

THE SYNTHESIS OF CERTAIN  $\pi$ -ALLYL  
TRANSITION METAL COMPLEXES INCLUDING  
 $\pi$ -PERFLUOROALLYLCOBALT TRICARBONYL

A thesis presented

by

Keith Stanley

in partial fulfillment of the requirements

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Chemistry

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A dissertation submitted to the Faculty of Graduate Studies of  
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### ABSTRACT

The reaction of perfluoroallyl iodide with iron ennea-carbonyl was shown to yield cis and trans-isomers of perfluoro-propenyliron tetracarbonyl iodide. The trans to cis isomerization was studied. Perfluoroallyl iodide with bis(tetracarbonyl cobalt) zinc gave, as one of the major products,  $\pi$ -perfluoroallylcobalt tricarbonyl and the reaction of this complex with triphenylphosphine was investigated.

A series of complexes containing the novel ligand  $\pi$ -2-trimethylsilylallyl was prepared and the spectral characteristics of the complexes compared to those of the unsubstituted  $\pi$ -allyl analogues.

The synthesis of bi- $\pi$ -allyldicobalt hexacarbonyl and its reaction with bromine to yield a novel carbonyl insertion product were studied.

The preparation of  $\pi$ -allyl compounds of iron, cobalt and nickel from bridging carbonyl complexes and tetraallyltin was investigated.

The complex,  $\pi$ -allyliron tricarbonyl triphenyltin was synthesized and its phosphine substitution product studied.

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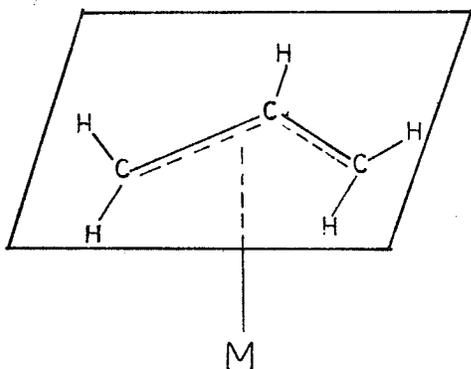
GENERAL INTRODUCTION

## General Introduction

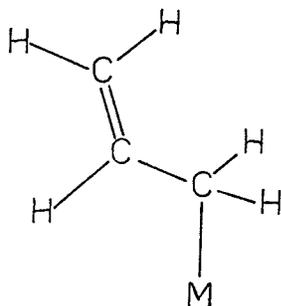
Since the synthesis of the first  $\pi$ -allyl transition metal complex in the early 1950's, and the subsequent proof of the  $\pi$ -allyl structure by Heck and Breslow in 1960 by  $^1\text{H}$  NMR<sup>(1)</sup>, the interest in  $\pi$ -allyl organometallic chemistry has been expanding. The synthesis, structural elucidation, and uses of  $\pi$ -allyl complexes have formed a significant proportion of organometallic research. Several reviews that indicate the importance of the work reported on this subject have appeared.<sup>(2,3,4)</sup>

This thesis presents some new work done in this area with specific attention to complexes of iron, cobalt and nickel.

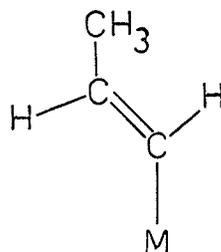
The configuration of the  $\pi$ -allyl metal system has been determined by x-ray crystal structure analysis<sup>(5)</sup> and  $^1\text{H}$  NMR<sup>(1)</sup> to show the three carbon atoms in an isosceles triangle with the protons in the same plane as the carbon atoms. In most  $\pi$ -allyl complexes, the three carbon atoms are nearly equidistant from the metal atom.



The allyl ligand can also bond to the metal by a  $\sigma$ -linkage.

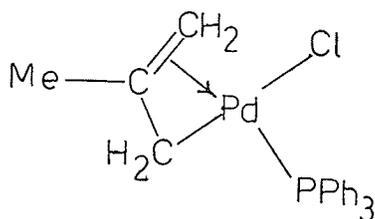


The  $\sigma$ -allyl group can rearrange to form the  $\sigma$ -propenyl group.



This rearrangement can be accomplished with catalytic amounts of HCl and has been studied with some iridium complexes.<sup>(6)</sup> In  $\sigma$ -perfluoroallyl complexes, (all protons on the ligand replaced by fluorine atoms), this rearrangement is usually very rapid. The proposed mechanism for this rearrangement of the  $\sigma$ -perfluoroallyl ligand will be discussed later.

The allyl ligand in some complexes has been shown to bond unsymmetrically to the metal through a  $\sigma$ -linkage and a  $\pi$ -linkage.<sup>(7)</sup>



This is referred to as a  $\sigma$ - $\pi$ -allyl group.

The theoretical treatment of the  $\pi$ -allyl group, and the bond formed between the delocalized  $\pi$ -electron system and the valence orbitals of the metal atom, has been attempted by several groups of workers and the conclusions reached are not always in agreement.<sup>(8)</sup> Stated simply, the  $\pi$ ,  $\pi_{\text{non-bonding}}$ , and  $\pi^*$  orbitals of the allyl group (see diagram on page 4a) participate in bonding the organic moiety to the metal. The filled bonding  $\pi$ -orbital acts as an electron donor to the empty d or hybridized d orbital of the metal in a  $\sigma$ -type bond. The empty antibonding  $\pi$ -orbital acts as an electron-acceptor in a  $\pi$ -type bond. The non-bonding orbital may act as a net electron donor or acceptor depending on the other ligands attached to the metal.<sup>(8)</sup>

This bond is usually referred to as the  $\pi$ -allyl linkage. Recent nomenclature changes proposed by Cotton<sup>(9)</sup> would refer to it as a trihapto ( $h^3$ ) linkage.\* This terminology indicates the number of carbon atoms involved in the multicenter bond.  $\pi$ -Cyclopentadienyl complexes would be designated pentahapto ( $h^5$ ) and  $\sigma$ -complexes mono-

\* - Official IUPAC notation: (1-3-h-propenyl)

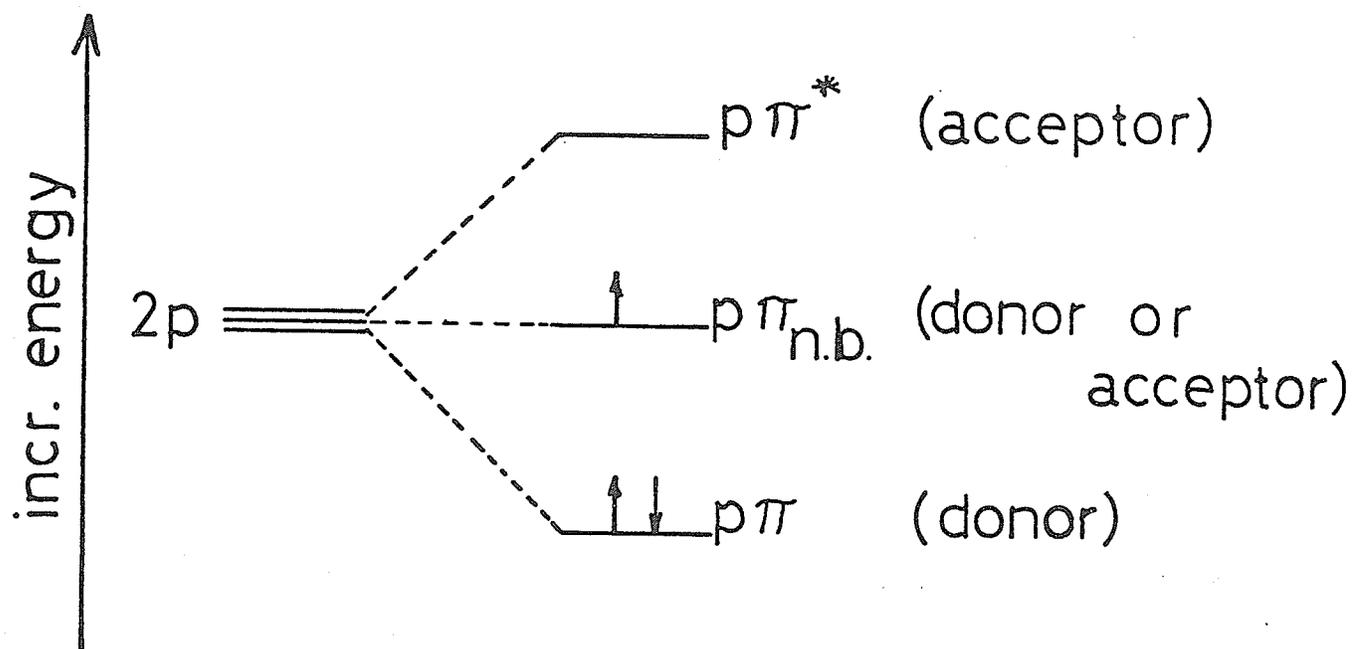


Diagram - The three  $2p$  atomic orbitals of the allyl group combine to give three  $p\pi$  molecular orbitals. The allyl radical ( $C_3H_5\cdot$ ) has three electrons in the delocalized  $\pi$  system.

hapto ( $h^1$ ). An unsymmetrically bound  $\sigma$ - $\pi$ -allyl would be designated (1- $h^1$ , 2,3- $h^2$ -allyl). This nomenclature will be used here only when the  $\pi$ -allyl group is contained in a larger cyclic ligand and confusion could arise by using the older terminology.

