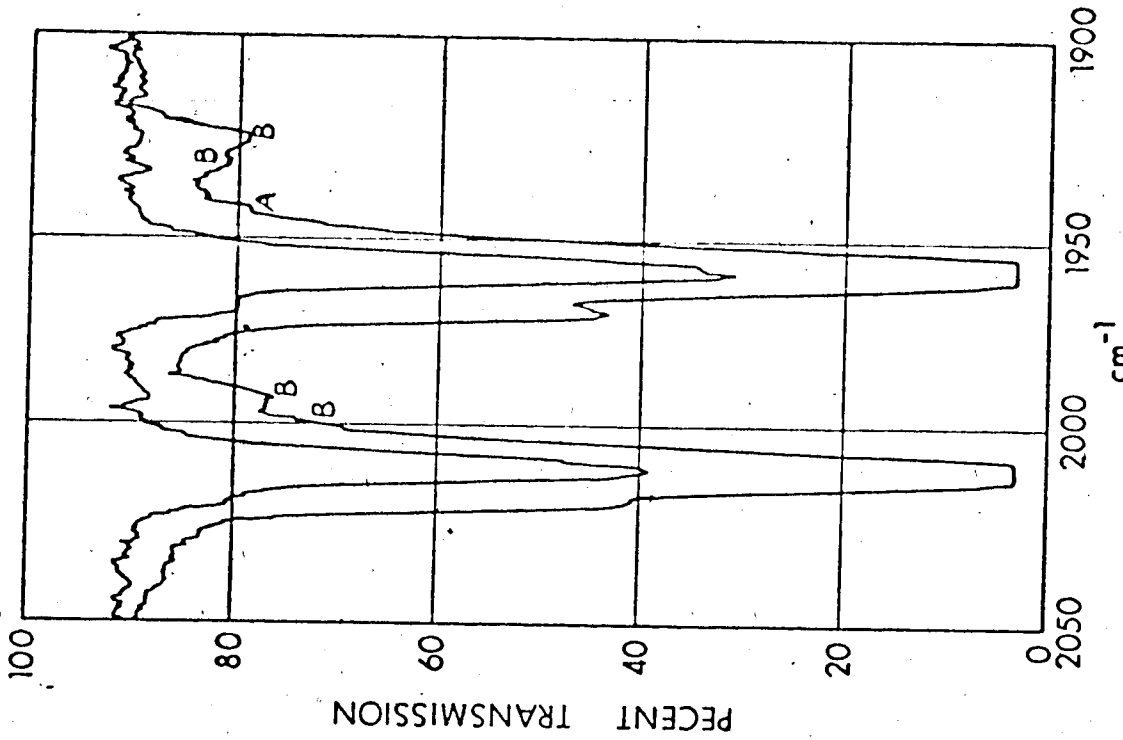
Thus, the inverse reduced mass of ^{13}CO is less than that of ^{12}CO . If we consider a single ^{12}CO mode at 2000 cm^{-1} , then the corresponding ^{13}CO frequency will be shifted down by 45 cm^{-1} .

For the case of mono- ^{13}CO substitution into $\text{L}_n\text{M}(\text{CO})_x$, the downfield shift of satellites will be divided between all CO vibrational bands, the total shift amounting to $\sim 45\text{ cm}^{-1}$. For compounds of type $\text{CpM}(\text{CO})_2\text{M}'\text{R}_3$, the stretching modes correspond to symmetric and antisymmetric bands. It is a feature of these compounds that one observes satellites ~ 14 and $\sim 31\text{ cm}^{-1}$ below these respective modes (cf., $\text{CpFe}(\text{CO})_2\text{SiF}_3$, ^{12}CO at 2036, 1988; ^{13}CO at 2022, 1957).

Utilizing these principles, satellites may be paired with the appropriate ^{12}CO bands since we expect, for the C_s rotamer, one satellite $\sim 14\text{ cm}^{-1}$ below the symmetric mode and a second, $\sim 31\text{ cm}^{-1}$ below the antisymmetric ^{12}CO mode. Similarly, for the C_1 rotamer, two pairs of satellites whose centroids occur $\sim 14\text{ cm}^{-1}$ and $\sim 31\text{ cm}^{-1}$ below each ^{12}CO mode, should be observed. This is demonstrated in Figure IV-VIII. For $\text{CpFe}(\text{CO})_2\text{Si}(\text{OC}_6\text{F}_5)_2\text{Me}$, the more intense ^{12}CO band is assigned to the C_s isomer on the basis of the position of the satellite labeled A.



CpFe(CO)₂Si(OC₆F₅)₂Me



CpFe(CO)₂SiMe(OC₆F₅)

Figure IV-VIII: Example of spectra showing ¹³C satellites used in assignment of rotamers to observed ¹²C bands. Bands labelled A correspond to C_S, those-labelled B correspond to C_I rotamer.

For $\text{CpFe}(\text{CO})_2\text{SiMe}_2(\text{OC}_6\text{F}_5)$, the more intense ^{12}C CO band is assigned to the C_1 isomer on the basis of the position of the satellites labeled B.

In practice, not all the satellites are observed due to the proximity of the symmetric stretching ^{12}C mode to the ^{13}C CO modes. Nevertheless, the large separation that is observed between the antisymmetric stretch and the corresponding satellites, allows assignment to be made.

The satellite region is scanned by running the spectrum of a concentrated solution of the appropriate compound in a nonpolar solvent, the solvent chosen being *n*-heptane. A nonpolar solvent such as *n*-heptane is important since the molecules will be free from solvation effects and sharp bands will be observed.

The basis for assignment of the two possible rotamers of $\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ compounds was just described. Essentially the same method was applied to $\text{CpMn}(\text{CO})_2\text{SR}_2$ compounds,¹⁰⁴ where the lone pair on sulfur produces the possibility of rotamers. In that study, variation of the R substituent (R = alkyl) produced no apparent changes in the rotamer populations.¹⁰⁴ In the present work, wholesale changes were observed when substituents were varied. The results of this study will be presented in part (Aiii) of this Chapter.

ii) Force Constant Results for C_s and C_1 Conformers of $CpFe(CO)_2SiR_3$

When infrared spectra trends for a series of related compounds are studied, C-O stretching force constants are particularly useful.^{12,42} In the present work, an energy factored force field analysis was carried out on $CpM(CO)_2M'R_3$ ($M = Fe, Ru; M' = C, Si, Sn$) compounds, utilizing the computer program MOLVIBS.¹⁰⁵ This program requires $(n + 1)$ frequencies to iterate for n force constants and predict all relevant carbonyl bands. Since there are two force constants for the C_s rotamer and three for the C_1 rotamer, the problem is solvable. Furthermore, it provides a check upon the assignments made according to the procedure described in part (Ai) of this Chapter. Thus, observed and predicted CO band positions were generally found to agree within $\pm 1 \text{ cm}^{-1}$.

In Table IV-15, a list of force constants and observed CO bands is presented for the C_s rotamer of $CpM(CO)_2M'R_3$ compounds. Similarly, in Table IV-16, the data for the C_1 rotamer is presented.

The expected trend of decreasing carbonyl stretching force constants with increasing electron releasing properties of the R substituents is observed.^{40,106} Thus, strong electron withdrawing groups such as F, Cl, or C_6F_5 cause a drift of electron density from iron to silicon. This either reduces π electron density within the

Table IV-15.

Force Constants^a and Observed Infrared Bands^b for the C_s Rotamer
of CpM(CO)₂M'X₂R (M = Fe, Ru; M' = C, Si, Sn) Compounds

Compound M-M'X ₂ R	Force Constants		Observed I.R. Bands ^c cm ⁻¹
	k	k _i	
Ru-SiCl ₃	16.62	0.40	2053, 2005; 2039, 1974
Ru-SiF ₃	16.57	0.42	2051, 2000; 2038, 1968
Fe-C ₂ F ₅	16.61	0.39	2051.5, 2005; 2038, 1972.5
Fe-C ₃ F ₇	16.61	0.39	2051, 2005; 2038, 1972.5
Fe-SiCl ₃	16.43	0.36	2038, 1995; 2025, 1962
Ru-SiCl ₂ H	16.39	0.40	2040, 1990.5; 2024, 1959
Ru-SiCl ₂ Ph	16.37	0.42	2039, 1987; 2026, 1957
Fe-SiF ₃	16.35	0.39	2036, 1988; 2022, 1957
Ru-SnCl ₂ Me ^d	16.35	0.39	2035.5, 1988.5; 2022, 1957
Ru-SnI ₂ Me	16.32	0.39	2033.5, 1986; 2020, 1955
Ru-SiCl ₂ Me	16.30	0.43	2035, 1982.5; 2019, 1952
Ru-SiMe ₂ Cl ^d	16.28	0.43	2034, 1981; 1953
Fe-SiCl ₂ H	16.23	0.38	2027, 1980; 2015, 1949
Ru-SiF ₂ Me ^d	16.22	0.45	2031, 1976; 2015, 1944
Fe-Si(OC ₆ F ₅) ₂ Ph	16.22	0.40	2029, 1980; 2014, 1948
Ru-SnMe ₂ Cl ^d	16.22	0.40	2030, 1978; 1946
Ru-SnMe ₂ I ^d	16.21	0.40	2030, 1977; 1946

Table IV-15 (continued)

Compound M-M'X ₂ R	Force Constants		Observed I.R. Bands ^c cm ⁻¹
	k	k _i	
Fe-Si(C ₆ F ₅) ₂ Ph	16.21	0.40	2027, 1980; 2014, 1948
Fe-SnCl ₂ Ph	16.19	0.34	2023, 1980.5; 2010, 1949
Fe-Si(SC ₆ F ₅) ₂ Ph	16.19	0.37	2025, 1979; 2011, 1949
Ru-SiMe ₂ F ^d	16.18	0.45	2029, 1974; 2014, 1944
Fe-SiCl ₂ Ph	16.17	0.39	2025, 1979; 2010, 1949
Fe-SiCl ₂ (CH=CH ₂)	16.17	0.40	2024, 1977; 2010, 1946
Fe-Si(SPh) ₂ Ph	16.17	0.37	2024, 1978; 2010, 1946
Fe-SnI ₂ Ph	16.16	0.33	2020.5, 1979.5; 2008, 1948
Fe-Si(OC ₆ F ₅) ₂ Me	16.13	0.39	2022, 1974; 2009, 1943
Fe-SnCl ₂ Me	16.13	0.35	2020, 1977; 2005, 1947
Fe-SiCl ₂ Me	16.12	0.40	2022, 1973; 2007, 1940
Fe-SiCl ₂ (<i>t</i> -Bu) ^d	16.11	0.39	2021.5, 1973; 2007, 1942
Fe-SiF ₂ H	16.11	0.38	2021, 1974; 2007, 1944
Fe-SiF ₂ Ph	16.10	0.41	2022, 1971; 2007, 1939
Fe-Si(C ₆ F ₅) ₂ Me	16.10	0.38	2020, 1973.5; 2007, 1942
Fe-Si(SC ₆ F ₅) ₂ Me	16.09	0.38	2020, 1971.5; 2005, 1943
Fe-SiPh ₂ Cl	16.08	0.38	2019, 1973; 1941
Fe-Si(OCH ₂ CF ₃) ₂ Me	16.07	0.40	2019.5, 1970; 1940
Fe-SiMe ₂ (OC ₆ F ₅)	16.06	0.39	2018, 1970; 1939
Fe-SiMe ₂ Cl	16.05	0.39	2018, 1970; 1939

Table IV-15 (continued)

Compound M-M'X₂R

	Force Constants		Observed I.R. Bands ^c cm ⁻¹
	k	k _i	
Fe-SiF ₂ (CH=CH ₂)	16.05	0.41	2018.5, 1969; 2005, 1942
Ru-SiPh ₃	16.05	0.44	2021, 1966; 2005, 1936
Fe-SnMe ₂ Cl	16.04	0.35	2015, 1971; 2002, 1940
Fe-SnMe ₂ I	16.02	0.35	2013, 1970; 2000, 1939
Fe-SiF ₂ Me	16.02	0.41	2017, 1966; 2003, 1934
Fe-SiPh ₂ F	16.02	0.39	2015.5, 1967; 2002, 1936
Fe-Si(SPh) ₂ Me	15.99	0.39	2013.5, 1966; 2001, 1934.5
Fe-Si(SET) ₂ Me	15.99	0.38	2013.5, 1966; 2000, 1935
Ru-SiPh ₂ Me	15.99	0.44	2017, 1961.5; 2002, 1931
Fe-SiMe ₂ F	15.97	0.41	2014, 1963; 1934
Fe-Si(OPh) ₂ Ph	15.94	0.40	2011.5, 1962; 1931
Fe-SiH ₃	15.93	0.39	2010, 1962; 1995, 1933
Ru-SiMe ₂ Ph	15.92	0.46	2013.5, 1956.5; 1997.5, 1926
Fe-Si(OMe) ₂ Me	15.89	0.43	2009, 1957; 1996, 1926
Fe-Si(OPh) ₂ Me	15.89	0.42	2008.5, 1957; 1993, 1926
Fe-Si(OMe) ₂ Ph	15.89	0.41	2008.5, 1958; 1996, 1927.5
Fe-SiMe ₂ (SC ₆ F ₅)	15.88	0.39	2008, 1958.5; 1993, 1928
Fe-Si(OEt) ₂ Ph	15.87	0.41	2007.5, 1957; 1926
Fe-Si(OEt) ₂ Me	15.86	0.41	2007, 1956; 1925
Fe-SiMe ₂ (C ₆ F ₅)	15.85	0.41	2006.5, 1955; 1925

Table IV-15 (continued)

Compound $M=M'X_2R$	Force Constants		Observed I.R. Bands cm^{-1}
	k	k_i	
Fe-Si(Oi-Pr) ₂ Ph	15.85	0.41	2007, 1956; 1993, 1924.5
Fe-Si(Oi-Pr) ₂ Me	15.84	0.42	2006, 1954; 1993, 1923.5
Fe-SiPh ₂ H	15.84	0.41	2006, 1955; 1990, 1925
Fe-Si(Ot-Bu) ₂ Me	15.83	0.43	2006.5, 1953; 1922
Fe-SiPh ₃	15.83	0.41	2005, 1954; 1990, 1924
Fe-SiPh ₂ Me	15.79	0.40	2002, 1952; 1988, 1919.5
Fe-SiMe ₂ (OPh)	15.78	0.42	2003, 1950.5; 1988, 1920
Fe-SiPh ₂ (OEt)	15.76	0.42	2001, 1950.5; 1988, 1918
Fe-SiPh ₂ (OMe)	15.76	0.42	2001, 1950.5; 1988, 1918
Fe-SiMe ₂ (OCH ₂ CF ₃)	15.86	0.42	2001, 1949; 1988, 1918
Fe-SiMe ₂ (Si-Pr)	15.75	0.41	2000, 1949; 1987, 1919
Fe-SiMe ₂ (p-C ₆ H ₄ F)	15.74	0.41	2000, 1949; 1985.5, 1917
Fe-SiMe ₂ OSiMe ₂ -Fe	15.73	0.44	2000, 1947; 1987, 1915.5
Fe-SiMe ₂ (SET)	15.73	0.43	2000, 1947; 1986, 1916.5
Fe-SiMe ₂ (SPh)	15.73	0.43	2000, 1947; 1986, 1916
Fe-SiMe ₂ (OH)	15.72	0.44	2000, 1945.5; 1986, 1915
Fe-SiMe ₂ (t-Bu)	15.71	0.41	1998, 1946.5; 1984, 1915.5
Fe-SiMe ₂ (Oi-Pr)	15.70	0.43	1998.5, 1944.5; 1984, 1914
Fe-SiMe ₂ (o-C ₆ H ₄ Me)	15.70	0.41	1997, 1946; 1983, 1915.5
Fe-SiMe ₂ Ph	15.70	0.41	1997, 1946; 1982.5, 1913

Table IV-15 (continued)

Compound M-M'X₂R

Compound M-M'X ₂ R	Force Constants		Observed I.R. Bands ^c , cm ⁻¹
	k	k _i	
Fe-SiMe ₃	15.69	0.43	1998, 1944; 1982.5, 1913
Fe-SiMe ₂ (Ot-Bu)	15.69	0.43	1998, 1944.5; 1984, 1914
Fe-SiMe ₂ (p-C ₆ H ₄ SiMe ₂)-Fe	15.69	0.41	1997, 1946; 1982.5, 1915
Fe-SiMe ₂ (OMe)	15.68	0.42	1997, 1944.5; 1982.5, 1913.5
Fe-SiEt ₂ Ph	15.68	0.42	1996.5, 1945; 1982.5, 1914
Fe-SiMe ₂ (p-C ₆ H ₄ Me)	15.68	0.41	1996, 1944.5; 1982, 1914
Fe-SiMe ₂ (p-C ₆ H ₄ OMe)	15.67	0.42	1996, 1944; 1982, 1913.5
Fe-SiMe ₂ (OEt)	15.67	0.42	1996, 1943.5; 1982, 1913
Fe-SiMe ₂ (t-Bu)	15.66	0.41	1998, 1946.5; 1984, 1915.5
Fe-SiMe ₂ (p-C ₆ H ₄ NMe ₂)	15.64	0.42	1994, 1942.5; 1980, 1911

^aUnits for force constants are millidynes/Å.

^bBand intensities are not assessed since rotamer populations are measured accurately in part (Aiii) of this chapter.

^cBands listed after the semicolon correspond to ¹³CO satellites.

^dThese compounds were incompletely characterized.

Table IV-16

Force Constants^a and Observed Infrared Bands^b for the C₁ Rotamer
of CpM(CO)₂M'X₂R (M = Fe, Ru; M' = C, Si, Sn) Compounds

Compound	Force Constants ^c		Observed I.R. Bands ^c , cm ⁻¹
	M-M'X ₂ R k ₁	k ₂ · k _i	
Fe-C ₃ F ₇	16.50	16.58	0.40 2047.5, 2001; 2036, 2033, 1969, 1965
Fe-C ₂ F ₅	16.49	16.59	0.39 2047, 2000.5; 2036, 2032, 1970, 1966
Ru-SiCl ₂ H	16.42	16.58	0.39 2045.5, 1997; 2028, 1963
Ru-SnCl ₂ Me ^d	16.42	16.56	0.37 2044, 1998; 1969, 1963
Ru-SnI ₂ Me	16.39	16.50	0.37 2040.5, 1995; 1996, 1961
Ru-SiCl ₂ Ph	16.37	16.52	0.44 2042.5, 1992; 1965, 1959
Ru-SiCl ₂ Me	16.34	16.54	0.41 2043.5, 1992; 2025, 1965, 1957
Fe-SiCl ₂ H ^e	16.27	16.34	0.39 2033, 1987; 1955, 1952
Ru-SiF ₂ Me ^d	16.23	16.46	0.44 2039, 1984; 2020, 1949
Fe-Si(SC ₆ F ₅) ₂ Ph	16.23	16.32	0.36 2029.5, 1984; 1956, 1952
Fe-SnCl ₂ Ph	16.22	16.43	0.33 2032, 1988; 1963, 1954
Fe-Si(SC ₆ F ₅) ₂ Me	16.20	16.32	0.37 2029, 1982; 2018, 2013, 1955, 1950
Fe-Si(OC ₆ F ₅) ₂ Me	16.18	16.35	0.40 2031.5, 1982; 2014, 1954, 1947
Fe-SiCl ₂ (CH=CH ₂) ^e	16.18	16.35	0.38 2039, 1983.5; 2018, 2014, 1955, 1949
Fe-SiCl ₂ (t-Bu) ^e	16.19	16.23	0.39 2039, 1983; 2015, 1947
Fe-SiCl ₂ Me	16.19	16.28	0.37 2028, 1981; 1953, 1949
Fe-SnI ₂ Ph	16.17	16.37	0.31 2027, 1986; 1960, 1951

Si l'on compare ces vers au "Flambeau vivant", pourtant, on remarquera que, bien que la figure de Madame Sabatier joue un rôle de protectrice et de guide dans ces deux poèmes, dans "Le Flambeau vivant", la lumière qui rayonne des yeux de la Présidente est plus intense que le feu solaire, tandis que dans "L'Aube spirituelle", la clarté du souvenir est égale à la splendeur du soleil levant.

Charmants Yeux, vous brillez de la clarté mystique
 Qu'ont les cierges brûlant en plein jour; le soleil
 Rougit, mais n'éteint pas leur flamme fantastique!

Astres dont nul soleil ne peut flétrir la flamme! (33)

"Le Flambeau vivant" ressemble en ce sens à "Harmonie du soir", car tous les deux empruntent l'image d'une source lumineuse plus forte que le soleil lui-même. Cette source, c'est le souvenir qui reste après le fait dans "Harmonie du soir"; dans "Le Flambeau vivant", c'est une flamme spirituelle: dans les deux poèmes, l'énergie psychique l'emporte donc sur l'énergie cosmique, selon le principe de la suprématie de l'Idéal sur le Réel auquel, comme nous avons vu, Baudelaire adhérerait en dépit des lois de la raison, il est vrai, mais fidèle à son esthétique. Seul le soleil de "L'Aube spirituelle" peut égaler l'intensité du souvenir parce que, lui aussi, a une valeur spirituelle, celle de la rédemption et du salut, tandis que dans les deux autres pièces le soleil représente ce qui avait été (l'amour dans "Harmonie du soir") et qui n'est plus, ou un emblème purement plastique sans aucune résonance spirituelle ("Le Flambeau vivant").

Si l'image solaire est utilisée comme symbole de ce qu'on pourrait appeler la femme solaire d'où irradie une chaleur spirituelle qui purifie et guérit, il y eut un moment dans la vie de Baudelaire où ce dernier

Table 16 (continued)

Compound, M-M'X ₂ R	Force Constants		Observed I.R. Bands ^c , cm ⁻¹
	k ₁	k ₂ k _i	
Fe-SiPh ₂ Cl	15.91	16.05 0.39	2014, 1965.5; 1996, 1937, 1931
Fe-SiMe ₂ (SC ₆ F ₅)	15.89	16.07 0.40	2014, 1964; 1997, 1937, 1929
Fe-SiMe ₂ (OPh)	15.88	15.95 0.41	2010, 1960; 1931, 1926
Fe-Si(OCH ₂ CF ₃) ₂ Me	15.84	16.01 0.43	2012, 1959; 1932, 1925
Fe-SiMe ₂ (C ₆ F ₅)	15.85	15.97 0.39	2011, 1960; 1996, 1993, 1933, 1926.5
Fe-SiMe ₂ (OC ₆ F ₅)	15.84	15.98 0.41	2010.5, 1959.5; 1994, 1931, 1925
Fe-SiPh ₂ F	15.83	15.98 0.39	2011, 1959.5; 1997, 1992, 1933, 1926
Fe-SiPh ₂ (OEt)	15.82	15.98 0.40	2009, 1960; 1931, 1924
Fe-SiMe ₂ Cl	15.81	15.99 0.41	2010, 1958; 1998, 1993, 1933, 1924
Fe-SiPh ₂ (OMe)	15.81	15.99 0.40	2009.5, 1959.5; 1931, 1924
Fe-SiMe ₂ (SET)	15.80	15.90 0.41	2006, 1954.5; 1995, 1991, 1927, 1923
Fe-Si(SET) ₂ Me	15.78	15.95 0.41	2008, 1957; 1996, 1990, 1930, 1920
Fe-SnMe ₂ Cl	15.78	15.96 0.35	2005, 1959; 1994, 1987, 1934, 1925
Fe-SiMe ₂ (SET)	15.77	15.95 0.41	2008, 1956.5; 1997, 1989, 1929, 1922
Fe-SiMe ₂ F	15.77	15.91 0.41	2007, 1953; 1995, 1989, 1927, 1921
Fe-SiMe ₂ (OMe)	15.75	15.9 0.41	2006, 1954; 1928, 1921
Fe-SiMe ₂ (OCH ₂ CF ₃)	15.77	15.90 0.42	2006, 1953.5; 1995, 1990, 1926, 1921
Fe-SnMe ₂ I	15.75	15.93 0.43	2003.5, 1956.5; 1991, 1985, 1933, 1924
Fe-SiMe ₂ (OEt)	15.73	15.95 0.41	2007, 1955; 1928, 1920
Fe-SiMe ₂ (Si-Pr)	15.73	15.94 0.41	2006, 1954.5; 1995, 1987, 1928, 1919
Fe-SiMe ₂ (O <i>i</i> -Pr)	15.75	15.90 0.39	2004, 1955; 1927, 1921
Fe-SiMe ₂ (<i>p</i> -C ₆ H ₄ F)	15.77	15.84 0.42	2004.5, 1953; 1991, 1988, 1923, 1920

Table 16 (continued)

Compound M-M'X ₂ R	Force Constants		Observed I.R. Bands ^c , cm ⁻¹	
	k ₁	k ₂		
Fe-SiMe ₂ (Ot-Bu)	15.75	15.88	0.41	2004, 1952.5; 1988, 1926, 1922
Fe-SiMe ₂ (o-C ₆ H ₄ Me)	15.74	15.84	0.41	2003, 1952.5; 1987, 1923, 1919
Fe-Si(OMe) ₂ Ph	15.73	15.83	0.42	2002, 1950; 1992, 1987, 1923, 1919
Fe-SiMe ₂ (OH)	15.73	15.84	0.43	2004, 1950; 1922, 1918
Fe-Si(OMe) ₂ Me	15.73	15.83	0.44	2004, 1949.5; 1992, 1988, 1921, 1917
Fe-SiMe ₂ (p-C ₆ H ₄ SiMe ₂)-Fe	15.73	15.82	0.42	2002, 1950.5; 1991, 1987, 1921, 1918
Fe-SiMe ₂ Ph	15.71	15.81	0.41	2001, 1950.5; 1986, 1922, 1917
Fe-SiMe ₂ (p-C ₆ H ₄ Me)	15.71	15.81	0.41	2001, 1950; 1985, 1921, 1917
Fe-SiEt ₂ Ph	15.69	15.84	0.41	2001.5, 1950; 1923, 1917
Fe-Si(OEt) ₂ Ph	15.68	15.83	0.41	2001.5, 1948; 1920, 1915
Fe-SiMe ₂ (p-C ₆ H ₄ OMe)	15.70	15.80	0.41	2000.5, 1949.5; 1984, 1920, 1916
Fe-Si(OEt) ₂ Me	15.66	15.81	0.43	2001, 1947.5; 1920, 1914
Fe-Si(Ot-Bu) ₂ Me	15.66	15.81	0.43	2001, 1947; 1920, 1914
Fe-Si(Oi-Pr) ₂ Me	15.66	15.78	0.43	2000, 1946; 1988, 1983, 1918.5, 1913
Fe-Si(Oi-Pr) ₂ Ph	15.65	15.78	0.44	1999.5, 1946; 1988, 1984, 1918, 1912
Fe-SiMe ₂ (p-C ₆ H ₄ NMe ₂)	15.68	15.75	0.42	1999, 1948; 1985, 1920, 1916

^a Units for force constants are millidynes/Å.

^b Band intensities are not assessed since rotamer populations are measured accurately in part (Aiii) of this Chapter.

^c Bands listed after the semicolon correspond to ¹³C satellites.

^d These compounds were incompletely characterized.

iron-CO bond, or causes enhanced π bond donation to iron from carbonyl carbon. The net effect of either, or more likely both of the above, is to raise the CO stretching force constants.⁴²

When analogous silicon/tin $\text{CpFe}(\text{CO})_2\text{M}'\text{R}_3$ ($\text{M}' = \text{Si}, \text{Sn}$) compounds are compared, the force constants are observed to be virtually constant (*cf.*, $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Me}$, C_s rotamer, $k = 16.12$ and C_1 rotamer, $k_1 = 16.19$ and $k_2 = 16.28$; $\text{CpFe}(\text{CO})_2\text{SnCl}_2\text{Me}$, C_s rotamer, $k = 16.13$ and C_1 rotamer, $k_1 = 16.17$ and $k_2 = 16.42$). This suggests that the iron-M' bond is very similar in these compounds.

Comparison of analogous iron/ruthenium $\text{CpM}(\text{CO})_2\text{SiR}_3$ ($\text{M} = \text{Fe}, \text{Ru}$) compounds, shows an increase of ~ 0.2 millidynes/Å when iron is replaced with ruthenium (*cf.*, $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Me}$, C_s rotamer, $k = 16.12$ and C_1 rotamer, $k_1 = 16.19$ and $k_2 = 16.28$; $\text{CpRu}(\text{CO})_2\text{SiCl}_2\text{Me}$, C_s rotamer, $k = 16.30$ and C_1 rotamer, $k_1 = 16.34$ and $k_2 = 16.54$). This indicates that either the ruthenium-CO π bond is weaker than the iron-CO π bond, or ruthenium-CO σ bond is stronger than the iron-CO σ bond.

There are two principal force constants for the C_1 rotamer, arising since each CO group is transoid to either X or R (see Figure I-I). If X is the disubstituent on silicon, then in the C_s rotamer each CO group is transoid to X. Dalton⁵⁷ has suggested that the C_1 force constant which more closely corresponds to the C_s force constant, may be assigned as the one arising from the CO group

transoid to X. This procedure was not adopted here since it is not clear how substituents so far removed from the CO ligands will effect CO force constants (*i.e.*, inductive or mesomeric effects, or a combination of both).

Force constants listed in Table IV-16 are presented arbitrarily, so that the lower force constant appears first. Comparison of the same compounds in Tables IV-15 and IV-16 reveals that generally the C_1 force constants are greater than C_s . The significance of this is not known.

iii) Rotamer Populations and Trends Observed for $CpM(CO)_2M'R_3$ Compounds

It was pointed out under part (Ai) of this Chapter that a large variation in rotamer populations for $CpM(CO)_2M'R_3$ compounds is observed when R substituents are varied. On a statistical basis, the C_1 rotamer is favored two to one over the C_s . However, temperature dependent infrared studies on $CpFe(CO)_2SiCl_2Me$ show $\Delta H \approx 1$ kcal/mole in favor of the C_s rotamer.¹⁰⁷ A similar study on a series of $CpFe(CO)_2GeX_2R$ compounds indicated enthalpy differences of 0.7 - 2.3 kcal/mole, in favor of the C_s conformer.¹⁰⁸

In the present work, several series of $CpM(CO)_2M'X_2R$ compounds were studied with a view towards determining what factors influence rotamer populations for these compounds. Measurement of band intensities, and hence populations, was

accomplished with the aid of a Model 310 Dupont Curve Resolver. This instrument permits resolution of up to seven overlapping Gaussian or Lorentzian curves and allows one to determine the individual peak heights. Typically, a spectrum was measured and the two sets of rotamer bands were resolved, establishing the peak heights of each rotamer for both the symmetric and antisymmetric stretching modes. Populations were then determined by calculating $\log T_0/T$ for each assigned rotamer and then normalizing. No correction for the statistical weighting was made, since only trends within a series were to be considered.

In the study concerned with $\text{CpFe}(\text{CO})_2\text{GeX}_2\text{R}$ compounds, the authors concluded that enthalpy differences between the two conformers of these compounds were controlled by a steric interaction between the carbonyl groups and substituents X and R.¹⁰⁸ Such a conclusion seems unlikely, since structural evidence (this will be discussed more fully in Chapter VI) suggests that for $\text{CpFe}(\text{CO})_2\text{M}'\text{R}_3$ compounds, R groups are closer to the Cp ring than to CO groups.^{36,109,110}

An NMR investigation of rotamers about the nickel-carbon bond in $\text{CpNiPPh}_3(\text{CH}_2\text{R})$ (R = alkyl, aryl) compounds indicated a steric interaction with the Cp ring such that R groups apparently prefer to be as far away as possible from the Cp moiety.¹¹¹ Conformational isomerization examined by infrared spectroscopy in

$(\pi\text{-C}_3\text{H}_4\text{X})\text{Co}(\text{CO})_2\text{PY}_3$ compounds also suggested that a steric interaction between the π -moiety and Y groups was operative.⁵⁶

The above evidence suggested that rotamer populations in $\text{CpM}(\text{CO})_2\text{M}'\text{R}_3$ compounds might be controlled by a steric or van der Waals interaction of R groups with the Cp ring. With this in mind, several series of $\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ compounds were prepared and some related $\text{CpM}(\text{CO})_2\text{M}'\text{X}_2\text{R}$ compounds were studied.

The following points were considered for arguments based on observed rotamer populations:

- (a) Compounds of formula $\text{CpM}(\text{CO})_2\text{M}'\text{X}_2\text{R}$ have the R groups cisoid to the Cp ring in the C_1 rotamer and X groups cisoid to the Cp ring in the C_s rotamer (see Figure I-I).
- (b) Compounds studied were considered to be free from solvation effects, since spectra were measured in *n*-heptane. Intermolecular interactions were assumed to be unimportant, since solutions were very dilute (10^{-3} M).
- (c) All spectra were measured at ambient temperature which is taken as 300°K.
- (d) The entropy difference between rotamers is assumed to be constant for all compounds studied, and to favor the C_1 rotamer by the statistical factor of $R\ln 2$.¹⁰⁷

Points (c) and (d) and Dalton's enthalpy determination

on $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Me}$ of 0.8 (-0.1, +0.7) kcal/mole,¹⁰⁷ allow evaluation of the difference in free energy between the rotamers of $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Me}$. The enthalpy value favors the C_s isomer and the entropy value favors the C_1 ; thus the free energy difference at 300°K favors the C_s rotamer by 0.4 kcal/mole. On the basis of a Boltzmann distribution of rotamers, the C_s isomer is predicted to be 66% populated at 300°K. This compares reasonably with the measured value of 74% in the present work.

A series of compounds of formula $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{R}$ (R = aryl) was first studied and the measured rotamer populations are presented in Table IV-17. These compounds were studied with a view towards investigating the possibility of an electronic influence controlling rotamer populations in the absence of any steric complication. However, only for the compound $\text{CpFe}(\text{CO})_2\text{SiMe}_2(\text{C}_6\text{F}_5)$ may one argue that a significant change in electronic influence is felt by the carbonyls, in comparison to the other compounds in Table IV-17. Thus, the force constants for the first seven compounds in Table IV-17 are all within 0.1 millidyne/Å of one another, whereas for $\text{CpFe}(\text{CO})_2\text{SiMe}_2(\text{C}_6\text{F}_5)$ the force constant is 0.15 millidyne/Å higher (see Tables IV-15 and IV-16). Therefore, the nearly constant observed populations of these compounds does not rule out an electronic effect; in fact, the large change observed for $\text{CpFe}(\text{CO})_2\text{SiMe}_2(\text{C}_6\text{F}_5)$ suggests an electronic preference

Table IV-17

Rotamer Populations of $\text{CpFe}(\text{CO})_2\text{SiMe}_2$ (aryl) Compounds

Compound, $-\text{SiR}_3$	$\%C_s^a$	$\%C_1^a$
$\text{SiMe}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$	87	13
$\text{SiMe}_2(p\text{-C}_6\text{H}_4\text{OMe})$	91	9
$\text{SiMe}_2(p\text{-C}_6\text{H}_4\text{Me})$	91	9
SiMe_2Ph	91	9
$\text{SiMe}_2(p\text{-C}_6\text{H}_4\text{SiMe}_2)$	91	9
$\text{SiMe}_2(p\text{-C}_6\text{H}_4\text{F})$	89	11
$\text{SiMe}_2(o\text{-C}_6\text{H}_4\text{Me})$	88	12
$\text{SiMe}_2(\text{C}_6\text{F}_5)$	7	93

^aPopulations were determined from observed carbonyl infrared bands as described in the text. Results of determinations upon the symmetric and antisymmetric modes generally agreed within two per cent of one another.

for a strong electron withdrawing group next to the Cp ring; however, an attractive van der Waals interaction may also be important in this case.

The results above prompted an investigation of the series $\text{CpFe}(\text{CO})_2\text{SiR}_2\text{X}$ ($\text{R} = \text{Me, Ph}$; $\text{X} = \text{electron withdrawing substituent}$) in order to gain further insight into the apparent preference for an electron withdrawing group cisoid to the Cp ring. The measured populations of these compounds are presented in Table IV-18.

The results show a strong favoring of the C_1 rotamer, indicating a preference for an electron withdrawing group cisoid to the Cp ring. The wide variation in steric properties of X in these compounds suggests that this preference may be the result of electronic factors. Two possibilities were considered, a preference for an electron withdrawing group transoid to CO, or an attractive van der Waals interaction between X and the Cp ring. Either of these possibilities would be consistent with small enthalpy differences between rotamers.

Next, the series $\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ was investigated, since here the C_s isomer should be favored if there is indeed a preference for an electron withdrawing group (X) cisoid to the Cp ring. The results are presented in Table IV-19 and are consistent with this hypothesis.

It is informative to note that when analogous $\text{X} = \text{Cl, F}$ compounds are compared, in every case the fluoro compound shows a lesser tendency to populate the C_s rotamer. This

Table IV-18
 Rotamer Populations of $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{X}$ and
 $\text{CpFe}(\text{CO})_2\text{SiPh}_2\text{X}$ Compounds

Compound, $-\text{SiR}_3$	$\%C_s^a$	$\%C_1^a$
SiMe_2Cl	11	89
SiMe_2F	20	80
$\text{SiMe}_2(\text{C}_6\text{F}_5)$	7	93
$\text{SiMe}_2(\text{OC}_6\text{F}_5)$	9	91
$\text{SiMe}_2(\text{SC}_6\text{F}_5)$	23	77
SiPh_2Cl	19	81
SiPh_2F	28	72

^aPopulations were determined from observed infrared carbonyl bands as described in text. Results of determinations upon the symmetric and antisymmetric modes generally agreed within two per cent of one another.

Table IV-19
Rotamer Populations of $\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ Compounds

Compound, $-\text{SiR}_3$	$\%C_s^a$	$\%C_1^a$
SiCl_2Me	74	26
SiF_2Me	59	41
$\text{Si}(\text{C}_6\text{F}_5)_2\text{Me}$	80	20
$\text{Si}(\text{OC}_6\text{F}_5)_2\text{Me}$	70	30
$\text{Si}(\text{SC}_6\text{F}_5)_2\text{Me}$	89	11
SiCl_2Ph	34	66
SiF_2Ph	20	80
$\text{Si}(\text{C}_6\text{F}_5)_2\text{Ph}$	70	30
$\text{Si}(\text{OC}_6\text{F}_5)_2\text{Ph}$	85	15
$\text{Si}(\text{SC}_6\text{F}_5)_2\text{Ph}$	59	41
SiCl_2H	52	48
SiF_2H	37	63
$\text{SiCl}_2(\text{CH}=\text{CH}_2)$	60	40
$\text{SiF}_2(\text{CH}=\text{CH}_2)$	41	59
$\text{SiCl}_2(t\text{-Bu})^b$	51	49

^aPopulations were determined from observed carbonyl infrared bands as described in the text. Results of determinations upon the symmetric and antisymmetric stretch generally agreed within two per cent of one another.

^bThis compound was incompletely characterized.

result seems inconsistent with a preference for an X substituent transoid to the CO group. However, this observation may be accommodated by the attractive van der Waals forces hypothesis, since such an attraction would depend upon intramolecular nonbonded distances. Thus, the shorter silicon-fluorine bond (with respect to the silicon-chlorine linkage) may result in a reduction in the attractive interaction between Cp ring protons and X. When $X = C_6F_5$, OC_6F_5 , and SC_6F_5 a strong preference for the C_S rotamer is observed. These groups should be well suited towards a favorable van der Waals interaction of the type described above.

Further examination of Table IV-19 shows that steric considerations are unimportant for these compounds (*cf.*, $CpFe(CO)_2SiCl_2H$, 52% C_S , $CpFe(CO)_2SiCl_2Me$, 74% C_S , $CpFe(CO)_2SiCl_2t-Bu$, 51% C_S). Thus, when only one bulky substituent is present on silicon, there is apparently no steric strain.

A series of $CpFe(CO)_2SiMe_2(YR')$ ($Y = O, S$; $R' =$ alkyl, Ph, C_6F_5) compounds were next studied in order to investigate the varying effects of Y and R' on rotamer populations. Results are presented in Table IV-20.