#### The 18-electron rule

In organometallic chemistry, the course of a reaction can often be elucidated or the structure of a molecule suggested by observing the empirical rule, "a valence shell (of a transition metal) containing 18 electrons gives stable complexes".<sup>(10)</sup> To use this rule, it is necessary to count the number of electrons which are formally in the valence shell of the metal atom. To do this, the number of electrons in the valence shell of the metal, (atom, cation or anion), is added to the number of electrons formally donated by the ligands to the metal. The ligands encountered in this work are well known and have been classified as to the number of electrons they formally contribute:  $\pi$ - $C_5H_5$ —5,  $\pi$ -allyl—3, CO—2, triphenylphosphine ( $PR_3$ )—2,  $\sigma$ -alkyl or  $\sigma$ -perfluoroalkyl—1. Most complexes considered have the metal in the formal zero oxidation state so that the number of valence electrons for the metal is: Fe—8, Co—9, and Ni—10.

$(\pi-C_5H_5)Fe(CO)(\pi-C_3H_5)$  can be used as an example of this counting procedure. Counting from left to right as the formula is written, the electrons add  $5 + 8 + 2 + 3 = 18$ .

There are many exceptions to this rule. An example of one type of

exception is the series of complexes  $(PR_3)_2NiR_2$ , where nickel frequently forms compounds in which it has a 16-electron environment and the molecule has a square-planar configuration.

While the 18-electron rule is used extensively, it must be emphasized that it is unsophisticated and provides no detailed insight into the chemistry of organometallic complexes.

#### Identification of $\pi$ -allyl complexes

The identification of  $\pi$ -allyl complexes and organometallic compounds in general, is accomplished by IR, NMR, and mass spectra. X-ray crystallography has been used to elucidate the structure of many organometallic complexes, but is usually the last stage of characterization and will not be discussed here..

Infrared spectroscopy is used extensively in the identification of organometallic compounds, especially for transition metal carbonyl complexes where the number of terminal carbonyl stretching modes and the relative intensities of these absorptions can be used to determine the geometry of the molecule. Group theory<sup>(11)</sup> is used to predict the carbonyl absorption pattern when the configuration of the molecule can be determined or postulated. If the molecule can exist in two or more configurations, the pattern for each possible geometrical isomer can be predicted and compared to the observed pattern, to determine in which configuration the molecule exists. The work done in this area has been collected in books<sup>(12)</sup> and reviews,<sup>(13)</sup> so that the synthetic chemist can refer to general or specific work to help interpret the terminal carbonyl vibration region of the spectrum ( $1850 - 2150 \text{ cm}^{-1}$ ),

without having to develop or appreciate fully all the implications of group theory. The IR spectra also enable the observer to identify bridging carbonyl groups ( $M-\overset{\text{O}}{\parallel}{C}-M$ ,  $1700 - 1850 \text{ cm}^{-1}$ ) and acyl groups ( $R-\overset{\text{O}}{\parallel}{C}-M$ ,  $1650 - 1750 \text{ cm}^{-1}$ ). The configuration of the organic moiety can often be determined from the IR spectra, such as in  $\sigma$ -allyl and  $\sigma$ -propenyl complexes where the C C stretching vibrations occur at different frequencies. The stretching vibrations of the  $\sigma$ -allyl group  $\left[ \nu(C=C=C) \right]$  have not been well characterized and are not an obvious characteristic of the IR spectra. The frequencies fall in the  $1000 - 1500 \text{ cm}^{-1}$  region but have been identified for only a few specific complexes.<sup>(14)</sup> The C-H vibration region is not useful at the present time and is most often not reported. Only a few  $\pi$ -allyl complexes have been thoroughly studied by IR.<sup>(14)</sup>

Mass spectroscopy is extremely useful in identifying organo-metallic complexes. In most cases, the parent ion can be recorded, although its relative intensity may be small, especially in some carbonyl complexes. For  $\pi$ -allyl complexes, the fragmentation pattern is usually straight forward and the loss of the CO groups and  $C_3H_5$  groups can be seen. Peaks at  $m/e$  41 ( $C_3H_5$ ) and  $m/e$  39 ( $C_3H_3$ ) are often found in the mass spectra of  $\pi$ -allyl complexes. In cases where the complex may be difficult to isolate in a form pure enough for an elemental analysis, a high resolution mass spectrum can be used to determine the elemental composition.

The most useful method for identifying a  $\pi$ -allyl group is NMR. A typical spectrum of a  $\pi$ -allyl group is two doublets and a multiplet (integration 2:2:1) downfield from the internal standard tetramethylsilane (TMS).

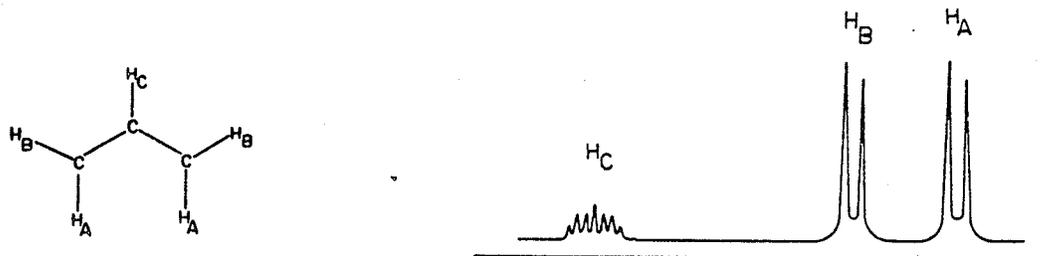


Figure 1 Typical  $^1\text{H}$  NMR spectrum of the  $\pi$ -allyl ligand

Preferential shielding of the A protons by the metal atom may explain  $\delta_A < \delta_B$ . The  $\text{H}_C$  resonance absorption appears as a multiplet at higher  $\delta$  values. Typical coupling constants in the NMR spectra of  $\pi$ -allyl complexes are  $J_{BC} \sim 7$  Hz,  $J_{AC} \sim 11$  Hz, and  $J_{AB} \sim 0$  Hz, (except when  $\text{H}_C$  is replaced by an electronegative group; then  $J_{AB} \sim 2$  Hz). Four-bond coupling has not been observed.

The  $^1\text{H}$  NMR spectra are more complex for compounds such as  $(\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_2$  and  $\text{Ni}(\pi\text{-C}_3\text{H}_5)_2$ , where rapid interconversion of isomers is possible and spectra of the sample at low temperature are required to determine the chemical shifts and coupling constants for the protons of the  $\pi$ -allyl groups in the different isomers.<sup>(15, 16)</sup> An even more intriguing study of  $\pi$ -allyl complexes by NMR that is receiving considerable attention is that of  $\sigma$ - $\pi$  conversion resulting in syn-anti proton exchange (where  $\text{H}_A$  is the anti-proton and  $\text{H}_B$  is the syn-proton). This subject was reviewed recently by Fedorov.<sup>(17)</sup> None of the complexes in this work show this phenomenon.

The use of  $^{19}\text{F}$  NMR has been very valuable in determining the structure of transition metal complexes containing a polyfluorinated

organic moiety. This was particularly useful in the differentiation between the  $\sigma$ -perfluoroallyl and  $\sigma$ -perfluoropropenyl ligands in a study by Pitcher and Stone.<sup>(18)</sup> This work will be discussed later in Section A.