Note that the thiol compounds exhibit a strong preference for the C_1 rotamer, especially when compared to the analogous alkoxy compounds. This again may be explained by bond length considerations and a favorable intramolecular

Table IV-20

Rotamer Populations of $\text{CpFe}(\text{CO})_2\text{SiMe}_2(\text{YR}')$

(Y = O, S) Compounds

Compound, $-\text{SiR}_3$	$\%C_s^a$	$\%C_l^a$
$\text{SiMe}_2(\text{OH})$	91	9
$\text{SiMe}_2(\text{OMe})$	92	8
$\text{SiMe}_2(\text{OEt})$	88	12
$\text{SiMe}_2(\text{OCH}_2\text{CF}_3)$	64	36
$\text{SiMe}_2(\text{O}i\text{-Pr})$	84	16
$\text{SiMe}_2(\text{O}i\text{-Bu})$	76	24
$\text{SiMe}_2(\text{OPh})$	91	9
$\text{SiMe}_2(\text{OC}_6\text{F}_5)$	9	91
$\text{SiMe}_2(\text{SEt})$	59	41
$\text{SiMe}_2(\text{S}i\text{-Pr})$	30	70
$\text{SiMe}_2(\text{SPh})$	8	92
$\text{SiMe}_2(\text{SC}_6\text{F}_5)$	23	77

^aPopulations were determined from observed infrared bands as described in text. Results of determinations upon symmetric and antisymmetric stretch generally agreed within two per cent of one another.

interaction between the sulfur lone pairs and the Cp ring protons. The shorter silicon-oxygen bond length apparently precludes an optimum interaction between the oxygen lone pairs and Cp ring protons. It is also interesting to note that for both $\text{CpFe}(\text{CO})_2\text{SiMe}_2(\text{OR}')$ ($\text{R}' = \text{CH}_2\text{CF}_3$, C_6F_5) compounds, a strong preference for the C_1 rotamer is observed. Since in these two compounds fluorine atoms are attached to R' , the possibility of an attractive van der Waals interaction exists.

The steric bulk of R' apparently is of secondary importance in these compounds. No obvious trends are observed, in keeping with results observed for $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{R}$ ($\text{R} = \text{H}, \text{Me}, t\text{-Bu}$) compounds.

To investigate further changes in Y and R' and how they affect rotamer populations, the series $\text{CpFe}(\text{CO})_2\text{Si}(\text{YR}')_2\text{R}$ ($\text{Y} = \text{O}, \text{S}$; $\text{R}' = \text{alkyl}, \text{Ph}, \text{C}_6\text{F}_5$; $\text{R} = \text{Me}$) was considered next and the results are presented in Table IV-21.

Trends in this series of compounds were most difficult to rationalize. This is the case since steric as well as electronic factors are apparently important for these complexes. Thus, consideration of the first five compounds in Table IV-21 shows that increasing steric bulk of R' counteracts a preference for OR' cisoid to the Cp ring. This effect is most dramatic for $\text{CpFe}(\text{CO})_2\text{Si}(\text{SR}')_2\text{Ph}$ when $\text{R}' = \text{Et}$, $\text{C}_s = 81\%$; $\text{R}' = i\text{-Pr}$, $\text{C}_s = 21\%$. Steric considerations are expected to be important for these

Table IV-21

Rotamer Populations of $\text{CpFe}(\text{CO})_2\text{Si}(\text{YR}')_2\text{R}$ Compounds

Compound, $-\text{SiR}_3$	$\%C_s^a$	$\%C_1^a$
$\text{Si}(\text{OMe})_2\text{Me}$	55	45
$\text{Si}(\text{OEt})_2\text{Me}$	48	52
$\text{Si}(\text{O}i\text{-Pr})_2\text{Me}$	39	61
$\text{Si}(\text{O}t\text{-Bu})_2\text{Me}$	28	72
$\text{Si}(\text{OPh})_2\text{Me}$	46	54
$\text{Si}(\text{OCH}_2\text{CF}_3)_2\text{Me}$	46	54
$\text{Si}(\text{OC}_6\text{F}_5)_2\text{Me}$	70	30
$\text{Si}(\text{SEt})_2\text{Me}$	48	52
$\text{Si}(\text{S}i\text{-Pr})_2\text{Me}$	38	62
$\text{Si}(\text{SPh})_2\text{Me}$	80	20
$\text{Si}(\text{SC}_6\text{F}_5)_2\text{Me}$	89	11
$\text{Si}(\text{OMe})_2\text{Ph}$	88	12
$\text{Si}(\text{OEt})_2\text{Ph}$	89	11
$\text{Si}(\text{O}i\text{-Pr})_2\text{Ph}$	82	18
$\text{Si}(\text{OPh})_2\text{Ph}$	22	78
$\text{Si}(\text{SEt})_2\text{Ph}$	81	19
$\text{Si}(\text{S}i\text{-Pr})_2\text{Ph}^c$	21	79
$\text{Si}(\text{SPh})_2\text{Ph}$	16	84
$\text{Si}(\text{OC}_6\text{F}_5)_2\text{Ph}$	85	15
$\text{Si}(\text{SC}_6\text{F}_5)_2\text{Ph}$	59	41

Table 21 (continued)

^aPopulations were determined from observed infrared bands as described in text. Results of determinations upon symmetric and antisymmetric stretch generally agreed within two per cent of one another.

compounds since R' will be in a position to interact with the Cp ring and there are two such interactions.

Further consideration of results in Table IV-21 shows that thiol compounds in the C_s isomer are sometimes highly favored when compared to analogous alkoxy compounds (cf., CpFe(CO)₂Si(SPh)₂Me, 80% C_s; CpFe(CO)₂Si(OPh)₂Me, 46% C_s). However, this is not the general trend it was for CpFe(CO)₂SiMe₂(YR') (Y = O, S) compounds, due to the importance of steric considerations as discussed above.

Rotamer populations of related CpM(CO)₂M'R₃ compounds were determined in order to study the effects of varying M and M' (M = Fe, Ru; M' = C, Si, Sn). The results are presented in Table IV-22. Surprisingly, virtually no change in rotamer populations was observed on varying M and M'. These results contradict Dalton's suggestion that increasing the size of the Group IV ligand atom should result in a decrease in enthalpy difference between rotamers.¹⁰⁷ The neglect of σ bonding considerations for these compounds by Dalton,¹⁰⁷ probably accounts for the anomaly.

There are some CpFe(CO)₂SiR₃ compounds which show only two ¹²CO bands in the carbonyl region. These are compounds such as CpFe(CO)₂SiPh₂Me, CpFe(CO)₂SiPh_nH_{3+n} (n = 1, 2), CpFe(CO)₂SiMe₂H, CpFe(CO)₂SiMe₂(t-Bu), and CpFe(CO)₂SiMe₂OSiMe₂Fe(CO)₂Cp. The satellite region of

Table IV-22

Rotamer Populations of $\text{CpM}(\text{CO})_2\text{M}'\text{R}_3$
 (M = Fe, Ru; M' = C, Si, Sn) Compounds

Compound, M - M'R ₃	%C _s ^a	%C _l ^a
Fe-SiCl ₂ Me	74	26
Fe-SnCl ₂ Me	77	23
Ru-SiCl ₂ Me	70	30
Ru-SnCl ₂ Me ^b	71	29
Fe-C ₂ F ₅ & -C ₃ F ₇	71	28
Fe-SiF ₂ Me	59	41
Fe-SnI ₂ Me	75	25
Ru-SiF ₂ Me ^b	50	50
Ru-SnI ₂ Me	75	25
Fe-SiCl ₂ Ph	34	66
Fe-SnCl ₂ Ph	63	37
Ru-SiCl ₂ Ph	38	62
Fe-SiF ₂ Ph	20	80
Fe-SnI ₂ Ph	66	34
Fe-SiMe ₂ Cl	11	89
Fe-SnMe ₂ Cl	8	92
Ru-SiMe ₂ Cl ^b	15	85
Ru-SnMe ₂ Cl ^b	9	91
Fe-SiMe ₂ F	20	80
Fe-SnMe ₂ I	6	94
Ru-SiMe ₂ F	23	77
Ru-SnMe ₂ I ^b	6	94

Table 22 (continued)

^aPopulations were determined from observed infrared bands as described in text. Results of determinations on the symmetric and antisymmetric modes generally agreed to within 2 per cent of one another.

^bThese compounds were incompletely characterized.

these compounds showed one ^{13}CO band below each ^{12}CO band; however, this cannot be taken as evidence for 100% population of the C_s isomer in these compounds, since the satellite bands could be degenerate. Only for the latter compound would it be reasonable to make this assignment, since there is a significant difference in the electronegativities of substituents on silicon. For the other compounds, it is felt that the similar electronegativities of groups on silicon result in degeneracy of the individual rotamer bands.

The compound $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_5$ was of interest since it also showed only two ^{12}CO bands; however, the satellite region showed two ^{13}CO bands below each ^{12}CO mode. This indicates the presence of solely the C_1 rotamer for this compound. Again, a strong van der Waals interaction with the Cp ring protons could be responsible for this observation.

B. Compounds of Type $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$

The infrared carbonyl bands observed for these compounds are listed in Table IV-23. When $\text{SiR}_3 = \text{SiX}_2\text{R}$, rotamers are again observed and examples are shown in Figure IV-IX.

There are four possible conformers for these compounds, assuming that the CO, H, and SiX_2R groups all lie in a plane and X and R groups stagger the CO ligand. These

Table IV-23
Observed Carbonyl Infrared Bands for
CpFe(CO)H(SiR₃)₂ Compounds.

Compound, -SiR ₃	Bands Observed ^a , cm ⁻¹
Ru-SiCl ₃	2039; 1994
SiCl ₃ ^b	2025; 1982
SiF ₃	2016; 1972
SiCl ₂ Ph	2015, 2005, 1993; 1953
SiF ₂ Ph ^c	2012, 2004, 2000
SiCl ₂ Me	2006, 1992; 1945
SiF ₂ Me	1993, 1981; 1935
SiMe ₂ Cl	1980, 1967, 1954; 1941, 1927
SiMe ₂ F	1969, 1960, 1950; 1923, 1914
SiMe ₂ (C ₆ F ₅)	1975, 1968.5, 1957.5; 1923, 1913
SiPh ₂ Me	1947; 1901
SiMe ₂ Ph	1944; 1899

^aSpectra were measured in *n*-heptane. Bands listed after semicolon correspond to ¹³C¹⁸O satellites.

^bThis compound prepared initially by W. Jetz, reference 6.

^cThis compound was incompletely characterized.

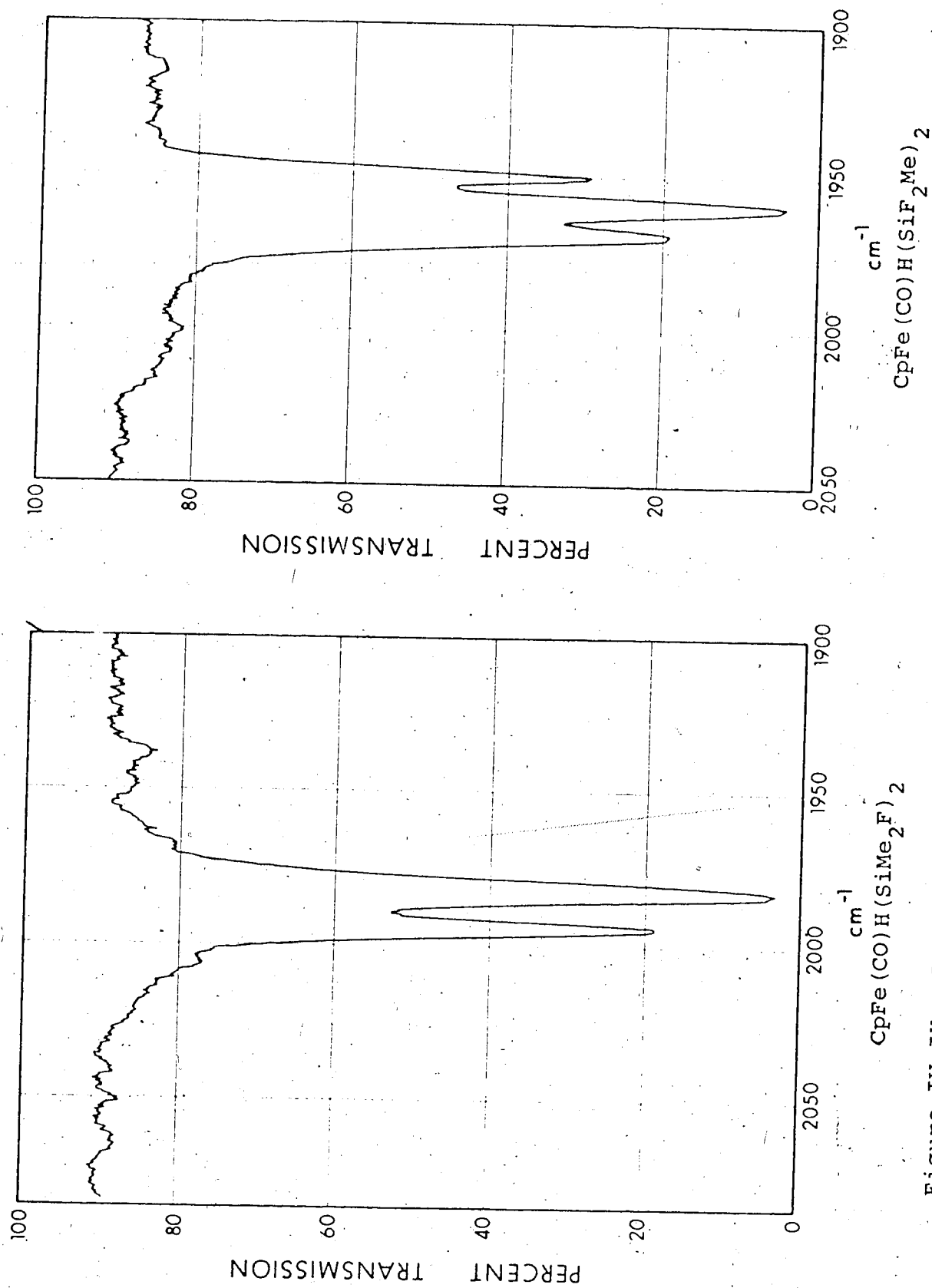


Figure IV-IX: Representative spectra of CpFe(CO)H(SiR₃)₂ compounds, exhibiting the rotamer phenomenon.

conformers are shown in Figure IV-X. (Crystal structures on three of these compounds indicate that they may be considered to possess a distorted tetragonal pyramidal structure with the Cp ring at the apex and SiR_3 groups trans to each other and in a plane with the H and CO ligands.^{65,11}

The compounds $\text{CpFe}(\text{CO})\text{H}(\text{SiX}_2\text{R})_2$ ($\text{SiX}_2\text{R} = \text{SiMe}_2\text{Cl}$, $\text{SiMe}_2(\text{C}_6\text{F}_5)$, SiCl_2Ph , SiF_2Ph) showed three of the four possible bands. We may expect conformers 3 and 4 in Figure IV-X to possess nearly equivalent CO bands. The compounds $\text{CpFe}(\text{CO})\text{H}(\text{SiX}_2\text{R})_2$ ($\text{SiX}_2\text{R} = \text{SiCl}_2\text{Me}$, SiF_2Me) showed two of the four possible bands. Here, there may be further degeneracy of some of the bands, or one of the conformers may be only slightly populated. The compounds $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_n\text{Ph}_{3-n})$ ($n = 1, 2$) showed only one ^{12}CO band. This is undoubtedly due to degeneracy of the various expected conformer bands. As before, the similar electronegativities of Me and Ph accounts for this degeneracy.

The position of the CO bands of these compounds appears to fall, with two exceptions, between the symmetric and antisymmetric bands of the analogous $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds. This comparison is presented in Table IV-24.

Formally, iron is considered to be oxidized from +2 to +4 on going from $\text{CpFe}(\text{CO})_2\text{SiR}_3$ to $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$. However, the results of Table IV-24 suggest little actual

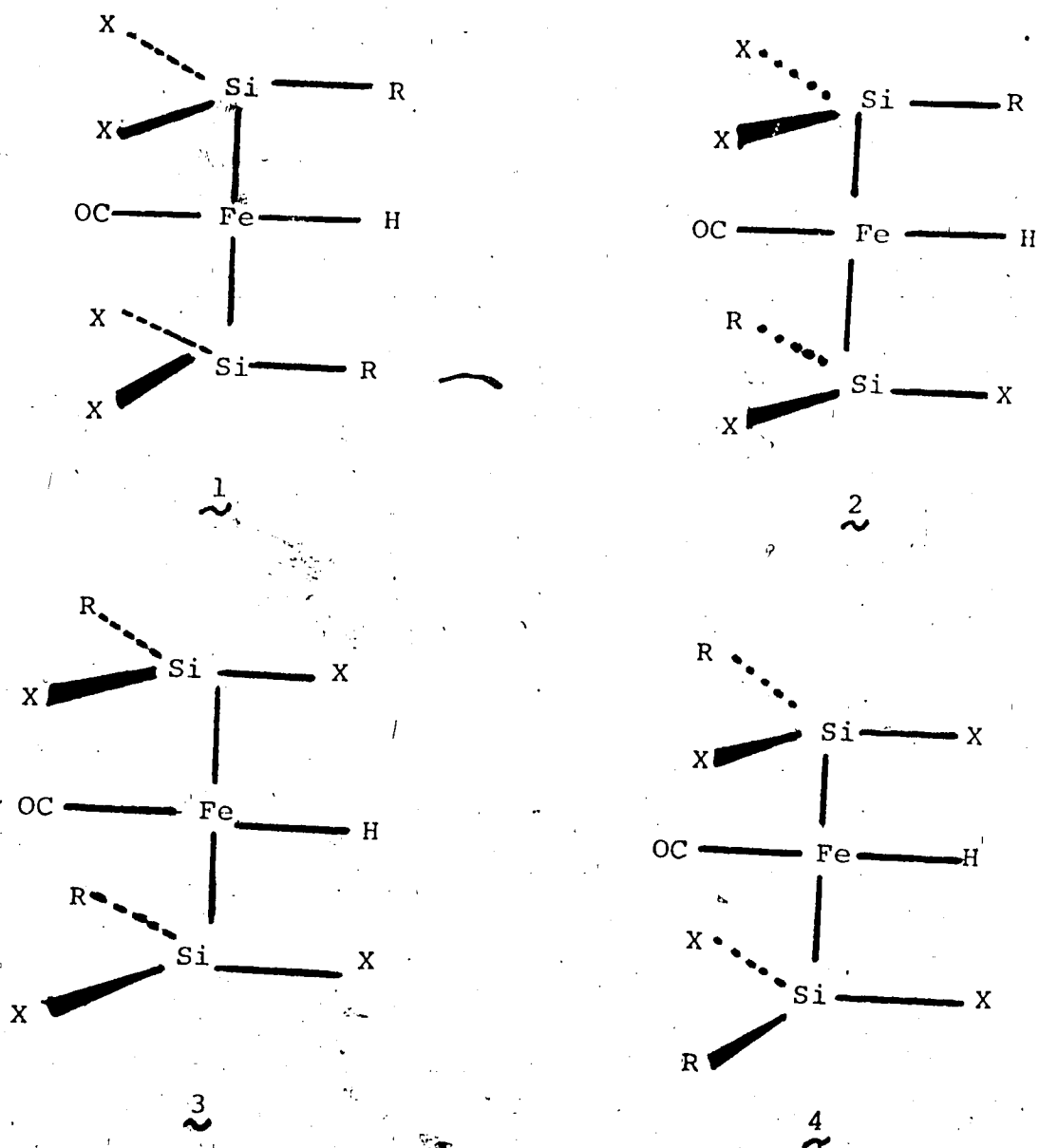


Figure IV-X: A view down the Cp-Fe axis (Cp group omitted), showing four possible conformers about the CO group.

Table IV-24

Comparison of C=O Stretching Frequencies^a of Analogous
CpFe(CO)₂SiR₃ and CpFe(CO)H(SiR₃)₂ Compounds

Compound, -SiR ₃	Band for CpFe(CO)H(SiR ₃) ₂ , cm ⁻¹	Bands for CpFe(CO) ₂ SiR ₃ , cm ⁻¹
SiCl ₃	2025	2038, 1995
SiF ₃	2016	2036, 1988
SiCl ₂ Ph	2004	2024, 1975
SiF ₂ Ph	2005	2023, 1972
SiCl ₂ Me	1999	2026, 1976
SiF ₂ Me	1987	2020, 1974
SiMe ₂ Cl	1967	2013, 1963
SiMe ₂ F	1960	2010, 1958
SiMe ₂ (C ₆ F ₅)	1966	2008, 1958
SiPh ₂ Me	1947	2002, 1952
SiMe ₂ Ph	1944	1997, 1946

^aWhere rotamers are observed, an average band value is reported.

change on proceeding from the formal +2 to +4 oxidation states. The implication of this data is that there is a similar charge density upon iron in both types of compounds.

Chapter V

Nuclear Magnetic Spectroscopy Results

The NMR spectra of all compounds prepared in the present work were routinely studied and further served to confirm the identity of these compounds. All spectra were recorded on Varian HA 56/60 $^{19}\text{F}/^1\text{H}$ or Varian HA 100 instruments and referenced to TMS or CFCl_3 .