### Experimental

Diethyl ether and tetrahydrofuran (THF) were dried by sodium in the presence of benzophenone and then distilled under vacuum. Pentane, hexane, and methylene chloride were sufficiently dry to be used without further purification. Benzene was distilled and only the middle fraction collected. Nitrogen gas ( $N_2$ ) was passed through a  $CaSO_4$  column to ensure dryness.

IR spectra were recorded on a Perkin-Elmer 337 instrument using double-beam techniques. The  $1601.4\text{ cm}^{-1}$  peak of polystyrene was used for calibration. For more accurate work, the spectra were expanded on an external recorder and calibrated with indene. The IR cells were stainless steel with KBr windows and a 0.1 mm path length. For air-sensitive samples, the filling ports were capped with 5 mm. silicone rubber septa and the cell was flushed with  $N_2$  using two syringe needles. The sample was prepared under  $N_2$  and introduced into the cell by syringe.

Mass spectra were obtained on a Finnigan 1015 quadrupole mass spectrometer using the gaseous or solid inlet systems.

The  $^1H$  and  $^{19}F$  NMR spectra were recorded with a Varian A-56/60A spectrometer with a variable temperature probe. The  $^1H$  spectra were

run with tetramethylsilane (TMS) as the internal standard ( $\delta = 0$  ppm). Positive  $\delta$  values refer to a downfield shift from TMS. The  $^{19}\text{F}$  spectra were run with  $\text{CFCl}_3$  as the internal standard ( $\delta = 0$  ppm). Positive  $\delta$  values refer to an upfield shift from  $\text{CFCl}_3$ .  $^{19}\text{F}$  chemical shifts were determined by generating side bands of the  $\text{CFCl}_3$  absorption with a Hewlett-Packard Wide Range Oscillator.

Conventional vacuum techniques were used when complexes were isolated or purified in vacuo. The vacuum rack was equipped with a mercury diffusion pump which allowed pressures of less than 0.01 mmHg to be obtained. The vacuum rack consisted of four directly connected U traps in which static, (closed to the manifold) or dynamic, (open to the manifold and pump) distillations could be carried out.

The samples for the NMR spectra were contained in 5 mm o.d. Pyrex sample tubes. Volatile compounds were distilled into the cooled ( $-80^\circ\text{C}$ ) sample tube in vacuo. Next the solvent and standard were distilled into the tube which was then sealed. Non-volatile samples were prepared under  $\text{N}_2$  and transferred to the sample tube by syringe and capped immediately. The sample tube was flushed with  $\text{N}_2$  before the introduction of the sample. Where a non-volatile compound was particularly sensitive to air, the solid was introduced into the sample tube under  $\text{N}_2$  and transferred to the vacuum rack. The sample was pumped down, the solvent and standard distilled into the tube and the tube sealed. In some cases, where partial decomposition of the sample occurred during the sample preparation, or in the recording of the spectrum, the insoluble paramagnetic material was centrifuged to the

bottom of the tube. This was useful for some samples but not all.

Melting points were taken on a Fisher-Johns Melting Point Apparatus and are uncorrected.

Elemental analyses were performed by the Alfred Bernhardt Laboratories in Germany. Analysis by high resolution mass spectrometry was obtained from the Department of Chemistry of the University of Alberta at Edmonton under the direction of Dr. A. M. Hogg.

The work presented here is divided into five sections to show the different areas of interest concerning the synthesis and reactions of  $\pi$ -allyl complexes. Included in Section A are two  $\sigma$ -perfluoropropenyl complexes which clarify some previous problems in the separation and identification of isomers of  $R_FFe(CO)_4I$  complexes, (where  $R_F$  = perfluoroalkyl).

SECTION A

Reactions of Perfluoroallyl Iodide ( $\text{CF}_2\text{:CFCF}_2\text{I}$ )

## Introduction

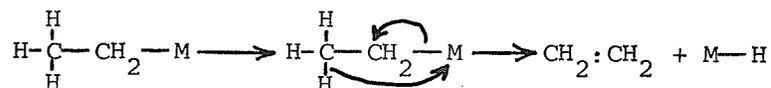
The synthesis of polyfluorinated organo-transition metal complexes has been an active field of study for the past twelve years, and several reviews have appeared on this topic.<sup>(19, 20, 21)</sup>

The majority of these complexes contain the organic moiety  $\sigma$ -bonded to the transition metal. The carbon atom bound to the metal is also bonded to at least one fluorine atom, i.e.,  $\text{CF}_3\text{CF}_2\text{-M}$ . In addition, there are many complexes where the fluorine atom is one carbon away from the carbon-metal bond. This type will not be discussed here but includes such ligands as  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ , pentafluorophenyl ( $\text{C}_6\text{F}_5$ ), and perfluorohexamethylbenzene  $\left[ \text{C}_6(\text{CF}_3)_6 \right]$ .

The synthesis of  $\sigma$ -bonded fluoroorganometallic complexes is interesting because of the high electronegativity of the fluorine atom on the carbon  $\alpha$  to the metal and the effect this has on the  $\sigma$ -character of the C-M bond and the possibility of some  $\pi$ -character in this bond as well. Investigation of these effects is difficult but it has been attempted. The results are discussed by Nyholm<sup>(19)</sup> and considered at best inconclusive. From an x-ray crystal structure, it is seen that the C-M bond distance is significantly shorter ( $\sim 5\%$ ) in fluorinated alkyl complexes compared to the hydrocarbon analogues. This stronger bond was considered to be due to the  $\pi$ -component in the linkage. The C-F stretching frequency for a series of  $\text{CF}_3\text{X}$  compounds was observed to shift to lower wavelengths when the halide atom X was replaced by a transition metal. This

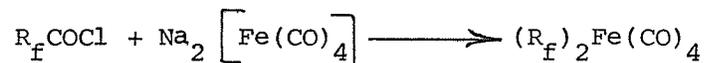
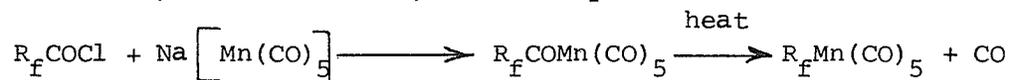
was thought to be due to backbonding from the metal to the fluoroalkyl group and the consequent shift of electron density to the  $\pi^*$  orbital of the C—F bond. Also, the carbonyl force constants for complexes of the type  $\text{RMn}(\text{CO})_5$  and  $\text{R}_f\text{Mn}(\text{CO})_5$  were compared<sup>(22)</sup> and the change related to backbonding to the  $\text{R}_f$  group. It was considered that the amount of backbonding to the  $\text{R}_f$  group was significant but small.

Generally, the fluorinated derivatives are more stable than the hydrocarbon analogues but the reasons for this are very speculative. The mode of decomposition for alkyl-metal complexes is thought to be olefin elimination:<sup>(23)</sup>



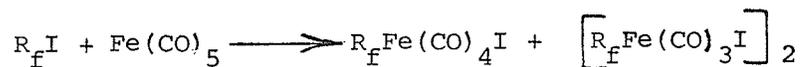
The mechanism for the decomposition of the fluorinated complexes has not been studied in any detail.

The synthesis of a number of  $\sigma$ -complexes has been reviewed by Stone and Treichel.<sup>(24)</sup> Some of the typical reactions and products are given here. For most reactions, the yields are small. The equations are often not balanced but just indicate the reactants and main product isolated. In many cases, this simplifies the situation, but most often, the side products are not known.



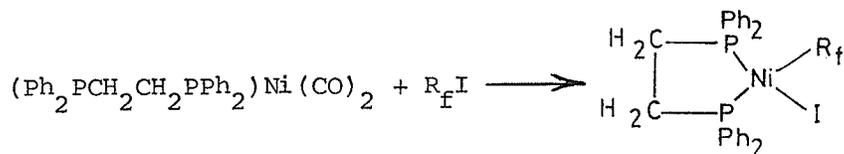
(where  $\text{R}_f = \text{C}_2\text{F}_5, n\text{-C}_3\text{F}_7$ )

A reaction that will be discussed later is:

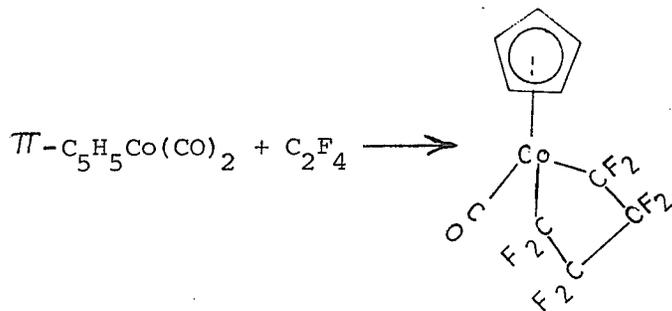
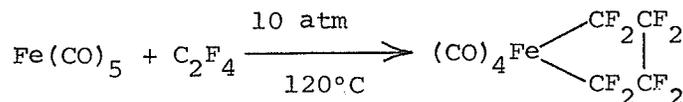


(where  $R_f = C_2F_5, n-C_3F_7$ )

Phosphine-substituted nickel carbonyls also react with perfluoroalkyl iodides.