A. Compounds of Type $\text{CpM}(\text{CO})_2\text{M}'\text{R}_3$ (M = Fe, Ru; M' = C, Si)

The observation of rotamers in the infrared carbonyl region of these compounds prompted temperature dependent NMR studies on some of these complexes. Unfortunately, the limiting low temperature spectrum anticipated for these compounds was not observed, likely due to a low barrier to rotation and to the small difference in free energy between the two conformers.¹¹³ The results obtained for $\text{CpFe}(\text{CO})_2\text{SiF}_2\text{Me}$ are typical; thus, a sample in CFCl_3 was cooled down to -80° and showed a sharp quartet in the ^{19}F NMR throughout. The coupling constant, $^3J_{\text{F-Me}}$ showed a slight decrease on cooling, 8.2 Hz at $+40^\circ$ to 6.5 Hz at -80° . This change may be attributed to changes in the rotamer populations with temperature, the spectrum at any one temperature being a weighted average of couplings and chemical shifts of each rotamer.^{114,115} Further

cooling of the sample produced broadening of all signals, including the CFCl_3 reference, indicating that the sample was precipitating out of solution.

The compound $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_5$ was of interest since its ^1H spectrum in acetone- d^6 showed an ABX_2 pattern for methylene protons as shown in Figure V-XI. The spectrum was assigned assuming equal coupling of ortho fluorines to the AB protons. On the basis of this assumption, $^2J_{\text{AB}} = 1.5 \text{ Hz}$, and $\delta_{\text{AB}} = 1.4 \text{ Hz}$; however, in CD_2Cl_2 the methylene protons were equivalent down to -40° , at lower temperatures the compound precipitated out of solution.

The results in acetone- d^6 appear to be consistent with the infrared study, which showed the presence of only the C_1 rotamer in *n*-heptane solution. However, if rotation about the iron- σ carbon bond is slow on the NMR time scale, then it is necessary to postulate a substantial barrier to rotation for this compound in acetone solvent. This is inconsistent with the NMR results in CD_2Cl_2 where rapid rotation about the iron- σ carbon bond must be occurring. Such a large change in the barrier to rotation for the same compound with solvent suggests an unusually important role for the solvent; thus, acetone could conceivably hydrogen bond to the methylene protons. Ideally these NMR investigations should have been carried out in *n*-heptane solution, then the role of solvent would have been unimportant and direct comparison with infrared results

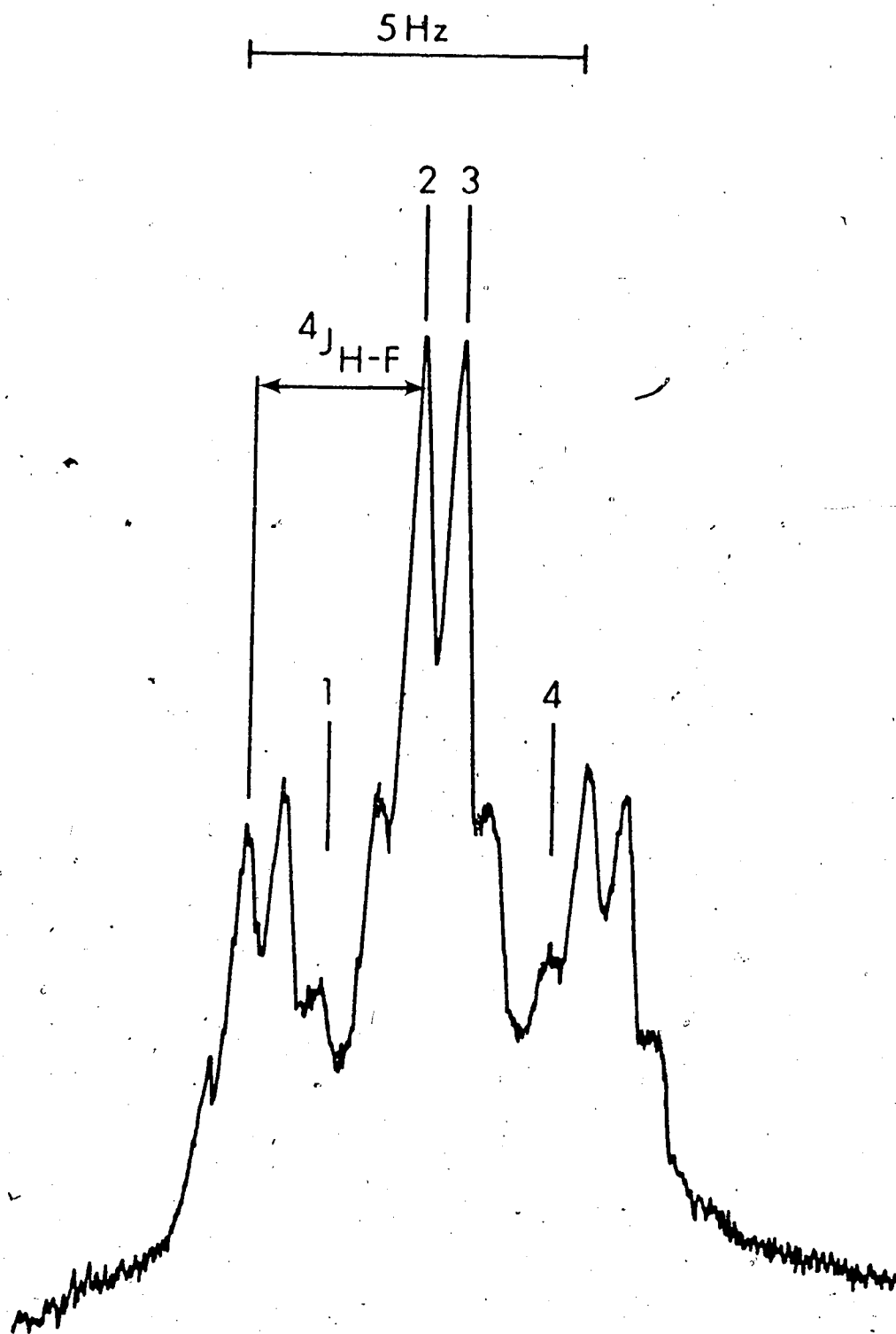


Figure V-XI. Methylene proton NMR spectrum in acetone-d⁶ of $\text{CpFe}(\text{CO})_2\text{CH}_2(\text{C}_6\text{F}_5)$, showing the AB resonance of an ABX_2 spin system.

would have been possible. Unfortunately, these compounds are insufficiently soluble in *n*-heptane for NMR spectra.

The compound $\text{CpFe}(\text{CO})_2\text{C}_3\text{F}_7$ exhibited nonequivalent α -fluorines in acetone- d^6 up to 70° , the temperature limit of solvent. This may be contrasted with the results for $\text{CpFe}(\text{CO})_2\text{C}_2\text{F}_5$ whose ^{19}F NMR in acetone- d^6 showed a simple A_2X_3 pattern. Both compounds showed the presence of rotamers in *n*-heptane in the infrared, in almost identical proportions (see Table IV-22). On cooling a sample of $\text{CpFe}(\text{CO})_2\text{C}_2\text{F}_5$ in acetone- d^6 from $+40^\circ$ to -40° $^3J_{\alpha-\beta}$ increased from 1.17 to 1.76 Hz. These results suggest that for the $-\text{C}_3\text{F}_7$ compound, both rotamers are interconverting rapidly on the NMR time scale, but on cooling, one rotamer is becoming more and more favored. Again, these results were obtained in acetone- d^6 , so that solvation may play a significant role.¹¹³ Limited solubility in other solvents including CD_2Cl_2 hampered further investigation, and the unusual behavior of these closely related compounds is not understood.

A list of chemical shifts observed for $\text{CpM}(\text{CO})_2\text{M}'\text{R}_3$ ($M = \text{Fe}, \text{Ru}; M' = \text{C}, \text{Si}$) is presented in Table V-25. The spectra were recorded in the indicated solvent and it is interesting to note the large chemical shift variation observed for the Cp protons. Thus, the Cp resonance of $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_5$ occurs at τ 5.09 in benzene and at τ 5.14 in CD_2Cl_2 . Other resonances were not affected significantly

Table V-25

Measured Chemical Shifts^a for $\text{CpM}(\text{CO})_2\text{M}'\text{R}_3$ (M = Fe, Ru; M' = C, Si) Compounds

Compound	Solvent	τ_{Cp}	$\tau_{\text{Si-Ph}}^b$	$\tau_{\text{Si-Me}}$	τ/ϕ for other moieties
Fe-SiPh ₂ Me	CDCl ₃	5.46	2.3-2.8	9.41	---
Fe-SiPh(Me)H	neat	5.49	2.3-2.8	9.34	Si-H, 4.78
Fe-SiMe ₂ Ph	CD ₂ Cl ₂	5.42	2.3-2.8	9.35	---
Fe-SiMe ₂ (<i>p</i> -C ₆ H ₄ NMe ₂)	C ₆ D ₆	5.90	2.3-3.4	9.20	NMe ₂ , 7.30
Fe-SiMe ₂ (<i>p</i> -C ₆ H ₄ OMe)	C ₆ D ₆	5.94	2.3-3.2	9.28	OMe, 6.57
Fe-SiMe ₂ (<i>p</i> -C ₆ H ₄ F)	C ₆ D ₆	6.00	2.3-3.3	9.37	---
Fe-SiMe ₂ (<i>p</i> -C ₆ H ₄ Me)	C ₆ D ₆	5.97	2.3-3.0	9.30	Me, 7.80
Fe-SiMe ₂ (<i>p</i> -C ₆ H ₄ SiMe ₂ -Fe)	C ₆ D ₆	5.98	2.3-3.0	9.25	---
Fe-SiMe ₂ (<i>o</i> -C ₆ H ₄ Me)	C ₆ D ₆	6.01	2.3-3.0	9.21	Me, 7.47
Fe-SiMe ₂ (C ₆ F ₅)	C ₆ D ₆	5.95	---	9.22	<i>o</i> -F, 123.8; <i>m</i> -F, 162.2; <i>p</i> -F, 150.0
Fe-Si(C ₆ F ₅) ₂ Me	C ₆ D ₆	5.99	---	9.01	<i>o</i> -F, 124.0; <i>m</i> -F, 159.0; <i>p</i> -F, 150.0

Table 25 (continued)

Compound	solvent	τ_{Cp}	$\tau_{\text{Si-Ph}}^b$	$\tau_{\text{Si-Me}}$	τ/ϕ for other moieties
Fe-Si(C ₆ F ₅) ₂ Ph	C ₆ D ₆	6.00	2.2-2.9	---	<i>o</i> -F, 112.8; <i>m</i> -F, 158.9; <i>p</i> -F, 149.8
Ru-SiPh ₂ Me	C ₆ D ₆	5.47	2.2-2.9	8.98	---
Ru-SiMe ₂ Ph	C ₆ D ₆	5.54	2.3-2.8	9.28	---
Ru-SiPh ₃	d ⁶ -acetone	4.82	2.4-2.8	---	---
Fe-SiEt ₂ Ph	C ₆ D ₆	5.98	2.3-2.9	---	Si-CH ₂ , 8.84; CH ₃ , 8.88
Fe-SiCl ₂ H	CDCl ₃	5.11	---	---	Si-H, 3.48
Fe-SiF ₂ H	CDCl ₃	5.03	---	---	Si-H, 3.67; F, 118.9
Fe-SiF ₂ Me	C ₆ D ₆	5.53	---	9.41	F, 89.2
Fe-SiMe ₂ F	CDCl ₃	5.19	---	9.40	F, 143.5
Fe-SiPh(F)Me	CDCl ₃	5.39	2.3-2.9	9.24	F, 130.0
Fe-SiPh ₂ Cl	CDCl ₃	5.31	2.3-2.8	---	---
Fe-SiPh ₂ F	CDCl ₃	5.23	2.3-2.8	---	F, 139.8

Table 25 (continued)

Compound	Solvent	τ_{Cp}	$\tau_{\text{Si-Ph}}^b$	$\tau_{\text{Si-Me}}$	τ/ϕ for other moieties
Fe-SiF ₂ Ph	C ₆ D ₆	5.65	2.3-2.8	---	F, 95.1
Fe-SiF ₃	C ₆ D ₆	5.55	---	---	F, 94.3
Ru-SiF ₃	acetone-d ₆	4.30	---	---	F, 81.1
Ru-SiCl ₃	CDCl ₃	4.59	---	---	---
Ru-SiCl ₂ Me	C ₆ D ₆	5.48	---	8.87	---
Ru-SiMe ₂ Cl	acetone-d ₆	4.50	---	9.24	---
Ru-SiCl ₂ Ph	C ₆ D ₆	5.57	2.0-2.9	---	---
Fe-SiMe ₂ (OC ₆ F ₅)	C ₆ D ₆	5.78	---	9.30	<i>o</i> -F, 152.0; <i>m</i> -F, 159.0; <i>p</i> -F, 161.5
Fe-Si(OC ₆ F ₅) ₂ Me	C ₆ D ₆	5.79	---	9.05	<i>o</i> -F, 154.0; <i>m</i> -F, 162.1; <i>p</i> -F, 163.3
Fe-Si(OC ₆ F ₅) ₂ Ph	C ₆ D ₆	6.05	2.4-3.2	---	<i>o</i> -F, 154.2; <i>m</i> -F, 162.3; <i>p</i> -F, 164.0

Table 25 (continued)

Compound	Solvent	τ_{Cp}	$\tau_{\text{Si-Ph}}^b$	$\tau_{\text{Si-Me}}$	τ/ϕ for other moieties
Fe-SiMe ₂ (SC ₆ F ₅) ₂	C ₆ D ₆	5.56	---	9.32	<i>o</i> -F, 128.3; <i>m</i> -F, 158.4; <i>p</i> -F, 151.3
Fe-Si(SC ₆ F ₅) ₂ Me	C ₆ D ₆	5.68	---	9.31	<i>o</i> -F, 129.0; <i>m</i> -F, 159.5; <i>p</i> -F, 151.6
Fe-Si(SC ₆ F ₅) ₂ Ph	C ₆ D ₆	5.91	2.2-3.1	---	<i>o</i> -F, 141.2; <i>m</i> -F, 160.0; <i>p</i> -F, 152.5
Fe-CH ₂ C ₆ F ₅	C ₆ D ₆	6.09	---	---	CH ₂ , 8.37; <i>o</i> -F, 142.2; <i>m</i> -F, 164.0; <i>p</i> -F, 159.4
Fe-C ₂ F ₅	acetone- _d ₆	4.73	---	---	α -F, 61.40; β -F, 80.43
Fe-C ₃ F ₇	acetone- _d ₆	4.71	---	---	α -F, 52.18; β -F, 112.5; γ -F, 77.60
Fe-SiMe ₂ (OCH ₂ CF ₃) ₂	C ₆ D ₆	5.72	---	9.54	OCH ₂ ', 6.26; CF ₃ ', 74.97
Fe-Si(OCH ₂ CF ₃) ₂ Me	C ₆ D ₆	5.76	---	9.58	OCH ₂ ', 6.14; CF ₃ ', 73.75

Table 25 (continued)

Compound	Solvent	τ_{CP}	$\tau_{\text{Si-Ph}}^b$	$\tau_{\text{Si-Me}}$	τ/ϕ for other moieties
Fe-SiCl(Me)(OCMe ₂ CF ₃)	C ₆ D ₆	5.81	---	9.08	CMe, 8.51, 8.57; CF ₃ , 83.47
Fe-Si(OMe) ₂ Me	C ₆ D ₆	5.71	---	9.42	OMe, 6.47
Fe-SiMe ₂ (OMe)	C ₆ D ₆	5.71	---	9.44	OMe, 6.65
Fe-Si(OMe) ₂ Ph	C ₆ D ₆	5.88	2.0-2.8	---	OMe, 6.41
Fe-SiPh ₂ (OMe)	C ₆ D ₆	5.89	2.1-2.9	---	OMe, 6.53
Fe-SiMe ₂ (OEt)	C ₆ D ₆	5.71	---	9.39	OCH ₂ , 6.37; Me, 8.84
Fe-Si(OEt) ₂ Ph	C ₆ D ₆	5.89	1.9-2.9	---	OCH ₂ , 6.11; Me, 8.75
Fe-SiPh ₂ (OEt)	C ₆ D ₆	5.85	2.1-2.8	---	OCH ₂ , 6.28; Me, 8.84
Fe-SiMe ₂ (OH)	C ₆ D ₆	5.72	---	9.39	OH, 7.35
Fe-SiMe ₂ (O ⁱ -Pr)	C ₆ D ₆	5.72	---	9.38	OCH, 5.98; Me, 8.83
Fe-Si(O ⁱ -Pr) ₂ Me	C ₆ D ₆	5.67	---	9.43	OCH, 5.78; Me, 8.82
Fe-Si(O ⁱ -Pr) ₂ Ph	C ₆ D ₆	6.11	2.1-3.1	---	OCH, 5.96; Me, 9.03

Table 25 (continued)

Compound	Solvent	τ_{Cp}	$\tau_{\text{Si-Ph}}$ ^b	$\tau_{\text{Si-Me}}$	τ/ϕ for other moieties
Fe-Si(Ot-Bu) ₂ Me	C ₆ D ₆	5.50	---	9.20	Me, 8.61
Fe-SiMe ₂ (Ot-Bu)	C ₆ D ₆	5.78	---	9.43	Me, 8.80
Fe-Si(OPh) ₂ Ph	C ₆ D ₆	5.97	1.8-3.2	---	---
Fe-SiMe ₂ OSiMe ₂ -Fe	C ₆ D ₆	5.71	---	9.29	---
Fe-SiMe ₂ (SEt)	C ₆ D ₆	5.71	---	9.27	SCH ₂ , 7.37; Me, 8.70
Fe-Si(SEt) ₂ Me	C ₆ D ₆	5.64	---	9.07	SCH ₂ , 7.31; Me, 8.75
Fe-Si(SEt) ₂ Ph	C ₆ D ₆	5.76	2.1-2.8	---	SCH ₂ , 7.36; Me, 8.79
Fe-SiMe ₂ (Si-Pr)	C ₆ D ₆	5.64	---	9.31	SCH, 6.93; Me, 8.69
Fe-Si(Si-Pr) ₂ Me	C ₆ D ₆	5.68	---	8.95	SCH, 6.62; Me, 8.59
Fe-SiMe ₂ (SPH)	C ₆ D ₆	5.67	2.4-3.1	9.39	---
Fe-Si(SPh) ₂ Me	C ₆ D ₆	5.80	2.2-3.1	9.19	---
Fe-Si(SPh) ₂ Ph	C ₆ D ₆	5.99	1.8-3.2	---	---

Table 25 (continued)

^aChemical shifts are all relative to TMS or CFC1₃. All ¹⁹F shifts are positive in ppm.

^bPhenyl resonances were generally broad; therefore, the range of the signal is reported.

by change of solvent.

The Cp resonance was observed to shift to higher τ value as groups upon M' become more electron releasing. This effect has been observed for similar compounds^{40,106} and is attributed to the increased electron density placed upon the metal, resulting in a greater shielding of the Cp protons.

Compounds possessing pentafluorophenyl groups are of interest since it is possible to correlate the para fluorine chemical shift to the electronic character of the group attached to the C_6F_5 ring.^{85,116,117} A list of ϕ_{para} values for selected C_6F_5X compounds is presented in Table V-26. A more positive ϕ_{para} value indicates that X is a π donating group (cf., when X = OH, $\phi_{para} = 171.0$; X = SiF_3 , $\phi_{para} = 143.0$).