Tetrafluoroethylene reacts to give cyclic products:

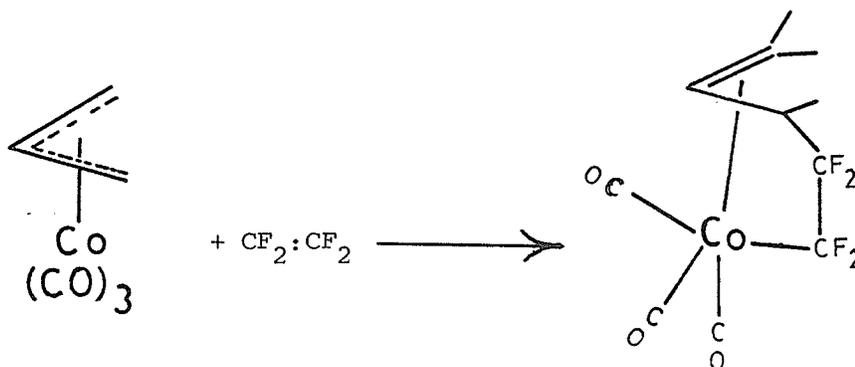
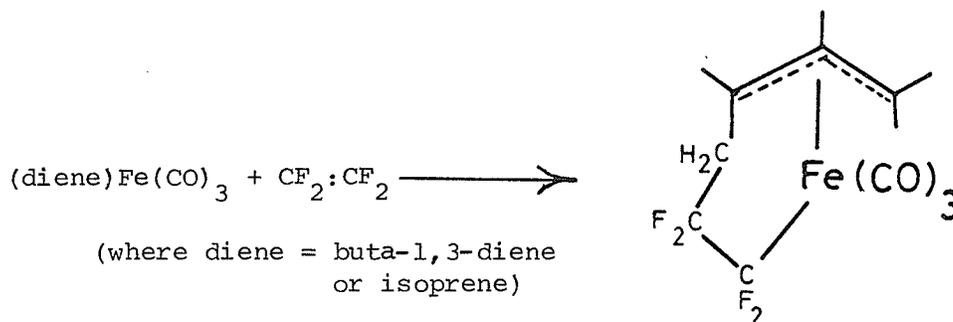


With dicobalt octacarbonyl, tetrafluoroethylene yields

$(CO)_4Co-CF_2CF_2-Co(CO)_4$ . With metal carbonyl hydrides, a typical reaction is: (17)

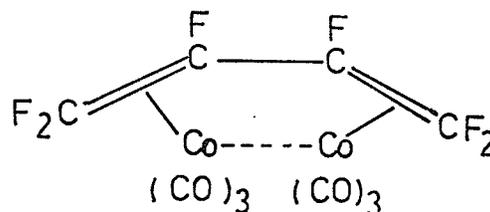
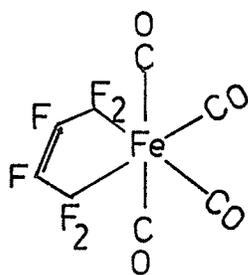


Fluoroolefins have been reacted with hydrocarbon  $\pi$ -complexes to produce some novel insertion products. Reactions of  $\text{CF}_2:\text{CF}_2$  are typical: (26, 27)

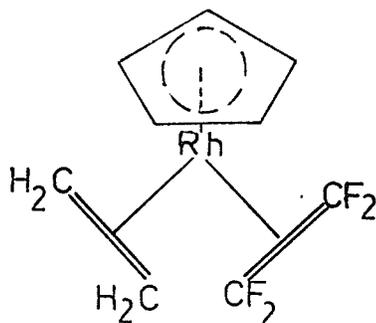


The synthesis of fluorocarbon  $\pi$ -complexes has not been so successful because many reactions which were expected to give a  $\pi$ -complex yielded instead novel  $\sigma$ -complexes. However, a number of  $\pi$ -complexes have been isolated and characterized.

The reactions of perfluorobutadiene with  $\text{Fe}(\text{CO})_5$  and  $\text{Co}_2(\text{CO})_8$  yield a  $\sigma$ -complex and a reported  $\pi$ -complex. (28)



Some  $\pi$ -tetrafluoroethylene derivatives have been synthesized and used to investigate the  $\pi$ -type bond formed. A  $^1\text{H}$  and  $^{19}\text{F}$  NMR study of  $(\pi\text{-C}_5\text{H}_5)\text{Rh}(\pi\text{-CH}_2\text{:CH}_2)(\pi\text{-CF}_2\text{:CF}_2)$ :

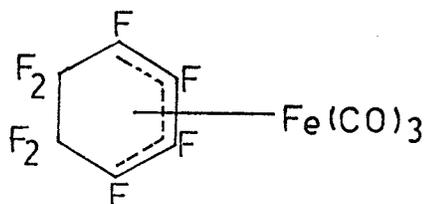


showed the bond to the fluoroolefin to be stronger than the  $\pi$ -bond to the olefin.<sup>(29)</sup> This was determined by the barrier to rotation for the two ethylene groups. An x-ray crystal structure of the complex (acetylacetonate) $\text{Rh}(\pi\text{-CH}_2\text{:CH}_2)(\pi\text{-CF}_2\text{:CF}_2)$  showed the  $\text{F}_2\text{C-M}$  carbon-metal bond distance to be 10% shorter than the  $\text{H}_2\text{C-M}$  bond length, again indicating a stronger metal-fluoroolefin bond.

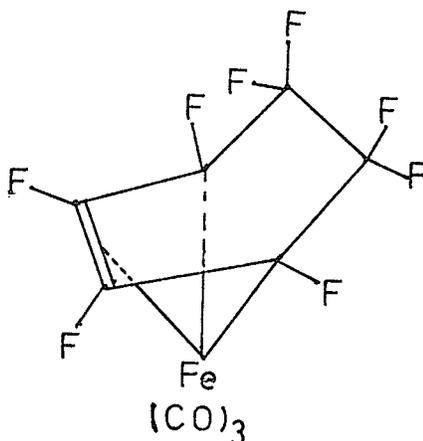
The donor properties of the tetrafluoroethylene are reasoned to be very much reduced compared to those of the ethylene due to the high electronegativity of the fluorine atoms. For the same reason, the acceptor properties of the fluoroolefin would be expected to be considerably enhanced. Since tetrafluoroethylene forms a stronger bond to Rh than does ethylene, it would seem that the  $\pi$ -contribution is very important to this linkage and the strength of the bond is due mainly to the back-donation of electrons from the metal to the empty  $\pi^*$  orbital of the ligand.