The results in Table V-26 indicate that the $CpFe(CO)_2$ moiety exerts little influence on ϕ_{para} values. Thus, both $CpFe(CO)_2C_6F_5$ and $CpFe(CO)_2CH_2C_6F_5$ have similar ϕ_{para} values, and since the CH_2 group is not expected to transmit a π effect, apparently the $CpFe(CO)_2$ moiety exerts little significant π influence. This is consistent with conclusions obtained for $C_6F_5Mn(CO)_nL_{5-n}$ ($n = 3, 4, 5$), where lack of influence of the $Mn(CO)_nL_{5-n}$ groups upon ¹⁹F chemical shifts was attributed to poor overlap of the π system of Mn with the aromatic π system.¹¹⁸

When $CpM(CO)_2C_6F_5$ ($M = Fe, Ru$) compounds are compared,

Table V-26

Para-Fluorine Chemical Shifts of a Selected
Series of C_6F_5X Compounds

Compound	δ para ($CFCl_3$, $\phi=0$)	Source
C_6F_6	163.0	ref. 116
$C_6F_5SiF_3$	143.0	ref. 85
$C_6F_5SiMe_2Br$	149.7	ref. 116
$CpFe(CO)_2Si(C_6F_5)_2Ph$	149.8	this work
$CpFe(CO)_2SiMe_2(C_6F_5)$	150.0	this work
$(C_6F_5)_2SiMe_2$	150.1	ref. 116
$CpFe(CO)H[SiMe_2(C_6F_5)]_2$	150.8	this work
$CpFe(CO)_2SiMe_2(SC_6F_5)$	151.3	this work
$CpFe(CO)_2Si(SC_6F_5)_2Me$	151.6	this work
$CpFe(CO)_2Si(SC_6F_5)_2Ph$	152.5	this work
$C_6F_5-SiMe_3$	152.9	ref. 116
$C_6F_5CH_2Br$	155.5	ref. 90
$C_6F_5CH_2OH$	155.6	ref. 116
$C_6F_5Mn(CO)_5$	158.7	ref. 118
$CpFe(CO)_2CH_2C_6F_5$	159.4	this work
$CpFe(CO)_2C_6F_5$	160.3	ref. 91
$(C_6F_5)_2CH_2$	160.8	ref. 90
$CpFe(CO)_2SC_6F_5$	161.0	ref. 85
$CpFe(CO)_2SiMe_2(OC_6F_5)$	161.5	this work
$CpRu(CO)_2C_6F_5$	162.5	ref. 91

Table 26 (continued)

Compound	ϕ para (CFCl ₃ , $\phi=0$)	Source
$\text{CpFe}(\text{CO})_2\text{Si}(\text{OC}_6\text{F}_5)_2\text{Me}$	163.3	this work
$\text{CpFe}(\text{CO})_2\text{Si}(\text{OC}_6\text{F}_5)_2\text{Ph}$	164.0	this work
$\text{C}_6\text{F}_5\text{OSiMe}_3$	167.6	ref. 85
$\text{C}_6\text{F}_5\text{OH}$	171.0	ref. 85

a larger ϕ_{para} value is observed for the ruthenium compound. This suggests that the $\text{CpRu}(\text{CO})_2$ moiety is possibly a weak π donor, certainly a better π donor than the $\text{CpFe}(\text{CO})_2$ moiety.

An interesting series is provided by compounds possessing fluorine atoms. A collection of ^{19}F chemical shifts is presented in Table V-27. Large positive ϕ values correspond to more shielded ^{19}F nuclei, shifts being referenced to CFCl_3 .

The compound $\text{CpFe}(\text{CO})_2\text{F}$ was recently prepared⁴⁹ and it is interesting to note that the fluorine nucleus does not exhibit a highly shielded value. (It is a feature of transition metal hydrido compounds that the hydrido resonance occurs in a highly shielded region mainly because of the diamagnetic shielding effect of metal orbitals.⁵⁹)

Trends within a series of related compounds such as those in Table V-27 are difficult to establish because of lack of understanding of factors influencing ^{19}F chemical shifts.¹¹⁹ However, fluorine nuclei attached to silicon appear to be more shielded than those attached to analogous carbon compounds. Also, increasing substitution of electron releasing groups upon silicon appears to produce shifts characteristic of increased shielding.

A list of observed couplings for $\text{CpM}(\text{CO})_2\text{M}'\text{R}_3$ ($\text{M} = \text{Fe, Ru}$; $\text{M}' = \text{C, Si}$) is presented in Table V-28. The

Table V-27

 ^{19}F NMR Chemical Shifts of Some π -Cyclopentadienyliron Compounds

Compound	Solvent	δ ppm (CFCl ₃ , $\phi = 0$)	Source
CpFe(CO) ₂ F	acetone	148.24	ref. 49
CpFe(CO)H(SiMe ₂ F) ₂	CDCl ₃	162.0	this work
CpFe(CO) ₂ SiMe ₂ F	CDCl ₃	143.5	this work
CpFe(CO) ₂ SiPh ₂ F	CDCl ₃	139.8	this work
CpFe(CO) ₂ SiPh(F)Me	CDCl ₃	130.0	this work
CpFe(CO) ₂ SiF ₂ H	CDCl ₃	118.9	this work
CpFe(CO)H(SiF ₃) ₂	C ₆ D ₆	98.6	this work
CpFe(CO) ₂ SiF ₂ (CH=CH ₂)	CDCl ₃	97.7	ref. 49
CpFe(CO) ₂ SiF ₂ Ph	C ₆ D ₆	95.1	this work
CpFe(CO) ₂ SiF ₃	C ₆ D ₆	94.3	this work
CpFe(CO) ₂ SiF ₂ Me	C ₆ D ₆	89.3	this work
CpFe(CO)H(SiF ₂ Me) ₂	CH ₃ CN	86.9	this work

Table 27 (continued)

Compound	Solvent	δ ppm (CFCl ₃ , $\phi = 0$)	Source
CpFe(PMe ₂ Ph) ₂ SiF ₂ Me	C ₆ D ₆	85.2	this work
CpRu(CO) ₂ SiF ₃	acetone	81.1	this work
CpFe(CO) ₂ CF ₃	CDCl ₃	-11.6	ref. 89
CpFe(CO) ₂ COCF ₃	CDCl ₃	80.1	ref. 89
CpFe(CO) ₂ C ₂ F ₅	acetone	α -F, 61.4; β -F, 80.4	this work
CpFe(CO) ₂ COC ₂ F ₅	CDCl ₃	α -F, 113.6; β -F, 80.3	ref. 89
CpFe(CO) ₂ C ₃ F ₇	acetone	α -F, 52.2; β -F, 112.5; γ -F, 77.6	this work
CpFe(CO) ₂ COC ₃ F ₇	CDCl ₃	α -F, 110.7; β -F, 126.2; γ -F, 81.0	ref. 89

Table V-28
 Measured Coupling Constants of $\text{CpFe}(\text{CO})_2\text{M}'\text{R}_3$
 ($\text{M}' = \text{C}, \text{Si}$) Compounds

Compound	Solvent	Observed Coupling Constant (Hz)
Fe-SiPh(Me)H	neat	$^3J_{(\text{Me-H})} = 3.5$
Fe-SiMe ₂ (C ₆ F ₅)	C ₆ D ₆	$^3J_{(m-F-p-F)} = 19.6;$ $^4J_{(o-F-p-F)} = 2.4;$ $^4J_{(o-F-Me)} = 1.4$
Fe-Si(C ₆ F ₅) ₂ Me	C ₆ D ₆	$^3J_{(m-F-p-F)} = 20.3;$ $^4J_{(o-F-p-F)} = 3.2;$ $^4J_{(o-F-Me)} = 1.4$
Fe-Si(C ₆ F ₅) ₂ Ph	C ₆ D ₆	$^3J_{(m-F-p-F)} = 20.6;$ $^4J_{(o-F-p-F)} = 3.7$
Fe-SiEt ₂ Ph	C ₆ D ₆	$^3J_{(\text{CH}_2\text{-Me})} = 3.1$
Fe-SiF ₂ H	CDCl ₃	$^2J_{(\text{H-F})} = 62.5$
Fe-SiF ₂ Me	C ₆ D ₆	$^3J_{(\text{F-Me})} = 8.2$
Fe-SiMe ₂ F	CDCl ₃	$^3J_{(\text{F-Me})} = 8.0$
Fe-SiPh(F)Me	CDCl ₃	$^3J_{\text{F-Me}} = 8.0$
Fe-SiMe ₂ (OC ₆ F ₅)	C ₆ D ₆	$^3J_{(m-F-p-F)} = 22.4;$ $^4J_{(o-F-p-F)} = 1.2;$ $^5J_{(o-F-Me)} = 1.1$
Fe-Si(OC ₆ F ₅) ₂ Me	C ₆ D ₆	$^3J_{(m-F-p-F)} = 22.3;$ $^4J_{(o-F-p-F)} = 2.4;$ $^5J_{(o-F-Me)} = 1.0$

Table 28 (continued)

Compound	Solvent	Observed Coupling Constant (Hz)
Fe-Si(OC ₆ F ₅) ₂ Ph	C ₆ D ₆	³ J _(m-F-p-F) = 22.3; ⁴ J _(o-F-p-F) = 1.8
Fe-SiMe ₂ (SC ₆ F ₅)	C ₆ D ₆	³ J _(m-F-p-F) = 21.3; ⁴ J _(o-F-p-F) = 0.8; ⁵ J _(o-F-Me) = 0.6
Fe-Si(SC ₆ F ₅) ₂ Me	C ₆ D ₆	³ J _(m-F-p-F) = 21.6; ⁴ J _(o-F-p-F) = 0.8; ⁵ J _(o-F-Me) = 0
Fe-Si(SC ₆ F ₅) ₂ Ph	C ₆ D ₆	³ J _(m-F-p-F) = 20.0; ⁴ J _(o-F-p-F) = 1.8
Fe-CH ₂ C ₆ F ₅	acetone-d ₆	³ J _(m-F-p-F) = 18.0; ⁴ J _(o-F-p-F) = 4.4; ⁴ J _(CH₂-o-F) = 2.3; ² J _{AB} = 1.5
Fe-C ₂ F ₅	acetone	³ J _{αβ} = 1.17
Fe-C ₃ F ₇	acetone	³ J _{αβ} = 1.3; ³ J _{βγ} = 0.7; ⁴ J _{αγ} = 12.2
Fe-SiMe ₂ (OCH ₂ CF ₃)	C ₆ D ₆	³ J _(CH₂-CF₃) = 8.8
Fe-Si(OCH ₂ CF ₃) ₂ Me	C ₆ D ₆	³ J _(CH₂-CF₃) = 8.8
Fe-SiMe ₂ (OEt)	C ₆ D ₆	³ J _(CH₂-Me) = 7.0
Fe-Si(OEt) ₂ Ph	C ₆ D ₆	³ J _(CH₂-Me) = 7.0
Fe-SiPh ₂ (OEt)	C ₆ D ₆	³ J _(CH₂-Me) = 7.0
Fe-SiMe ₂ (Oi-Pr)	C ₆ D ₆	³ J _(CH-Me) = 6.0

Table 28 (continued)

Compound	Solvent	Observed Coupling Constant (Hz)
Fe-Si(O <i>i</i> -Pr) ₂ Me	C ₆ D ₆	³ J _(CH-Me) = 6.2
Fe-Si(O <i>i</i> -Pr) ₂ Ph	C ₆ D ₆	³ J _(CH-Me) = 5.6
Fe-SiMe ₂ (SEt)	C ₆ D ₆	³ J _(CH₂-Me) = 7.2
Fe-Si(SEt) ₂ Me	C ₆ D ₆	³ J _(CH₂-Me) = 7.6
Fe-Si(SEt) ₂ Ph	C ₆ D ₆	³ J _(CH₂-Me) = 7.2
Fe-SiMe ₂ (S <i>i</i> -Pr)	C ₆ D ₆	³ J _(CH-Me) = 6.8
Fe ²⁺ -Si(S <i>i</i> -Pr) ₂ Me	C ₆ D ₆	³ J _(CH-Me) = 6.4

couplings observed are quite normal for these compounds. Even the five bond couplings observed for $\text{CpFe}(\text{CO})_2\text{Si}(\text{YC}_6\text{F}_5)_x\text{Me}_{3-x}$ ($\text{Y} = \text{O}, \text{Si}; x = 1, 2$) are not unusual, since related compounds show similar values.⁸⁵

The small α, β -fluorine coupling observed for $\text{CpFe}(\text{CO})_2\text{R}_f$ ($\text{R}_f = \text{C}_2\text{F}_5, \text{C}_3\text{F}_7$) is consistent with results observed on related transition metal- C_2F_5 and $-\text{C}_3\text{F}_7$ compounds.^{120,121}

B. Compounds of Type $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$

A list of measured chemical shifts for these complexes is presented in Table V-29. Again, τ values of the Cp resonance of these compounds were found to be markedly affected by solvent. For example, the Cp resonance of $\text{CpFe}(\text{CO})\text{H}(\text{SiF}_3)_2$ occurs at τ 5.35 in benzene, at τ 4.75 in CD_2Cl_2 , and at τ 4.57 in CH_3CN . The Cp resonance also shifts to lower τ value as electron withdrawing groups are placed upon silicon. This effect was discussed for $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds.

It is informative to note that τ Si-Me shifts to a less shielded value as one increases chlorine substitution at silicon. This effect was also observed for $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds,⁶ and results presented in Table V-25 indicate a similar trend when $\text{CpFe}(\text{CO})_2\text{SiMe}_x\text{R}_{3-x}$ ($\text{R} = \text{C}_6\text{F}_5, \text{OC}_6\text{F}_5, \text{SC}_6\text{F}_5; \text{R} \neq \text{F}; x = 1, 2$) compounds are compared. When fluorosilyl compounds are considered, however, such a

Table V-29

Chemical Shifts for CpFe(CO)H(SiR₃)₂ Compounds

SiR ₃	Solvent	τ_{Cp}	$\tau_{\text{Si-Ph}}$	$\tau_{\text{Si-Me}}$	$\tau_{\text{Fe-H}}$	$\delta_{\text{F}} (\text{CFCl}_3, 0 \text{ ppm})$
SiPh ₂ Me	CD ₂ Cl ₂	5.39	2.3-2.8	9.38	22.76	---
SiCl ₂ Ph	CD ₂ Cl ₂	5.69	2.1-3.0	---	23.28	---
SiMe ₂ Ph	CD ₂ Cl ₂	5.70	2.3-2.7	9.22, 9.38	23.74	---
SiCl ₂ Me	C ₆ D ₆	5.68	---	8.97	22.88	---
SiF ₂ Me ^a	C ₇ D ₈	5.69	---	9.45	24.25	102.1
SiF ₃	CD ₂ Cl ₂	4.75	---	---	24.12	98.6
SiMe ₂ Cl	CDCl ₃	5.11	---	9.09, 9.18	23.85	---
SiMe ₂ F	CDCl ₃	5.30	---	9.38, 9.43	24.05	162.0
SiMe ₂ (C ₆ F ₅)	C ₆ D ₆	6.06	---	9.18, 9.26	23.20	<i>o</i> -F, 123.8; <i>m</i> -F, 158.7; <i>p</i> -F, 150.8
SiCl ₃ ^b	cyclohexane	4.73	---	---	21.6	---
CpRu(CO)H(SiCl ₃) ₂ ^c	C ₆ D ₆	5.33	---	---	18.34	---

^aThe Si-F resonance is an ABMX₃ spin system, and the centre of this resonance is reported here.

^bReference 6.

^cSee discussion in text concerning the spectrum of this compound in CH₃CN.

shift to lower τ value is not observed (*cf.*, $\text{CpFe}(\text{CO})_2\text{SiMe}_2\text{F}$, $\tau_{\text{Me}} = 9.40$; $\text{CpFe}(\text{CO})_2\text{SiF}_2\text{Me}$, $\tau_{\text{Me}} = 9.41$; $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{F})_2$, $\tau_{\text{Me}} = 9.38, 9.43$; $\text{CpFe}(\text{CO})\text{H}(\text{SiF}_2\text{Me})_2$, $\tau_{\text{Me}} = 9.45$).

This might reflect reduced charge separation within the silicon-fluorine bond arising from $p\pi-d\pi$ back donation.

In support of this hypothesis, comparison of force constant results on analogous $\text{CpFe}(\text{CO})_2\text{SiX}_x\text{R}_{3-x}$ ($X = \text{Cl, F}$; $\text{R} = \text{Me, Ph}$; $x = 3, 2, 1$) compounds, shows that the fluoro compounds invariably possess a lower force constant than do the chloro compounds (see Tables IV-15 and IV-16). This is consistent with increased charge density upon silicon, arising from $p\pi-d\pi$ back donation from fluorine, and would not be expected from a consideration of electronegativity alone.

The pairs of Me groups on each silicon in compounds of formula $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{R})_2$ are diastereopic, so two Me resonances are expected and observed. This effect is very noticeable for $\text{CpFe}(\text{CO})\text{H}(\text{SiF}_2\text{Me})_2$, where here the fluorines are nonequivalent as shown in Figure V-XII and show an AB spin pattern.

The high field proton resonance due to Fe-H or Ru-H falls in the region τ 18-25, consistent with observations on similar compounds.⁶⁰

A list of coupling constants observed for $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ compounds is presented in Table V-30. The observation of ^{29}Si satellites about the high field

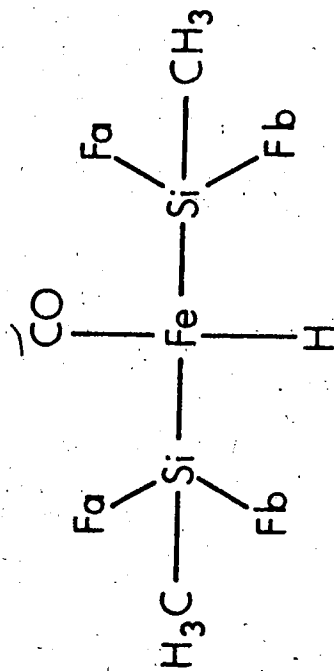


Figure V-XII. A view down the Cp-iron axis (Cp not shown) indicating the diastereopic fluorines on silicon.

②

Table V-30

Measured Coupling Constants for CpFe(CO)H(SiR₃)₂ Compounds

SiR ₃	Solvent	Observed Coupling Constants (Hz)	² J _(²⁹Si-H) (Hz)
SiCl ₂ Me	CH ₃ CN	---	14
SiF ₂ Me ^a	C ₇ D ₈	³ J _(F-Me) = 6.5; ³ J _(F-H) = 3.8, 14.8	--
SiF ₃	CH ₃ CN	³ J _(F-H) = 12.5	38
SiMe ₂ F	CDCl ₃	³ J _(F-Me) = 8.0, ³ J _(F-H) = 8.5	16
SiMe ₂ (C ₆ F ₅)	C ₆ D ₆	³ J _(m-F-p-F) = 20.4; ⁴ J _(o-F-p-F) = 2.4	--
		⁵ J _(o-F-Me) = 2.1	
SiCl ₃ ^b	CH ₃ CN	¹ J _(⁵⁷Fe-H) = 14.5	20
CpRu(CO)H(SiCl ₃) ₂	CH ₃ CN	---	27

^aIn CH₃CN all fluorines coupling equivalently to the high proton such that

³J_(F-H) = 14.5 Hz. See text for discussion.

^bReference 6.

proton of some of these compounds is of interest. Since ^{29}Si is only 4.7% abundant, highly concentrated solutions are necessary for observation of these satellites. Thus, it was found that CH_3CN was the only solvent in which these compounds were sufficiently soluble to produce sharp, high quality spectra. The spectrum of $\text{CpFe}(\text{CO})\text{H}(\text{SiF}_3)_2$ serves to illustrate these points and is presented in Figure V-XIII. The high field proton resonance is coupled to the six equivalent ^{19}F nuclei and ^{29}Si satellites are clearly observable about the five more intense peaks. That these satellites were indeed authentic and not spinning side bands was verified by varying the spin rate of the NMR tube. This did not affect the position of the satellites.

The proton spectrum of $\text{CpFe}(\text{CO})\text{H}(\text{SiF}_2\text{Me})_2$ in toluene showed nonequivalent coupling of the AB fluorines to the high field proton, however, this coupling was equivalent in CH_3CN . This solvent effect was temperature invariant in the above solvents; however, a 1:9 (vol/vol) mixture of CH_3CN in toluene, when used as solvent, produced temperature dependent coupling effects as shown in Figure V-XIV whereby the two nonequivalent couplings of 6.8 and 12.4 Hz at $+80^\circ$ became equivalent at -80° , and of value 12.5 Hz. That this was a solvent effect and not the consequence of fluorine groups becoming equivalent was verified by running the ^{19}F spectra.