The reaction of octafluorocyclohexa-1,3 or 1,4-diene with

$\text{Fe}_3(\text{CO})_{12}$  was reported to yield the first fluorocarbon-metal tetrahapto linkage: (31)



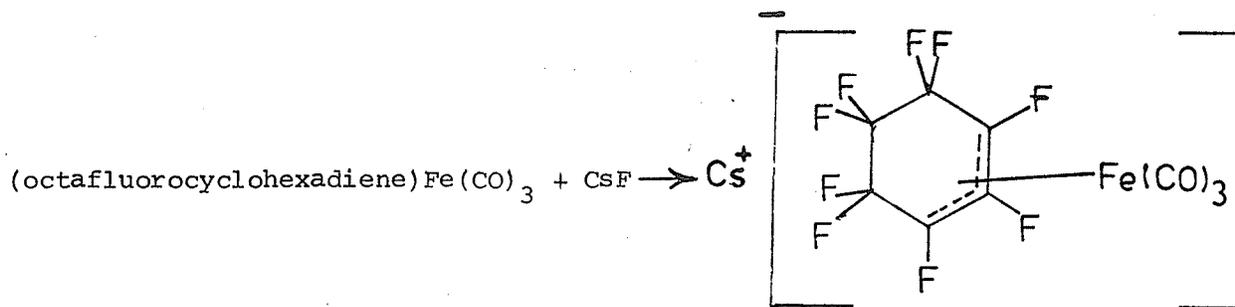
but a crystal structure showed that the ligand was coordinated to the metal by two  $\sigma$ -bonds and a single dihapto bond. (32)



octafluorocyclohexadieneiron tricarbonyl

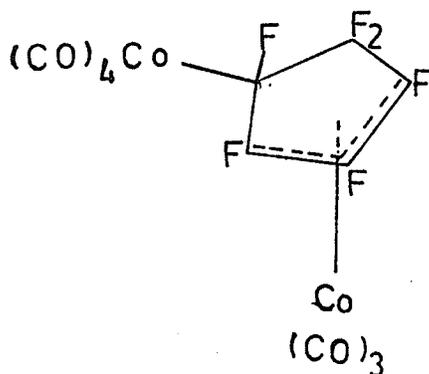
The reactions of perfluorocyclopentadiene with  $\text{Co}_2(\text{CO})_8$  and  $\text{Fe}(\text{CO})_5$  were reported to give several complexes where the  $\text{C}_5\text{F}_5$  group was coordinated by monohapto and dihapto bonds. No pentahapto linkage was reported. (33)

Attempts to prepare a  $\pi$ -perfluoroallyl linkage have been partially successful in that a  $\pi$ -allyl group is contained in a cyclic system. The two compounds shown below have been reported to contain the  $\pi$ -perfluoroallyl system bonded to a metal.



The  $^{19}\text{F}$  NMR spectrum, while not complete, indicated a  $\pi$ -allyl group. (34)

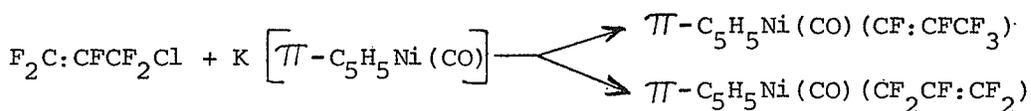
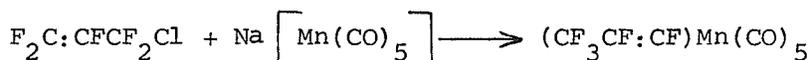
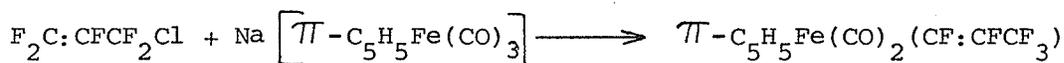
One of several products of perfluorocyclopentadiene with  $\text{Co}_2(\text{CO})_8$  was shown by x-ray crystallography to contain a trihapto linkage. (35)



Only the crystal structure of this complex was reported.

Attempts to synthesize a "pure" perfluoro- $\pi$ -allyl complex have not been successful. It was presumed that if the  $\sigma$ -perfluoroallyl complex was prepared, the complex would decarbonylate to the  $\pi$ -perfluoroallyl complex. This did not occur. For the Fe and Mn complexes, the  $\sigma$ -allyl group rapidly rearranged to the  $\sigma$ -propenyl

group precluding the  $\pi$ -allyl complex formation.<sup>(36)</sup> For the Ni complex, this rearrangement was also observed as well as the stable  $\pi$ -C<sub>5</sub>H<sub>5</sub>Ni(CO)( $\sigma$ -CF<sub>2</sub>CF:CF<sub>2</sub>) complex. This complex, however, did not decarbonylate.<sup>(37)</sup>



The allyl to propenyl rearrangement has been studied by Goldwhite, Rowsell and Valdez<sup>(38)</sup> for the complex  $\text{F}_2\text{C}:\text{C}(\text{Cl})\text{CF}_2\text{Mn}(\text{CO})_5$  and a bimolecular process was postulated. This will be discussed later.

The reason for the  $\pi$ -C<sub>5</sub>H<sub>5</sub>Ni(CO)( $\sigma$ -CF<sub>2</sub>CF:CF<sub>2</sub>) not decarbonylating to form a  $\pi$ -allyl complex can only be speculated. The nucleophilic attack by the double bond of the allyl group must not be strong enough to displace the carbonyl group. This will also be discussed in more detail later.

The work in this section presents the reactions of perfluoroallyl iodide with  $\text{Fe}_2(\text{CO})_9$  and  $\text{Zn} \left[ \text{Co}(\text{CO})_4 \right]_2$  to prepare a stable  $\pi$ -perfluoroallyl derivative. This was successful for the reaction of  $\text{C}_3\text{F}_5\text{I}$  with  $\text{Zn} \left[ \text{Co}(\text{CO})_4 \right]_2$ . The reaction of  $\text{C}_3\text{F}_5\text{I}$  with  $\text{Fe}_2(\text{CO})_9$  gave only  $\sigma$ -perfluoropropenyl complexes. The products of this reaction were thoroughly studied because of the previous interest<sup>(43, 46)</sup>

shown in the cis- and trans-isomers of  $R_f\text{Fe}(\text{CO})_4\text{I}$  complexes,

(where  $R_f = \text{CF}_3$ ,  $\text{C}_2\text{F}_5$ , and  $\text{C}_3\text{F}_7$ ).

## Experimental

### Preparation of Perfluoroallyl Chloride (C<sub>3</sub>F<sub>5</sub>Cl) and Perfluoroallyl Iodide (C<sub>3</sub>F<sub>5</sub>I)

Perfluoroallyl chloride was prepared following a procedure given in a U.S. patent.<sup>(39)</sup> Trifluorochloroethylene and chlorodifluoromethane were pyrolyzed in a quartz tube flow system at 700°C in a 2:1 mole ratio respectively. The products were trapped at -111°C and fractionally distilled under vacuum with a dry ice condenser. The C<sub>3</sub>F<sub>5</sub>Cl fraction was identified by IR and NMR spectra. The C<sub>3</sub>F<sub>5</sub>Cl was obtained in 95% purity with a yield of 35%. Following the method of Miller and Fainberg,<sup>(40)</sup> 100 g (0.6 mol) C<sub>3</sub>F<sub>5</sub>Cl was added to 160 g (1.06 mol) sodium iodide in 600 ml acetone. The reaction was allowed to proceed for ten days with occasional stirring. The precipitated NaCl was filtered off and the acetone solution added to 2000 ml H<sub>2</sub>O. The C<sub>3</sub>F<sub>5</sub>Cl layer was separated from the aqueous layer, dried with MgSO<sub>4</sub> and distilled. The 53 - 55°C fraction was collected and kept at 0°C to reduce decomposition. The yield was 75 g (49%).

### Reaction of C<sub>3</sub>F<sub>5</sub>I with Fe<sub>2</sub>(CO)<sub>9</sub>

Fe<sub>2</sub>(CO)<sub>9</sub> was prepared from Fe(CO)<sub>5</sub> in bright sunlight in a Pyrex flask. The Fe(CO)<sub>5</sub> was decanted off leaving the Fe<sub>2</sub>(CO)<sub>9</sub>, which was washed with petroleum ether and dried in vacuo.

C<sub>3</sub>F<sub>5</sub>I (3 g, 5 mmol) and Fe<sub>2</sub>(CO)<sub>9</sub> (1 g, 2.7 mmol) were reacted

in refluxing pentane under  $N_2$  for one hour. The solvent was removed in vacuo at room temperature. The reaction flask was then warmed with hot water ( $50^\circ C$ ). A mixture of red crystals and a rust powder sublimed (0.01 mm) onto the upper, cool region of the flask. The crystals were removed by scraping and placed in a subliming tube (15 cm long with 1 cm inside diameter). The crystals were resublimed (0.01 mm) by warming the lower 2 cm with hot water. The red isomer crystallized higher on the tube, the rust isomer lower. If the sublimation was done at  $75^\circ C$ , a greater percentage of the product sublimed as the red isomer. At  $30^\circ C$ , approximately equal amounts of each isomer were obtained. Both products were moderately air stable. The red crystals melted at  $61^\circ C$ , the rust powder at  $56^\circ C$ . The yield was 15%. Both isomers gave the same parent ion, (m/e 426), in the mass spectrometer. Elemental analysis of a mixture of the two isomers calculated for  $C_3F_5Fe(CO)_4I$ :  
 C 19.74%, F 22.30%, I 29.80% found: C 20.04%, F 22.93% and I 30.23%.

Reaction of  $C_3F_5I$  with  $Zn[Co(CO)_4]_2$

$Hg[Co(CO)_4]_2$  was prepared following the method by Brauer. <sup>(41)</sup>  
 $Hg[Co(CO)_4]_2$  was stirred with excess granulated zinc in toluene under  $N_2$  for two hours. <sup>(42)</sup> The Zn and Hg were removed by filtration and the toluene removed in vacuo from the product  $Zn[Co(CO)_4]_2$ .  
 $C_3F_5I$  (0.6 g, 2.4 mmol) and  $Zn[Co(CO)_4]_2$  (5 g, 1.2 mmol) were reacted in pentane at room temperature under  $N_2$  until CO evolution had ceased. The pentane was removed in vacuo at  $-30^\circ C$ . The products

were then distilled into the trapping system at room temperature (0.01 mm). The initial products were analyzed by IR and NMR, and the two major components separated and purified by successive trap to trap dynamic distillations. Two compounds (liquids at room temperature) were isolated. The lower melting compound (mp  $-15^{\circ}\text{C}$ ) was fairly unstable above  $0^{\circ}\text{C}$  and an elemental analysis could not be performed. The higher melting compound (mp  $5^{\circ}\text{C}$ ) was stable up to  $35^{\circ}\text{C}$  under vacuum. The yields were approximately 20% and 25% respectively. The thermally stable liquid was purified before elemental analysis by crystallization from pentane at  $-80^{\circ}\text{C}$ . Elemental analysis calculated for  $\text{C}_3\text{F}_5\text{Co}(\text{CO})_3$ : C 26.31%, F 34.66% found: C 26.43%, F 34.75%.

Reaction of  $\pi\text{-C}_3\text{F}_5\text{Co}(\text{CO})_3$  with  $\text{PPh}_3$

$\pi\text{-C}_3\text{F}_5\text{Co}(\text{CO})_3$  (1 g, 3.6 mmol) and  $\text{PPh}_3$  (0.95 g, 3.6 mmol) were reacted in pentane at room temperature for one hour under vacuum in a sealed reaction flask. The solution turned from light yellow to dark orange. No CO was evolved. The solvent was removed in vacuo and the products dissolved in a minimum amount of methylcyclohexane at  $70^{\circ}\text{C}$  under  $\text{N}_2$ . The solution was centrifuged to settle the insoluble materials and decanted under  $\text{N}_2$ . On slow cooling to  $0^{\circ}\text{C}$ , a yellow crystalline product was obtained. Decanting the solution and cooling it to  $-80^{\circ}\text{C}$  gave a different crystalline product. Separate recrystallizations from methylcyclohexane gave the two products. The less soluble product had a mp  $110^{\circ}\text{C}$  (with decomposition and evolution of a gas). Elemental analysis calculated for

$C_3F_5Co(CO)_3PPh_3$ : C 53.80%, H 2.82%, F 17.71%, P 5.83% found:  
C 54.39%, H 2.89%, F 18.34%, P 5.82%. The more soluble product  
had a mp 123°C. Elemental analysis calculated for  $C_3F_5Co(CO)_3PPh_3$ :  
C 53.80%, H 2.82%, F 17.71%, P 5.82% found: C 53.87%, H 2.83%,  
F 17.85%, P 5.64%.

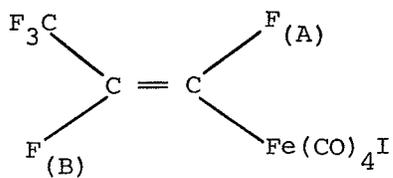
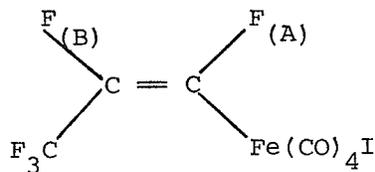
## Results and Discussion

### Reaction of $C_3F_5I$ with $Fe_2(CO)_9$

The two isomeric products isolated from this reaction both have a parent ion in the mass spectrum at  $m/e$  426 with the successive loss of four carbonyl groups. The elemental analysis indicates the formula  $C_3F_5Fe(CO)_4I$ .

The  $^{19}F$  NMR spectra of the two isomers (Table I) indicated that the perfluoropropenyl ligand was present, rather than the perfluoroallyl group. This rearrangement to the perfluoropropenyl group was not unusual in light of the reported reactions of perfluoroallyl chloride with transition metal complexes. (36, 37) The  $^{19}F$  NMR spectra of the two groups, (allyl and propenyl) are easily distinguishable. (36, 37) The coupling constants and chemical shift values are quite different. The spectrum of the perfluoroallyl ligand is very similar to that of  $CF_2:CF CF_2X$ , (where  $X = Cl, Br$  and  $I$ ). The integrations for the resonance absorptions are 2:1:1:1. The perfluoropropenyl ligand gives integrations 3:1:1. Both spectra are first order.

The configuration of the  $CF_3$  and  $Fe(CO)_4I$  groups about the C:C olefinic bond must be established. These groups can be either cis or trans to each other about this bond.

transcis

It has been shown<sup>(36)</sup> that  $J_{A,B}$  (trans) for fluoroolefins is in the range 115 to 124 Hz and  $J_{A,B}$  (cis) = 19 to 58 Hz. The  $J_{A,B}$  value taken from the spectra obtained here (Table I) is 130 Hz, indicating the arrangement to be exclusively trans.

The use of the terms cis and trans in the rest of the discussion will be used to designate the configuration of the  $R_f$  group and the iodine atom about the transition metal and the arrangement about the C:C bond must be understood to be trans.

There are two possible configurations of the ligands about the metal atom. The two isomers are:

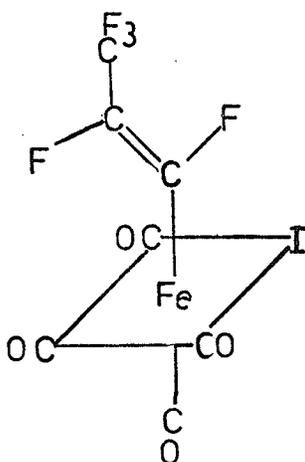
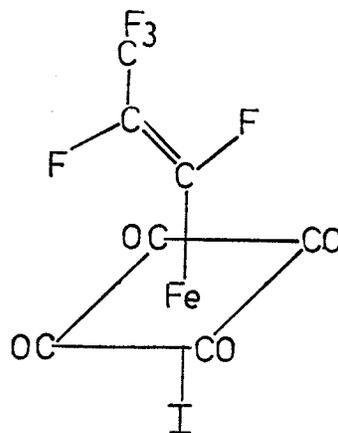
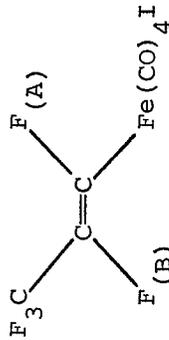
cistrans

TABLE I

IR and NMR spectra (a) of cis and trans  $\text{CF}_3\text{CF}:\text{CFFe}(\text{CO})_4$ 

Complex	$\nu(\text{CO}) \text{ cm}^{-1}$	$\delta_{\text{CF}_3} \text{ (c)}$	$\delta_{\text{A}}$	$\delta_{\text{B}}$	$J_{\text{A,B}} \text{ (d)}$	$J_{\text{A,CF}_3}$	$J_{\text{B,CF}_3}$
<u>cis</u> - $\text{CF}_3\text{CF}:\text{CFFe}(\text{CO})_4$ (rust crystals)	2141.5 (2.9) (b) 2093.1 (10) 2071.4 (6) 2055.0 (0.8) ( $^{13}\text{C}$ -0)	66.0	92.5	159.3	130	22	11
<u>trans</u> - $\text{CF}_3\text{CF}:\text{CFFe}(\text{CO})_4$ (red crystals)	2147.2 (0.7) 2088.2 (10) 2052.4 (0.6) ( $^{13}\text{C}$ -0)	66.2	87.9	161.9	130	22	11

(a) Methylcyclohexane solution for IR: THF solution for NMR with 10%  $\text{CFCl}_3$ 

(b) Numbers in parentheses refer to relative intensities.

(c)  $\delta$  values in ppm upfield from  $\text{CFCl}_3$ .