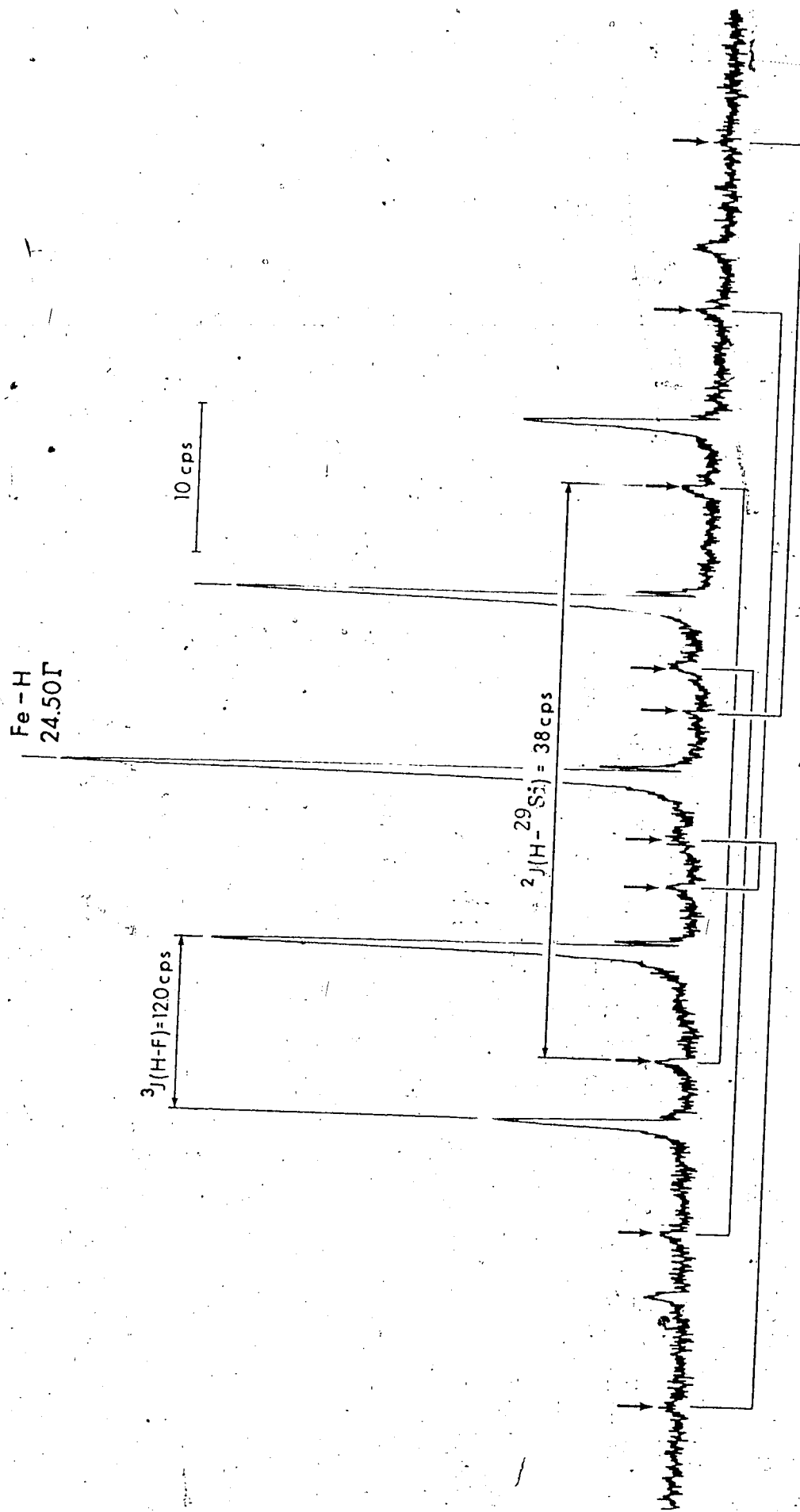


Figure V-XIII: High field proton resonance in CH_3CN of $\text{CpFe(CO)H(SiF}_3)_2$, showing the indicated coupling constants. Arrows mark ^{29}Si satellites.

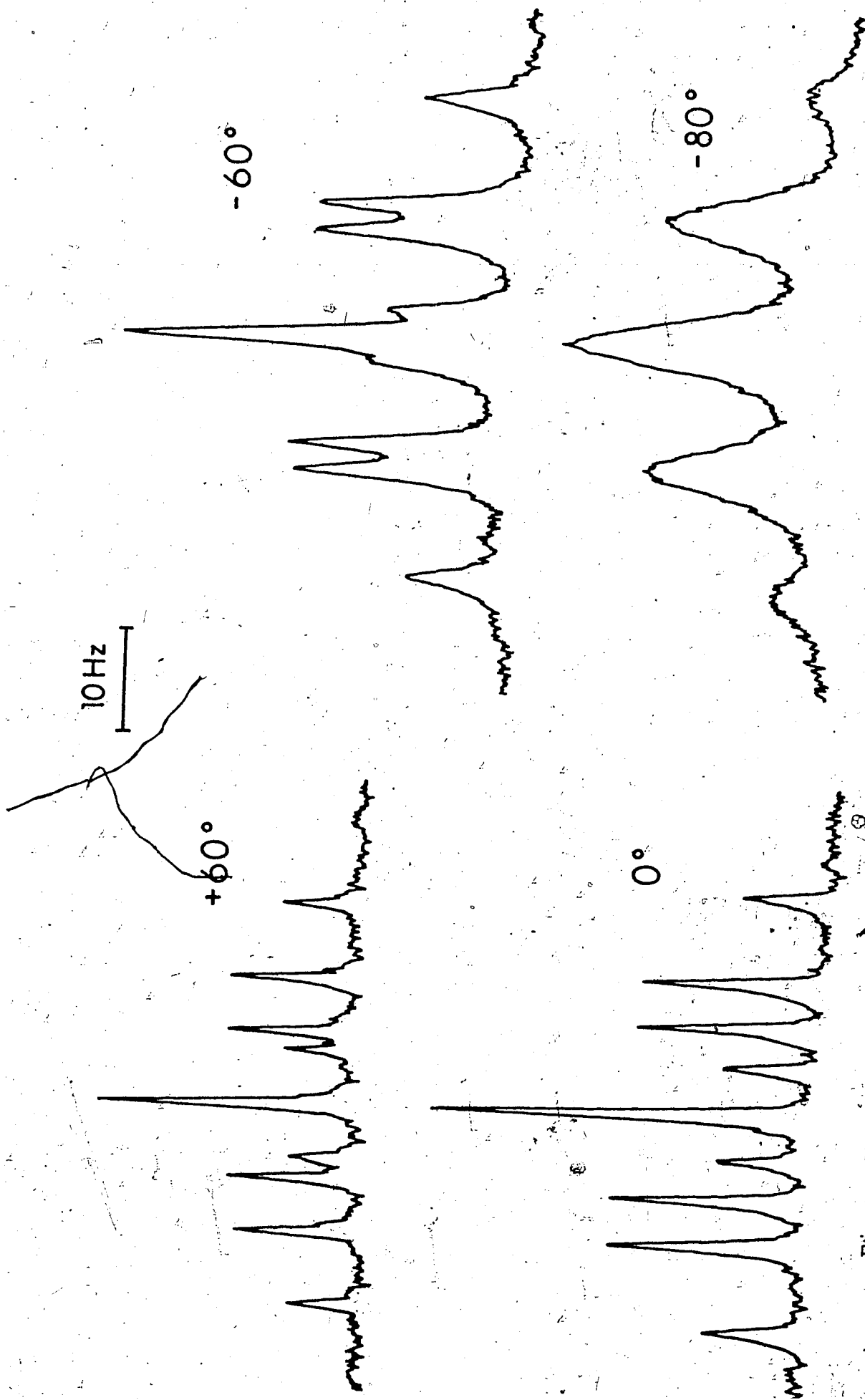


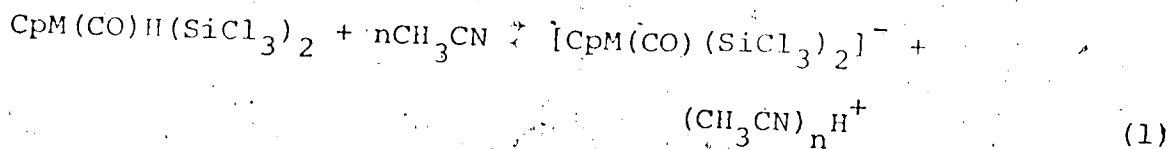
Figure V-XIV: Temperature dependent PMR spectrum of the high field proton resonance of CpFe(CO)H(SiF₂Me)₂ in 1:9 (vol/vol) CH₃CN:toluene.

An ABMX₃ spin system was observed throughout the temperature range in the mixed solvent, its appearance varying due to the aforementioned coupling change. Also the ¹⁹F spectrum in CH₃CN was consistent with an ABMX₃ spin system, where AB corresponds to the fluorine nuclei of CpFe(CO)H(SiF₂Me)₂.

The acidity of CpFe(CO)H(SiCl₃)₂ in CH₃CN has been established by observation of two Cp resonances in the NMR spectrum (their ratios yielded a pK_a value of 2.6).⁵⁸ A similar study was conducted in the present work upon all the hydrido compounds prepared. Only the compound CpRu(CO)H(SiCl₃)₂ showed two Cp resonances in CH₃CN arising from the equilibrium given in equation (1), and their ratios yielded a pK_a value of 2.4 (a 0.215 M solution showed two Cp resonances at τ 4.18 due to CpRu(CO)H(SiCl₃)₂ and τ 4.85 due to [CpRu(CO)₂(SiCl₃)₂]⁻ in an integrated ratio of 75.5 to 15.0). The comparable pK_a values for CpM(CO)H(SiCl₃)₂ (M = Fe, Ru) compounds, and the lack of dissociation of any of the other hydrido compounds,^a suggests that the SiCl₃ group is unique in

^aThe compounds CpFe(CO)H(SiMe₂Ph_{3-x})₂ (x = 1, 2) do not react with Et₃N in *n*-hexane. The compound CpFe(CO)H(SiCl₂Me)₂ reacts with Et₃N in CH₂Cl₂ to form an equilibrium which favors the neutral compound. This suggests that this compound is a weak acid while the former two compounds show no acidic tendencies.¹²²

these complexes. It may cause the metal-hydrogen bond to dissociate due to strong removal of charge density away from the transition metal. Although this effect may be largely a bonding in nature, it could also reflect significant acidic property of the SiCl_3 group.



C. Compounds of Type $\text{CpFe}(\text{CO})_{2-n}(\text{PMe}_2\text{Ph})_n\text{SiR}_3$ ($n = 1, 2$)

A list of chemical shifts observed for these compounds is presented in Table V-31. The position of the Cp resonance is relatively insensitive to changes in group attached to silicon, unlike analogous $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds.

All resonances are in the expected locations and asymmetry about the Cp-Fe axis⁸⁷ produces nonequivalent Si-Me resonances for $\text{CpFe}(\text{CO})\text{L}(\text{SiMe}_2\text{Ph})$ ($\text{L} = \text{PPh}_3, \text{PMe}_2\text{Ph}$) compounds. Of more interest is the nonequivalence of the phosphorus-Me resonance observed for the $n = 2$ compounds. A pair of deceptively simple $X_3\text{AA}'X_3$ ¹²³ resonances is generally observed, as shown in Figure V-XV.

The possibility of a rapid intramolecular rearrangement through a planar intermediate has been raised for the tetrahedral compound $(\text{PMe}_2\text{Ph})_2\text{Co}(\text{CO})\text{NO}$, but was not observed.⁶⁷ Compounds of formula $\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiR}_3$ might also undergo the process proposed by Wright and

Table V-31

Chemical Shifts Observed for $\text{CpFe}(\text{CO})_{2-n}(\text{PMe}_2\text{Ph})_n\text{SiR}_3$ ($n = 1, 2$) Compounds

Compound	Solvent	τ_{Cp}	τ_{Ph}	$\tau_{\text{P-Me}}$	$\tau_{\text{Si-Me}}$
$\text{CpFe}(\text{CO})(\text{PPh}_3)_2\text{SiMe}_2\text{Ph}$	C_6D_6	5.91	2.1-3.0	---	9.35, 9.69
$\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})_2\text{SiMe}_2\text{Ph}$	CDCl_3	5.91	2.3-2.9	8.46, 8.75	9.47, 9.51
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiMe}_2\text{Ph}$	C_6D_6	6.21	2.1-3.0	8.73	9.27
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiMe}_3$	C_6D_6	6.28	2.3-3.0	8.64, 8.78	9.52
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiPh}_2\text{Me}$	C_6D_6	6.07	2.2-3.1	8.75	9.19
$\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})_2\text{SiPh}_2\text{Me}$	C_6D_6	5.98	2.1-3.0	8.87, 9.08	9.14
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiPh}_3$	CS_2	6.17	2.0-3.0	8.65, 8.80	---
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiCl}_3$	CD_2Cl_2	5.95	2.3-2.8	8.20, 8.35	---
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiF}_2\text{Me}^a$	C_6D_6	6.09	2.2-3.8	8.37, 8.43	9.10

^a 19F chemical shift occurs at 85.2 ppm relative to CFCl_3 .



10Hz

Figure V-XV: PMR spectrum of phosphorus-Me groups of $\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiPh}_3$ showing a pair of deceptive simple $\text{X}_3\text{AA}'\text{X}_3$ resonances. The Me groups on each phosphorus are diastereopic, but each phosphorus atom is symmetry related. This accounts for the two Me resonances.

Mawby.⁶⁷ If such a process did occur, then one should observe an $X_6AA'X'_6$ ^{133,124} spectrum, where X and X' correspond to the phosphorus-Me protons. Such a spin system was observed at the high temperature limit for $CpFe(PMe_2Ph)_2SiMe_2Ph$; the temperature dependent NMR spectrum in CS_2 solvent for this compound is shown in Figure V-XVI. The compound $CpFe(PMe_2Ph)_2SiPh_2Me$ showed a similar temperature dependent spectrum, the process being reversible for both compounds. The other bisphosphine compounds prepared showed nonequivalent phosphorus-Me resonances up to 80°.

The results suggest that rapid intramolecular rearrangement can occur for some of these compounds, depending upon the substituents on silicon. This rearrangement has been postulated to proceed through a planar intermediate,⁶⁷ and might be facilitated in the compounds studied in the present work by the bulky substituents which may be expected to significantly distort the geometry towards a planar one. Since ^{31}P to $Cp-^1H$ coupling was observed throughout, a dissociative process was ruled out.

A list of coupling constants observed for $CpFe(CO)_{2-n}(PMe_2Ph)_nSiR_3$ ($n = 1, 2$) is presented in Table V-32. Coupling of phosphorus to Cp ring protons has been observed for related compounds.⁶⁶

The Δ values presented in Table V-32 refer to the separation of the outer sharp lines of the deceptively simple $X_nAA'X'_n$ ($n = 3, 6$) spin system.¹²⁴ This value is

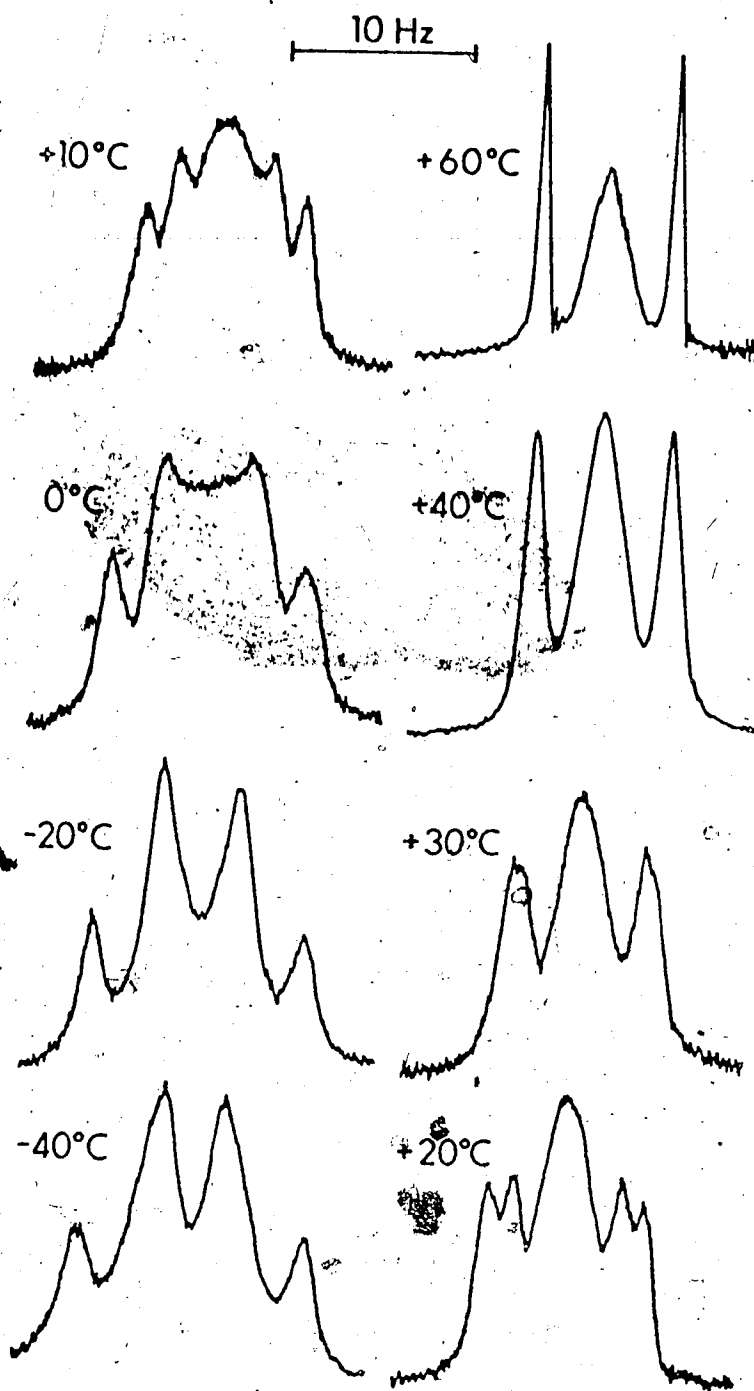


Figure V-XVI: Temperature dependent PMR spectra in CS_2 of the phosphorus-Me resonance of $\text{CpFe}(\text{Ph})_2\text{SiMe}_2\text{Ph}$. The lower temperature spectra are the result of two overlapping deceptively simple $X_3AA'X_3'$ spectra, the high temperature spectrum corresponds to a deceptively simple $X_6AA'X_6'$ spectra.

Table V-32

Measured Coupling Constants of $\text{CpFe}(\text{CO})_{2-n}(\text{PMe}_2\text{Ph})_n\text{SiR}_3$ ($n = 1, 2$) Compounds

Compound	Solvent	Observed Coupling Constants (Hz)	Δ^a (Hz)
$\text{CpFe}(\text{CO})(\text{PPh}_3)_2\text{SiMe}_2\text{Ph}$	C_6D_6	$^3J_{(\text{P-Cp})} = 2.0$	---
$\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})_2\text{SiMe}_2\text{Ph}$	CDCl_3	$^3J_{(\text{P-Cp})} = 1.6$; $^2J_{(\text{P-Me})} = 9.0$	---
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiMe}_2\text{Ph}$	C_6D_6	$^3J_{(\text{P-Cp})} = 1.6$	7.4
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiMe}_3$	C_6D_6	$^3J_{(\text{P-Cp})} = 1.4$	7.8
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiPh}_2\text{Me}$	C_6D_6	$^3J_{(\text{P-Cp})} = 1.6$	7.4
$\text{CpFe}(\text{CO})(\text{PMe}_2\text{Ph})_2\text{SiPh}_2\text{Me}$	C_6D_6	$^3J_{(\text{P-Cp})} = 1.3$; $^2J_{(\text{P-Me})} = 9.0$	---
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiPh}_3$	CS_2	$^3J_{(\text{P-Cp})} = 2.0$	7.6
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiCl}_3$	CD_2Cl_2	$^3J_{(\text{P-Cp})} = 1.4$	8.4
$\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiF}_2\text{Me}$	C_6D_6	$^3J_{(\text{P-Cp})} = 1.3$; $^3J_{(\text{F-Me})} = 8.1$	7.4

^a Δ refers to the measured distance between the outer sharp lines of the deceptively simple $X_{AA'X'_n}$ ($n = 3, 6$) spectra. See text for further discussion.

actually $|J_{AX} + J_{AX'}|^{124}$ and remains quite constant despite variation of substituents on silicon.

Chapter VI

X-Ray Structural Results

The infrared results discussed in Chapter IV concerning the rotamer phenomenon of $\text{CpFe}(\text{CO})_2\text{SiR}_3$ and related compounds, and also for $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ compounds, necessarily involved a study of these complexes in solution. The solvent *n*-heptane was used in those studies, since in that solvent molecules may be considered free from solvation effects. Also, because solution concentrations were very dilute ($\sim 10^{-3}$ M), molecules of these compounds were considered free of intermolecular interactions. With the above points in mind, the infrared studies conducted in Chapter IV may be considered to be an investigation of these compounds in an isolated state, similar to a dilute gaseous state.