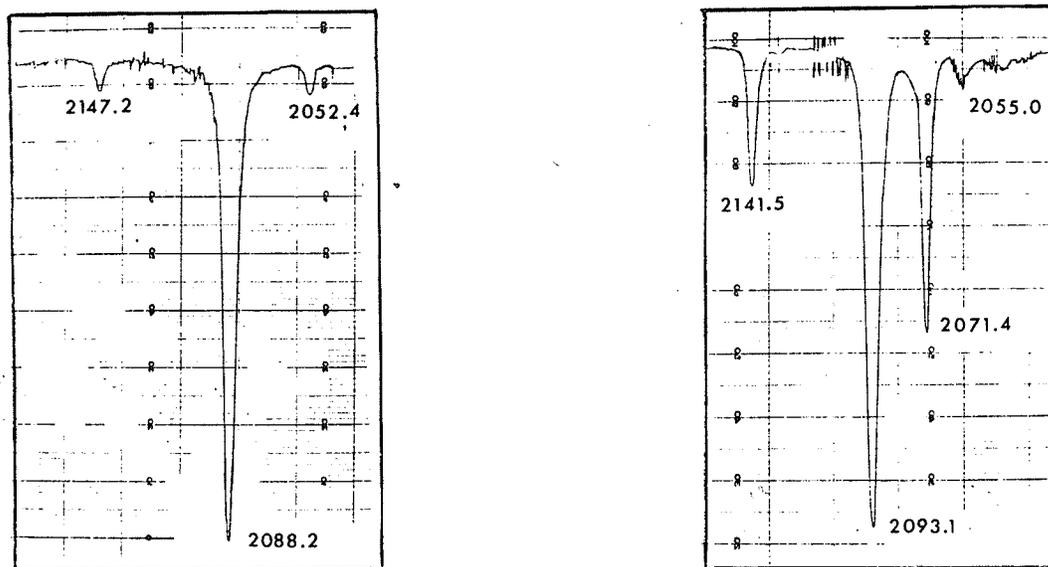
(d) J values in Hz.

The IR absorption band pattern in the terminal carbonyl vibration region of the spectrum, (1900 - 2150  $\text{cm}^{-1}$ ), is used to determine in which configuration the molecule exists in solution. The pattern expected for each isomer was predicted by Pitcher and Stone<sup>(43)</sup> from the geometrical arrangement of the ligands and group theory.

The cis-configuration corresponds to the point group  $C_s$  (local symmetry of the carbonyl groups), and should show four C-O IR active absorptions, ( $2A_1 + B_1 + B_2$ ). The more symmetrical trans-configuration with  $C_{4v}$  symmetry is expected to give rise to two IR active bands, ( $A_1 + E$ ). The intensity of the  $A_1$  band depends on the non-planarity of the four equatorial carbonyl groups and the iron atom, and therefore is expected to be weak.

Also expected to be observed in the IR spectra are bands due to  $^{13}\text{C}$ -O vibrations. These are very weak and usually  $\sim 40 \text{ cm}^{-1}$  lower than the intense absorption with which they are associated.

From the recorded spectra in Fig.2, it is seen that the red isomer has the trans-configuration. The bands at 2147.2 and 2088.2  $\text{cm}^{-1}$  are the  $A_1$  and E modes respectively. The 2052.4  $\text{cm}^{-1}$  absorption is assigned to a  $^{13}\text{C}$ -O vibration.



trans-isomer - (red crystal)

cis-isomer - (rust crystal)

Figure 2 IR carbonyl absorption bands of cis- and trans- $\text{CF}_3\text{CF:CFFe}(\text{CO})_4\text{I}$

The rust isomer has three  $^{12}\text{C-O}$  bands and a band at  $2055.0\text{ cm}^{-1}$  which is assigned to a  $^{13}\text{C-O}$  stretching vibration. It was noted that four IR active  $^{12}\text{C-O}$  absorptions were predicted for the cis-isomer. However, it has been shown for the complexes cis- $\text{Fe}(\text{CO})_4\text{I}_2$  (44, 45) and  $(\text{CF}_2)_4\text{Fe}(\text{CO})_4$  (43) (which must exist in the cis-form because of the nature of the bidentate ligand), that two of the frequencies are accidentally degenerate and are observed as the most intense absorption ( $2093.1\text{ cm}^{-1}$  for this complex). The rust crystals are therefore the cis-isomer.

The cis- and trans-isomers for a similar complex,  $\text{Fe}(\text{CO})_4\text{I}_2$ , have been isolated and studied. (44, 45) The cis-form (preferred configuration at room temperature), was converted to the trans-form

with UV irradiation and the two isomers separated by fractional recrystallization from hexane at  $-80^{\circ}\text{C}$ . The two isomers were identified by the carbonyl absorption patterns.

The cis- and trans-isomers of  $\text{CF}_3\text{CF}:\text{CFFe}(\text{CO})_4\text{I}$  could be separated by sublimation. The isomerization of the trans-form to the cis-form in THF solution was followed by the change in the IR and NMR spectra with time. The pure trans-isomer was dissolved in anhydrous THF at  $-20^{\circ}\text{C}$  in the NMR sample tube, and the tube sealed at  $-80^{\circ}\text{C}$  under vacuum. At  $-5^{\circ}\text{C}$ , only the NMR spectra due to the trans-form was recorded. Above  $0^{\circ}\text{C}$ , the appearance of the cis-form was observed. The sample was left at room temperature for three days and the NMR spectrum recorded again. Only the spectrum of the cis-form could be seen at  $25^{\circ}\text{C}$ . Above this temperature, the sample began to decompose and the resonance peaks collapsed due to paramagnetic species in the solution.

A methylcyclohexane solution of pure trans-isomer for the IR spectrum was prepared at  $-10^{\circ}\text{C}$  and introduced into the cell by syringe at room temperature. The absorption bands due to the trans-form decreased in intensity and the bands assigned to the cis-form appeared and increased in intensity. After 30 minutes, the solution contained a 1:1 mixture of the two isomers. From the NMR and IR spectra of a solution that had been standing for three days at room temperature, ( $25^{\circ}\text{C}$ ), it was estimated that the ratio of cis:trans isomers was 19:1.

From this ratio, the energy difference between the cis- and trans-isomers can be determined by using the Boltzmann equation:

$$\frac{N_c}{N_t} = \frac{g_c}{g_t} e^{\Delta E/RT}$$

where:  $N$  is the population of each isomer at  $T = 298.2$  K,  $g$  is the structural degeneracy for the isomer, and is determined from a consideration of the number of equivalent ways of forming a particular structure, and  $R = 1.99$  cal  $K^{-1}$  mole $^{-1}$ . From the IR and NMR spectra  $N_c / N_t = 19/1$ , and from the geometry of the two isomers,  $g_c / g_t = 4/1$ . From this calculation,  $\Delta E = 920$  cal/mole.

It was also estimated from the IR and NMR spectra that the rate of isomerization, (trans  $\longrightarrow$  cis) is 20x as rapid at 25°C compared to the rate at 0°C. Using the Arrhenius relationship:

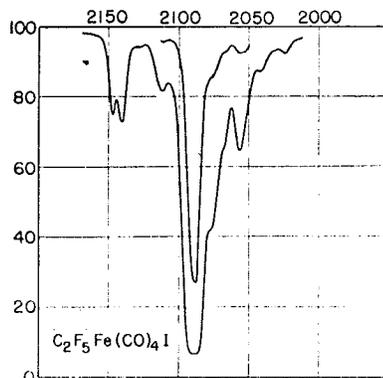
$$\left[ \frac{T_1 T_2}{T_1 - T_2} \right]_R \ln \frac{k_{273.2 \text{ K}}}{k_{298.2 \text{ K}}} = -E_{\text{activation}}$$

it is determined that the barrier to trans  $\longrightarrow$  cis isomerization is  $E_a = 19,400$  cal/mole.

It must be emphasized that the estimates used for the determination of  $\Delta E$  and  $E_a$  were not obtained under rigidly controlled conditions and error in the calculated energy values could be as high as 20%.