To support further suggestions put forth in Chapter IV regarding factors controlling the distribution of rotamers in $\text{CpFe}(\text{CO})_2\text{SiR}_3$ and related compounds, structural evidence will now be presented. The structural results are available through a number of X-ray crystallographic analyses on $\text{CpFe}(\text{CO})_2\text{M}'\text{R}_3$ and $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ compounds. A comparison of the structures of closely packed molecules in the solid state with the essentially isolated molecules of solution studies involves many uncertainties. Despite this drawback, it is felt useful information can be obtained from a comparison of solid state and solution results.

A. Compounds of Type $\text{CpFe}(\text{CO})_2\text{M}'\text{R}_3$

Crystal structures on $\text{CpFe}(\text{CO})_2\text{SnPh}_3$,^{109a}
 $\text{CpFe}(\text{CO})_2\text{SnPh}_2\text{Cl}$,¹²⁵ $\text{CpFe}(\text{CO})_2\text{SnCl}_2\text{Ph}$,^{37b} $\text{CpFe}(\text{CO})_2\text{SnCl}_3$,¹²⁶
 and $\text{CpFe}(\text{CO})_2\text{SnBr}_3$ ^{109c} have established two important
 features of these compounds. Firstly, intramolecular
 nonbonded distances are such that groups attached to
 tin are closer to the Cp ring than they are to the CO
 ligands. Secondly, one observes various orientations of
 the SnR_3 moiety with respect to the $\text{CpFe}(\text{CO})_2$ moiety
 in these crystal structures. These two points will now
 be considered.

i) Intramolecular Nonbonded Distances in
 $\text{CpFe}(\text{CO})_2\text{M}'\text{R}_3$ Compounds

Using the cell constants and fractional coordinates
 reported by Bryan and coworkers for the above com-
 pounds,^{37b,109,125,126} nonbonded intramolecular contacts
 less than 3.5 Å were evaluated to determine possible
 interactions between Cp hydrogens and groups bonded to
 M' , and between CO ligands and groups bonded to M' . Since
 the Cp hydrogens were only located in $\text{CpFe}(\text{CO})_2\text{SnCl}_3$,
 the Cp hydrogen atom fractional coordinates for all these
 compounds were determined as follows. Using the computer
 program XRAY:MMMR,¹²⁷ fractional coordinates for the
 Cp ring centroid and Cp carbon atoms were determined in
 the framework of a rigid hindered rotor treatment.¹²⁸

The Cp hydrogens were then assumed to be in the same plane as the Cp carbon atoms and at a distance of 1.0 Å away from them. On this basis, fractional coordinates for Cp hydrogen atoms were generated, and nonbonded distances were evaluated using the computer program DRILL.^a

The results of these calculations are presented in Table VI-33. The determined nonbonded intramolecular contact of Cl to Cp-H of 2.87 Å in $\text{CpFe}(\text{CO})_2\text{SnCl}_3$ ¹²⁶ agrees with the value of 2.88 Å obtained by the aforementioned treatment, which is gratifying agreement.

The important result of Table VI-33 is the lack of any nonbonded contacts below 3.5 Å between the CO ligands and groups attached to tin. However, some quite close nonbonded contacts are observed between Cp hydrogens and groups bonded to tin. This supports the argument presented in Chapter IV that observed rotamer populations are largely controlled by an interaction of groups attached to M' and the Cp ring hydrogens, rather than an interaction of groups bound to M' and CO ligands, as was suggested.¹⁰⁸ Further, it was postulated in Chapter IV that rotamer populations may be influenced by a van der Waals attractive interaction between an electron withdrawing substituent on M' and Cp hydrogens. From Table VI-33

^aDr. J. Takats, private communication. The program was modified at the University of Alberta for the IBM 360/67.

Table VI-33
 Nonbonded Intramolecular Contacts Shorter than
 3.5 Å for CpFe(CO)₂SnR₃ Compounds

Compound	Calculated Nonbonded Intramolecular Contacts. ^a
CpFe(CO) ₂ SnCl ₂ Ph	Cl to Cp-H: 3.05 Å Cl' to Cp-H': 3.48 Å
CpFe(CO) ₂ SnPh ₂ Cl	none
CpFe(CO) ₂ SnCl ₃	Cl to Cp-H: 2.88 Å Cl' to Cp-H: 3.19 Å Cl' to Cp-H': 3.16 Å
CpFe(CO) ₂ SnBr ₃	Br to Cp-H: 3.10 Å

^aCalculated in the manner described in the text. Primes denote different atoms. For example, in CpFe(CO)₂SnCl₃, two different Cl atoms have nonbonded intramolecular contacts less than 3.5 Å with the same Cp-H atom.

it can be seen that such interactions are feasible, due to close contact between halogen atoms and Cp hydrogens.

The compound $\text{CpFe}(\text{CO})_2\text{SnPh}_2\text{Cl}$ shows no contacts less than 3.5 Å of the type being considered. This is the case because this compound possesses nearly ideal C_s symmetry in the X-ray structure.¹²⁵ This necessarily means that the Cl atom is transoid to the Cp ring; therefore, no Cl-Cp hydrogen interaction is possible. Even so, no interaction between the Cl atom and CO-ligands was observed.

Accurate molecular models of this compound and others containing phenyl groups indicate no abnormally short phenyl hydrogen intramolecular contacts. Thus, phenyl hydrogens were not included in the above treatment.

Preliminary X-ray results on $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Ph}$ show this compound to possess near ideal C_s symmetry.¹²⁹ Using data at a refined R factor stage of 23%, the following nonbonded intramolecular contacts were found: Cl to Cp-H, 3.18 Å; Cl to Cp-H', 3.27 Å, Cl' to Cp-H, 3.10 Å. There were no other contacts of the type being considered and although these results are expected to have large standard deviations, they provide useful comparative values. Thus, the above results are similar to those obtained for $\text{CpFe}(\text{CO})_2\text{SnCl}_2\text{Ph}$; and surprisingly suggest that altering the Fe-M' bond length produces little change in nonbonded contacts between Cp hydrogens and

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Preliminary X-ray results on $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Ph}$ show this compound to possess near ideal C_s symmetry.¹²⁹ Using data at a refined R factor stage of 23%, the following nonbonded intramolecular contacts were found: Cl to Cp-H, 3.18 Å; Cl to Cp-H', 3.27 Å, Cl' to Cp-H, 3.10 Å.

There were no other contacts of this type being considered and although these results are expected to have large standard deviations, they provide useful comparative values. Thus, the above results are similar to those obtained for $\text{CpFe}(\text{CO})_2\text{SnCl}_2\text{Ph}$; and surprisingly suggest that altering the Fe-M' bond length produces little change in nonbonded contacts between Cp hydrogens and

substituents on M'. Molecular models of these compounds disclose that tilting of the Cp ring as defined by the angle at the iron atom between M' and the Cp ring centroid apparently allows similar nonbonded contacts between Cp hydrogens and R groups to be maintained, despite variation in the iron-M' bond length. Tilting of the Cp ring in complexes of formula Cp_2MX_2 is a well recognized phenomenon.¹³⁰ This ring tilting effect in $\text{CpFe}(\text{CO})_2\text{M}'\text{R}_3$ compounds may be expressed conveniently by the angle $\text{Cp}(\text{centroid})-\text{Fe}-\text{M}'$, and the results are given in Table VI-34.

In Chapter IV, it was found that rotamer populations were invariant to changes in M-M'. This agrees with the above structural evidence insofar as the intramolecular nonbonded contacts are concerned. The rotamer populations are unaffected by changes in M-M' is consistent with a tilting of the Cp ring away from or towards groups attached to M', such that a favorable van der Waals contact may be maintained between Cp hydrogens and electron withdrawing substituents attached to M' (cf., $\text{CpFe}(\text{CO})_2\text{SnCl}_2\text{Ph}$, $\text{Cp}(\text{centroid})-\text{Fe}-\text{Sn} = 119^\circ$; $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Ph}$, $\text{Cp}(\text{centroid})-\text{Fe}-\text{Si} = 130^\circ$).

Selected M-M' bond lengths are presented in Table VI-35. It is apparent that a significant shortening of the iron-M' bond is observed on going from tin to silicon. This trend continues as M' becomes carbon, as one might

Table VI-34

Variation in the Tilting of the Cp Ring
in $\text{CpFe}(\text{CO})_2\text{M}'\text{R}_3$ Compounds as Defined by
the Angle at Iron between M' and the Cp Ring Centroid

Compound	$\angle \text{Cp}(\text{centroid})\text{-Fe-M}'$	Reference
$\text{CpFe}(\text{CO})_2\text{SnPh}_3$ (Molecule 1)	124°	109a
$\text{CpFe}(\text{CO})_2\text{SnPh}_3$ (Molecule 2)	120°	109a
$\text{CpFe}(\text{CO})_2\text{SnPh}_2\text{Cl}$	122°	125 ^a
$\text{CpFe}(\text{CO})_2\text{SnCl}_2\text{Ph}$	119°	37b
$\text{CpFe}(\text{CO})_2\text{SnCl}_3$	125°	126
$\text{CpFe}(\text{CO})_2\text{SnBr}_3$	122°	109c
$\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Ph}$	130°	129 ^a

^aThis angle was not available in the reference; therefore it was determined with the aid of DRILL.

Table VI-35

M-M' (M = Fe, Ru; M' = C, Si, Sn) Bond Lengths
 Applicable to $\text{CpM}(\text{CO})_2\text{M}'\text{R}_3$ Compounds

Compound	M-M' Length, Å	Reference
$\text{CpFe}(\text{CO})_2\text{SnCl}_2\text{Ph}$	2.467(2)	37b
$\text{CpFe}(\text{CO})\text{H}(\text{SiCl}_3)_2^a$	2.252(3)	112
$\text{CpFe}(\text{CO})_2(\sigma\text{-Cp})$	2.11(2)	131
$[\text{Me}_3\text{Si}(\text{CO})_3\text{RuSiMe}_2]_2$	2.507(8) ^b	132
$[\text{Me}_3\text{Si}(\text{CO})_3\text{RuSnMe}_2]_2$	2.686(2) ^c	133

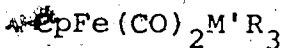
^aThe iron-silicon bond length for $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Ph}$ is not reported here, since the structure is still not completely refined, R factor is 21% at present.

^bThis value corresponds to the terminal Ru-SiMe₃ bond length. The two bridging Ru-Si bond lengths are 2.391(7) Å and 2.491(8) Å.

^cThis value corresponds to the terminal Ru-SnMe₃ bond length. The two bridging Ru-Sn bond lengths are 2.638(2) Å and 2.694(2) Å.

have expected that a critical point would be reached where the iron-M' bond becomes so short that the Cp ring may no longer be able to tilt sufficiently away from the substituents on M'. Results of Chapter IV gave no evidence that this was occurring for iron-carbon compounds investigated since both rotamers were observed for $\text{CpFe}(\text{CO})_2\text{C}_2\text{F}_5$ and $-\text{C}_3\text{F}_7$ compounds. Also, for $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_5$, only the C_1 rotamer was observed in the infrared, suggesting an attractive interaction between Cp hydrogens and the C_6F_5 group.

ii) Orientation of $\text{M}'\text{R}_3$ and $\text{CpFe}(\text{CO})_2$ Moieties in



Bryan and coworkers^{37b, 109, 125, 126} have established that various orientations of the SnR_3 group with respect to the $\text{CpFe}(\text{CO})_2$ moiety are possible. ORTEP drawings viewed down the tin-iron bond are shown in Figures VI-XVII through VI-XXII. The orientation of the two independent molecules of $\text{CpFe}(\text{CO})_2\text{SnPh}_3$, of $\text{CpFe}(\text{CO})_2\text{SnPh}_2\text{Cl}$, and of $\text{CpFe}(\text{CO})_2\text{SnCl}_2\text{Ph}$, shown in Figures VI-XVII, VI-XVIII, VI-XIX, and VI-XXII, establish the close to ideal C_s symmetry of these compounds in the crystalline state. However, $\text{CpFe}(\text{CO})_2\text{SnBr}_3$ and $\text{CpFe}(\text{CO})_2\text{SnCl}_3$, shown in Figures VI XX and VI-XXI, both deviate markedly from C_s symmetry, and are in fact moving towards eclipsed conformers. These results provide evidence for a low

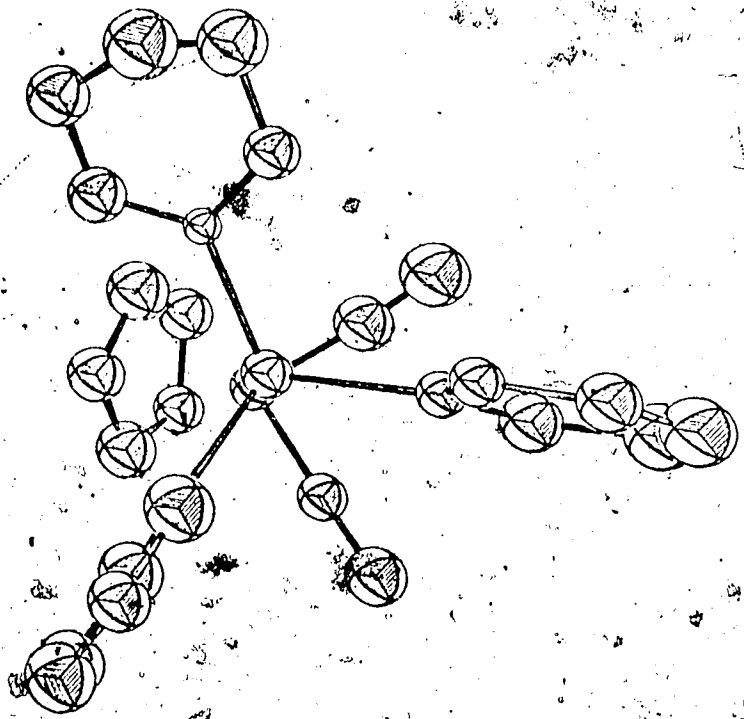


Figure VI-XVIII. A view down the tin-iron bond of CpFe(CO)₂SnPh₃ (molecule 2).

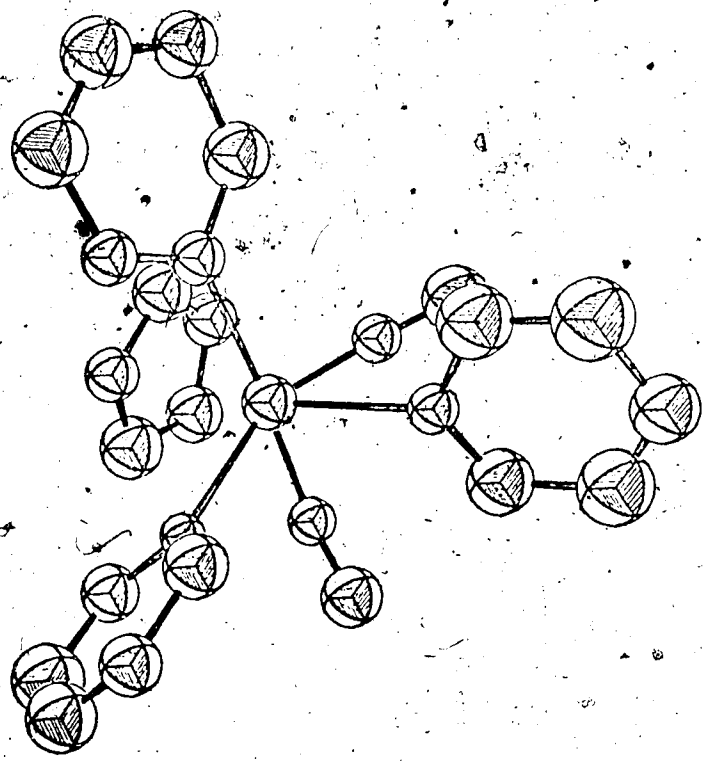


Figure VI-XVII. A view down the tin-iron bond of CpFe(CO)₂SnPh₃ (molecule 1).

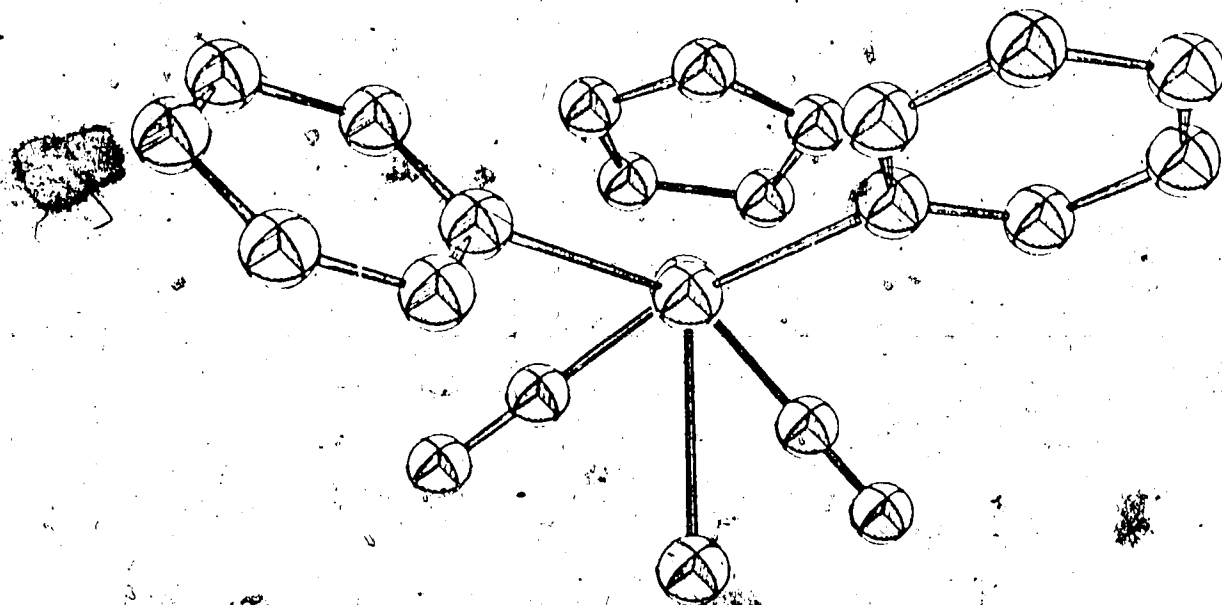


Figure VI-XIX: A view down the tin-iron bond of $\text{CpFe}(\text{CO})_2\text{SnPh}_2\text{Cl}$.

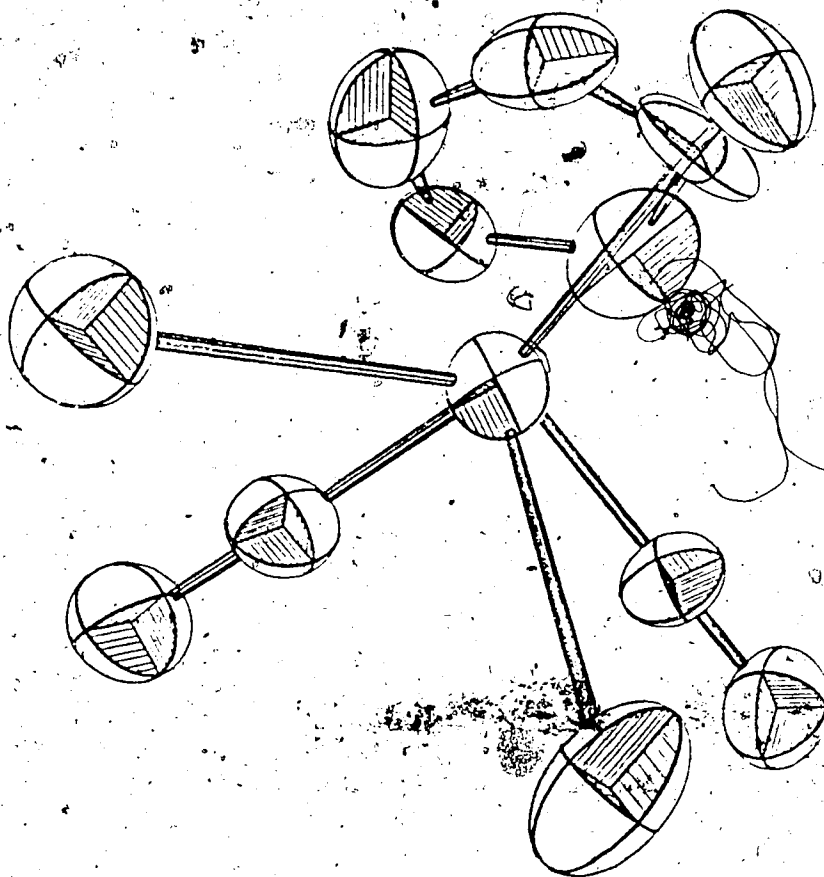


Figure VI-XX: A view down the tin-iron bond of $\text{CpFe}(\text{CO})_2\text{SnBr}_3$.

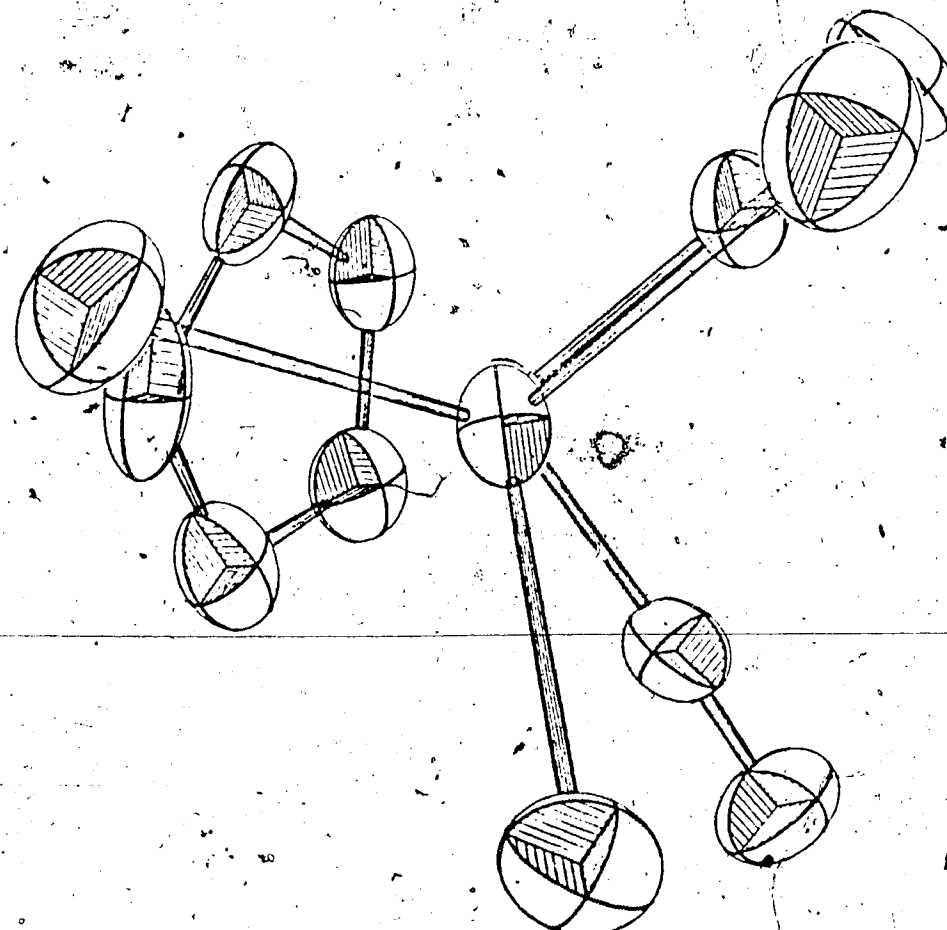


Figure VI-XXI: view down the tin-iron bond of $\text{CpFe}(\text{CO})_2\text{SnCl}_3$.

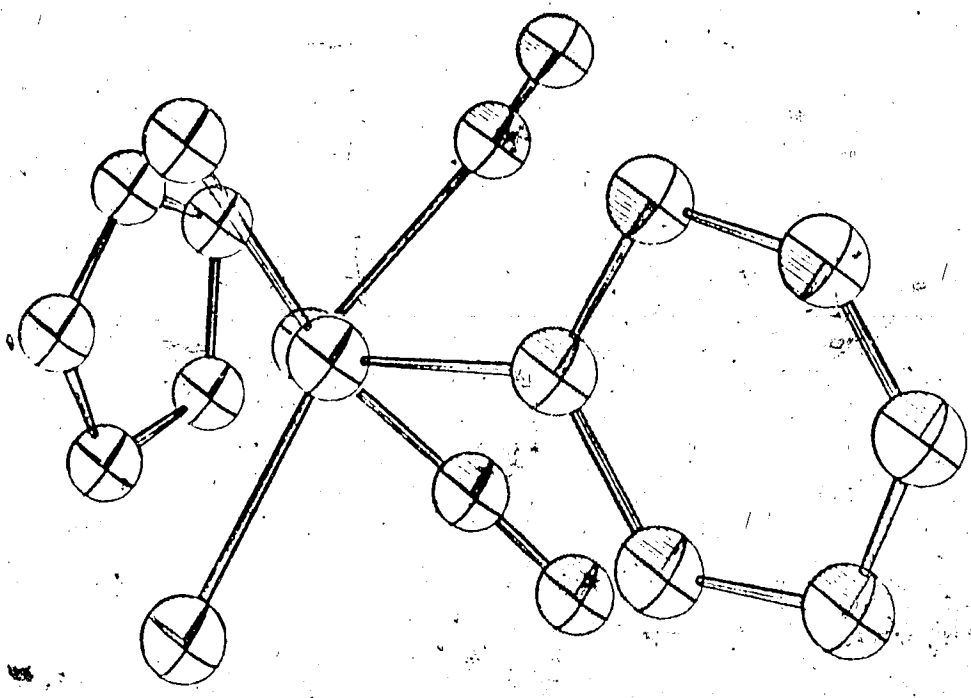


Figure VI-XXII: A view down the tin-iron bond of $\text{CpFe}(\text{CO})_2\text{SnCl}_2\text{Ph}$.

rotational barrier between the two halves of these molecules.^{107,108} The close to eclipsed forms observed for $\text{CpFe}(\text{CO})_2\text{SnBr}_3$ and $-\text{SnCl}_3$ suggest that a favorable interaction between halogen atoms and Cp hydrogens may be responsible for these conformations, a possibility not suggested by Bryan.^{37b,109,125,126}

In Figure VI-XXIII, theORTEP drawing for $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Ph}$ viewed down the silicon-iron bond is presented. This compound is very similar in geometric appearance to the analogous tin compound shown in VI-XXII.

Interestingly, none of the above structures showed a staggered C_1 rotamer of the type diagrammed in Figure I-I. However, a recent communication on structures of $\text{CpFe}(\text{CO})_2\text{P}(\text{CF}_3)_2$ and $\text{CpFe}(\text{CO})_2\text{F}(\text{O})(\text{CF}_3)_2$ shows both of these molecules in such a conformation.¹³⁴ A sample of $\text{CpFe}(\text{CO})_2\text{P}(\text{CF}_3)_2$ was kindly provided by Dr. R. C. Dobbie,¹³⁵ and an infrared of this compound showed two strong ^{12}CO bands at 2049 and 2008 cm^{-1} . A scan of the ^{13}CO satellite region disclosed bands at 2039 and 2033 cm^{-1} assignable to ^{13}CO satellites of the C_1 rotamer ^{12}CO mode at 2049 cm^{-1} , ^{13}CO satellites at 1978 and 1972 cm^{-1} were also observed, assignable to ^{13}CO satellites of the C_1 rotamer ^{12}CO mode at 2008 cm^{-1} . On closer inspection of the ^{12}CO mode at 2008 cm^{-1} , a weak shoulder at 2005 cm^{-1} was observed. This shoulder is reproducible and could reflect

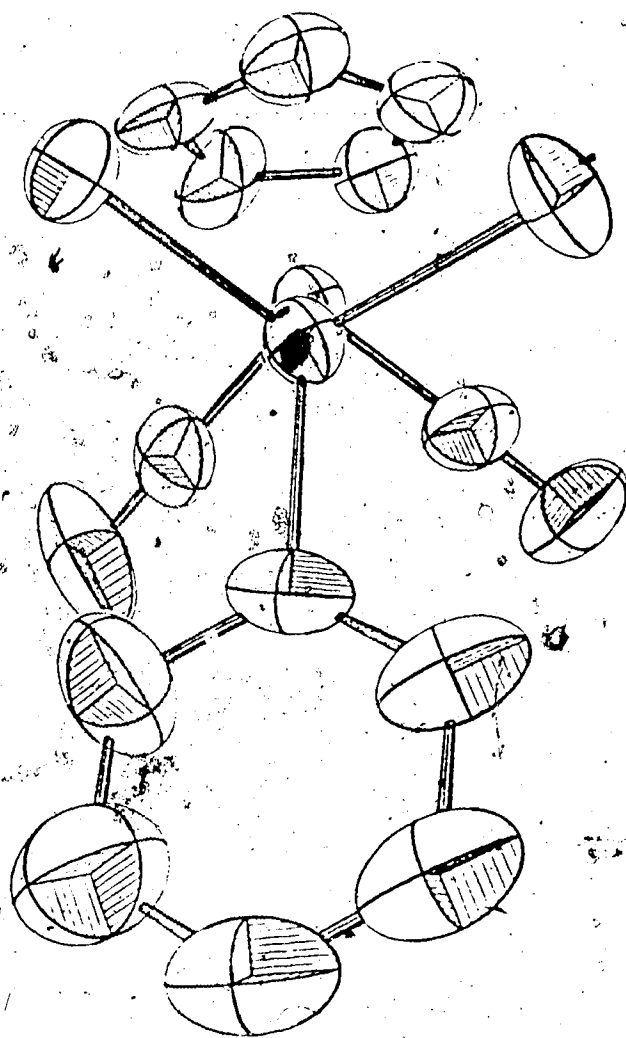


Figure VI-XXIII: A view down the silicon-iron bond of $\text{CpFe}(\text{CO})_2\text{SiCl}_2\text{Ph}$.

a small percentage of the C_s rotamer for this compound. Its intensity is such ($\sim 5\%$ of the 2008 cm^{-1} band) that a ^{13}C CO satellite would not be detectable next to the satellite corresponding to those arising from the C_1 rotamer.

The infrared results on $\text{CpFe}(\text{CO})_2\text{P}(\text{CF}_3)_2$ are in agreement with the structural results, in that an overwhelming population of the C_1 rotamer is observed in solution and the X-ray structure shows the C_1 conformer. This result is very gratifying, in that solid state and solution results are consistent. The strong preference for the C_1 rotamer in $\text{CpFe}(\text{CO})_2\text{P}(\text{CF}_3)_2$ is again consistent with a favorable van der Waals attraction, this time between the lone pair on phosphorus and the Cp hydrogens. It is interesting to note that the iron-phosphorus bond length of $2.265(3)\text{ \AA}$ in this compound¹³⁴ is nearly identical with the iron-silicon bond length expected for $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds (cf., Table VI-35).

B. Compounds of Type $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$

The structure of $\text{CpFe}(\text{CO})\text{H}(\text{SiCl}_3)_2$ has been reported¹¹² and may be considered a distorted tetragonal pyramid with the Cp ring centroid as the apex and SiCl_3 groups trans to each other in the basal plane. The iron atom

is raised towards the Cp ring and Cl atoms are staggered with respect to CO groups. Essentially the same structural features were observed for $\text{CpFe}(\text{CO})_2(\text{SiMe}_2\text{Ph})_2$ ¹³⁶ and $\text{CpFe}(\text{CO})\text{H}(\text{SiF}_2\text{Me})_2$ ¹³⁷. In the former compound, two Me groups on one silicon and a Me and Ph group on the other silicon, straddle the CO ligand to produce conformer 2 shown in Figure IV-X. In the latter compound, the groups bound to silicon straddle the CO ligand symmetrically, so that a Me and F unit produce conformer 3 shown in Figure IV-X. These results support the assignment of rotamers observed in solution for these compounds to the conformers shown in Figure IV-X.

CONCLUSIONS

A series of $\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds have been prepared by the following synthetic methods:

- (a) Cleavage of the iron-iron bond, thermally, by interaction of $[\text{CpFe}(\text{CO})_2]_2$ and HSiR_3 in a sealed tube.
- (b) Metathetical reaction of chlorosilanes with $\text{CpFe}(\text{CO})_2$, reaction performed in THF solvent.
- (c) Displacement of chloro groups in $\text{CpFe}(\text{CO})_2\text{SiCl}_x\text{R}_{3-x}$ ($x = 1, 2, 3$) applying AgBF_4 as a fluorinating agent.⁸³
- (d) Displacement of chloro groups in $\text{CpFe}(\text{CO})_2\text{SiCl}_x\text{R}_{3-x}$ ($x = 1, 2, 3$) by HYR' ($Y = \text{O}, \text{S}$; $\text{R}' = \text{alkyl}, \text{Ph}, \text{C}_6\text{F}_5$) to yield alkoxy and thioxy compounds.

These reactions were fully discussed in Chapter II, and were applied to the synthesis of a wide range of $\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ compounds. The $\text{C}\equiv\text{O}$ infrared spectra of these and related compounds was investigated in order to gain insight into factors influencing the rotamer phenomenon^{54, 57, 108} observed whenever two different substituents are bonded to a Group IV element. Also, $\text{C}\equiv\text{O}$ infrared results were used to obtain qualitative information about the electron density distribution within these complexes.

Nuclear magnetic resonance investigations were conducted on these compounds; however, the low rotational barrier about the metal-metal bond prevented observation of limiting spectra, time averaged spectra being generally observed down to -80° . The compounds $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_5$ and $\text{CpFe}(\text{CO})_2\text{C}_3\text{F}_7$ appeared to show limiting low temperature spectra; however, on warming samples to $+70^{\circ}$, no change was observed. It seemed likely that these results reflect solvation effects, since they were obtained in acetone- d_6 . The spectrum of $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_5$ measured in CD_2Cl_2 showed that rapid rotation about the iron- σ carbon bond was occurring down to -40° . A more complete investigation was frustrated by limited solubility in desirable solvents.

Results presented in Chapter IV, concerning trends in measured rotamer populations for several series of $\text{CpFe}(\text{CO})_2\text{SiX}_2\text{R}$ compounds, strongly suggest that an attractive van der Waals interaction between an electronegative X or R substituent and the Cp moiety determines the population ratio. Of minor importance was a steric effect between bulky substituents on silicon and the Cp ligand, this effect becoming more substantial when two bulky groups were present. Further support for the above hypothesis was presented in Chapter VI, in the form of structural evidence.

Carbonyl substitution reactions involving some

$\text{CpFe}(\text{CO})_2\text{SiR}_3$ compounds with PMe_2Ph or HSiR_3 were investigated. Replacement of carbonyl ligands by phosphines is a well established reaction of organometallic chemistry.⁶⁶ The synthesis of $\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiR}_3$ compounds was carried out in order to investigate possible temperature dependent NMR behavior. The results were discussed in Chapter V and are consistent with a rapid intramolecular rearrangement through a planar intermediate for some of these compounds. The proposed rearrangement depends upon the group R in SiR_3 and it was suggested that the steric bulk of $\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiR}_3$ molecules may produce significant distortion toward a planar structure, facilitating the rearrangement process.

Substitution of a carbonyl group by two fragments of a neutral molecule such as HSiR_3 is an example of an oxidative elimination reaction.^{24,25} This reaction yields compounds of formula $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ and these compounds were studied spectroscopically. Their mass spectra were of particular interest since no parent molecular ion was observed despite large variation in conditions within the mass spectrometer. Further, the ion of highest m/e observed always corresponded to a fragment of formula $[\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)(\text{SiR}_2)]^+$. This suggests a favorable fragmentation pathway to a silylene ion.

Rotamers were observed in the $\text{C}=\text{O}$ infrared spectra

of $\text{CpFe}(\text{CO})\text{H}(\text{SiX}_2\text{R})_2$ compounds; in some cases three carbonyl stretching modes were observed. Four possible conformers were proposed to account for the above, and structural evidence is consistent with the proposal.

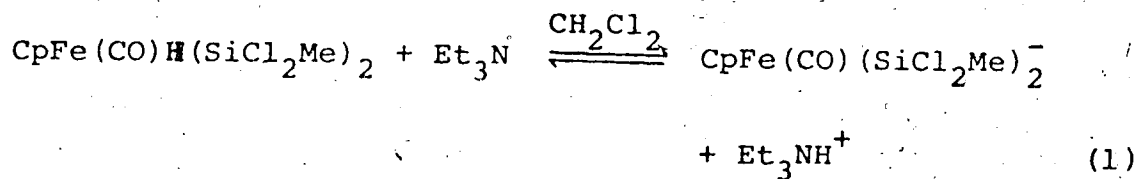
Further interest in $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ complexes arose from NMR results. The high field resonance, arising from the Fe-H proton, showed in favorable cases satellites corresponding to three-bond coupling from the 4.7% abundant ^{29}Si . Fluorosilyl complexes of $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ showed three-bond ^{19}F to high field proton coupling, and for the compound $\text{CpFe}(\text{CO})\text{H}(\text{SiF}_2\text{Me})_2$ this coupling was markedly solvent and temperature dependent.

Finally, the kinetics of the reductive elimination reaction between $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ and PPh_3 was investigated and compared with a similar study conducted on $\text{CpMn}(\text{CO})_2\text{H}(\text{SiPh}_3)$.⁶¹ The resultant activation parameters of $\Delta H^\ddagger = 32.4 \pm 1.4$ kcal/mole and $\Delta S^\ddagger = 18 \pm 4$ eu, are remarkably similar to those reported for $\text{CpMn}(\text{CO})_2\text{H}(\text{SiPh}_3)$.⁶¹ This suggests that similar reaction pathways are involved in each case.

Suggestions for Further Investigations

Of prime importance to the rotamer study on $\text{CpM}(\text{CO})_2\text{M}'\text{X}_2\text{R}$ compounds would be further crystallographic investigation. A likely candidate would be $\text{CpFe}(\text{CO})_2\text{CH}_2\text{C}_6\text{F}_5$, whose structure should possess the staggered C_1 conformer, consistent with infrared results. The compound $\text{CpRu}(\text{CO})_2\text{SiCl}_2\text{Ph}$ would be of interest since its structure could be compared with $\text{CpFe}(\text{CO})_2\text{M}'\text{Cl}_2\text{Ph}$ ($\text{M}' = \text{Si}, \text{Sn}$) structures. Also, the structure of $\text{CpFe}(\text{CO})_2\text{SiMe}_2(\text{SC}_6\text{F}_5)$ would provide additional information concerning the ring tilting effect and the possible role of sulfur lone pairs on conformers adopted.

A more complete study of the acidic properties of $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ compounds is required. Continuing investigation by the author has established that $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_x\text{Ph}_{3-x})$ ($x = 1, 2$) complexes show no acidic properties, whereas $\text{CpFe}(\text{CO})\text{H}(\text{SiCl}_2\text{Me})_2$ appears to be a weak acid since it forms an equilibrium according to equation (1).



The equilibrium lies far to the left hand side and reaction of the above hydride with Et_4NBr in CH_2Cl_2 was slow and incomplete, frustrating attempts to isolate the anion.

The most surprising aspect of this investigation was the behavior of $\text{CpFe}(\text{CO})\text{H}(\text{SiF}_2\text{Me})_2$ when treated according to equation (1). The reaction was vigorous, even at low temperatures, and resulted in rapid decomposition to $[\text{CpFe}(\text{CO})_2]_2$, $\text{CpFe}(\text{CO})_2\text{SiF}_2\text{Me}$, as well as insoluble material. This suggested a competition between H^+ loss and reductive elimination. A small scale reaction of the hydride with PMe_2Ph at room temperature resulted in rapid elimination to yield $\text{CpFe}(\text{CO})\text{PMe}_2\text{Ph}(\text{SiF}_2\text{Me})$. This indicates unusual facile loss of silane from $\text{CpFe}(\text{CO})\text{H}(\text{SiF}_2\text{Me})_2$ (cf., reaction of $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ with PPh_3 , $k_{\text{obs}} = 1.38 \times 10^{-4} \text{ sec}^{-1}$ at 69.9°). Further investigation of reductive elimination reactions involving $\text{CpFe}(\text{CO})\text{H}(\text{SiR}_3)_2$ compounds with phosphines would be desirable, and kinetic data of the type obtained for $\text{CpFe}(\text{CO})\text{H}(\text{SiMe}_2\text{Ph})_2$ would be of interest.

The NMR studies on $\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{SiR}_3$ compounds suggested that a polytopal rearrangement process was occurring on the NMR time scale for $\text{SiR}_3 = \text{SiMe}_2\text{Ph}$, SiPh_2Me . Further studies on $\text{CpFe}(\text{PMe}_2\text{Ph})_2\text{R}$ ($\text{R} =$ halogen, perfluoroalkyl, GeR_3 , SnR_3) will be undertaken to determine the extent of this process. Experiments are also under consideration which will be designed to further support the initial interpretation of NMR results presented in Chapter V.

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