The isolation of the cis- and trans-forms in this work clarifies previous studies done on complexes of this type. Stone et al<sup>(43, 46)</sup> prepared a series of  $R_f \text{Fe}(\text{CO})_4 \text{I}$  complexes where  $R_f = \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7$ . The products were sublimed and the IR spectra in the carbonyl region used to designate the complexes as cis or trans. The initial assignment was the cis-form.<sup>(46)</sup> An unequivocal conclusion was not reached

and the reasons for this can be shown by examining the IR spectrum of  $C_2F_5Fe(CO)_4I$ :



from Ref. (43)

Figure 2a IR carbonyl absorption bands of  $C_2F_5Fe(CO)_4I$

The carbonyl frequencies were listed as:

2146 (w) ( $cm^{-1}$ )	Abbreviations:
2140 (w)	(vw) very weak
2112 (vw)	(w) weak
2087 (vs)	(vs) very strong
2073 (sh)	(sh) shoulder
2056 (w) $^{13}C-O ?$	

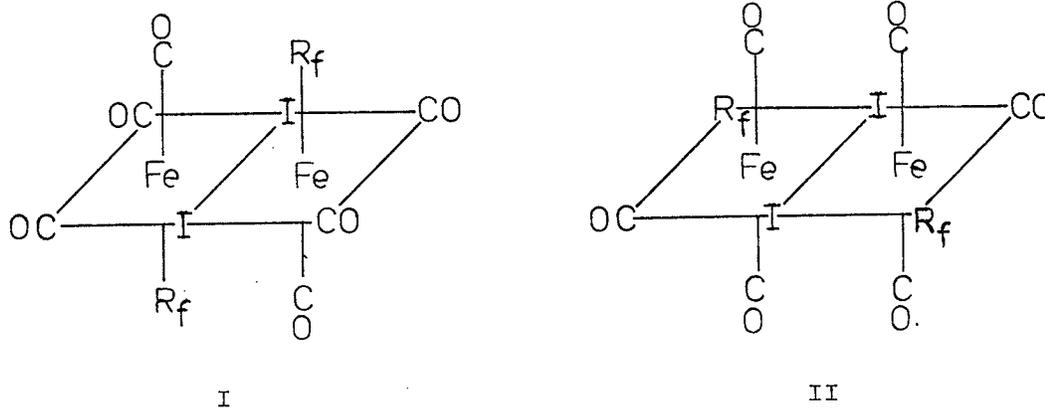
It was concluded later that this complex existed mainly in the trans-form but the presence of so many bands did not rule out the possibility of the cis-form. The band at  $2056\text{ cm}^{-1}$  was thought to be either a  $^{13}C-O$  vibration or a band due to the cis-isomer. (43)

From the present work, this spectrum can now be interpreted with some certainty. The absorptions at  $2146$  and  $2087\text{ cm}^{-1}$  are due to the predominant trans-form. Bands at  $2140$ ,  $2073\text{ cm}^{-1}$ , and a third band under the broadened  $2087\text{ cm}^{-1}$  absorption would be due to the cis-form, and  $2056\text{ cm}^{-1}$  is a  $^{13}C-O$  vibration from the trans-isomer. The pair of bands at  $2146$  and  $2140\text{ cm}^{-1}$  show that both the cis- and trans-forms are present. This same separation of  $6\text{ cm}^{-1}$  is shown in

cis- and trans- $\text{CF}_3\text{CF:CFFe}(\text{CO})_4\text{I}$ , ( $5.7 \text{ cm}^{-1}$ ).

For some reason, the two isomers could not be separated by sublimation. The carbonyl absorption band at  $2112 \text{ (w) cm}^{-1}$  is interesting. This band was not observed for the cis- and trans-isomers of  $\text{CF}_3\text{CF:CFFe}(\text{CO})_4\text{I}$  and must be present only for the perfluoroalkyl complexes. It may result from a lowering of the local carbonyl symmetry so that the IR inactive  $B_1$  mode for the trans-configuration becomes slightly IR active. This would result in a weak absorption as was seen in trans- $\text{Fe}(\text{CO})_4\text{I}_2$  by Pankowski and Bigorgne. (44)

This weak absorption could also be due to a small amount of dimeric compound which cosublimed with the monomer. On the basis of the IR data the configuration of the dimer was considered to be one of configurations shown below: (43)



The dimer is iodine-bridged because of the absence of any bridging C-O absorptions in the IR spectrum. Where  $R_f = \text{C}_2\text{F}_5$ , this dimer is reported to give the C-O absorption bands ( $\text{cm}^{-1}$ ): 2110 (m), 2075 (vs), and 2053 (s). (43) It can be seen that if a small amount of this dimer were present in the solution of the monomer, only the

2110  $\text{cm}^{-1}$  band would not be hidden by absorptions due to the monomer. The dimeric product was sublimed at a temperature not very much higher than that required for the monomer, and co-sublimation with the monomer was possible. (46)

The dimeric  $\left[ \text{CF}_3\text{CF}:\text{CFFe}(\text{CO})_3 \right]_2$  was prepared by heating a mixture of the monomers at 70°C for three hours in a sealed tube. The dimer was sublimed at 120°C and the yield was very poor. It could not be characterized fully because of the small amount of the product obtained and its low solubility in all solvents. The IR spectrum (in  $\text{CH}_2\text{Cl}_2$ ) showed the C-O stretching frequencies ( $\text{cm}^{-1}$ ): 2116.2 (5), 2079.6 (10) and 2057.7 (6.8). The configuration of the molecule (diag. I or II) cannot be determined from the IR because both are predicted to give similar spectra.

The attempt to obtain the  $^{19}\text{F}$  NMR spectrum was only partially successful because of the solubility problem and only a quartet at  $\delta = 67.5$  ppm with a measured splitting of 13 and 23 Hz was recorded. This is assigned to the  $\text{CF}_3$  fluorines as shown for the  $\sigma$ -perfluoropropenyl group as seen in Table I.

King et al (47) have synthesized two complexes which are of interest to the question of this isomerization.  $(\text{CF}_3)_2\text{CFFe}(\text{CO})_4\text{I}$  was reported to give the C-O absorption bands ( $\text{cm}^{-1}$ ):

2146 (w)  
2118 (w)  
2086 (s)  
2052 (w)

which indicated only the trans-form. From the bulkiness of the  $(\text{CF}_3)_2\text{CF}$

group, one would predict that the cis-isomer would not be the preferred configuration.  $n\text{-C}_7\text{F}_{15}\text{Fe}(\text{CO})_4\text{I}$  gave the C-O absorption bands ( $\text{cm}^{-1}$ ):

2140 (m)  
2114 (w)  
2090 (s)  
2076 (s)  
2051 (w)

Abbreviations:

(m) medium  
(w) weak  
(s) strong

which indicates the cis-form to be the isomer isolated. In both these cases, no mention as to the configuration of molecules was made in the original report.

Reaction of  $C_3F_5I$  with  $Zn[Co(CO)_4]_2$

This reaction proceeded rapidly at room temperature so that within 10 minutes the evolution of carbon monoxide had ceased. After the solvent had been removed in vacuo at  $-30^\circ C$ , the products were distilled into the trapping system, (described earlier in the General Introduction - Experimental), and an NMR sample was prepared. The  $^{19}F$  NMR spectrum indicated that all the  $C_3F_5I$  had reacted. The spectrum also indicated the presence of three new complexes, one of which had only a transient existence.

The resonance absorption at  $\delta = 41.6$  ppm (upfield from the internal standard  $CFCl_3$ ) was an octet very similar to the pattern for the perfluoromethylene group in  $CF_2:CFCF_2I$ , (see Table II).

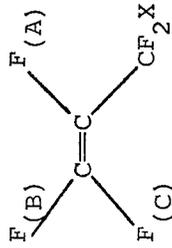
After standing at room temperature for one hour, or upon further trap to trap distillations, this octet absorption was not present in the  $^{19}F$  NMR spectrum of the product mixture.

It is seen in the complex  $\pi-C_5H_5Ni(CO)CF_2CF:CF_2$  that the coupling constants do not change when the perfluoroallyl group is  $\sigma$ -bonded to a metal atom.<sup>(37)</sup> It has also been observed that the chemical shift of a  $-CF_2$ -group  $\sigma$ -bonded to cobalt shifts downfield in comparison to the  $\delta$  values for the  $-CF_2-I$  system,<sup>(48)</sup> (see Table II). From these data, it was concluded that the complex which had a transient existence contained a  $\sigma$ -perfluoroallyl ligand. The complete  $^{19}F$  NMR spectrum of this group could not be recorded because the concentration of this short-lived complex in the reaction mixture was very low, ( $\sim 10\%$ ), and the single fluorine resonance

TABLE II

<sup>19</sup>F NMR Chemical Shift Values for -CF<sub>2</sub>-I and -CF<sub>2</sub>-Co Systems

Compound	$\delta_{CF_2}$ (b)	$\delta_B$	$\delta_C$	$\delta_A$	$J_{B,C}^{(b)}$	$J_{A,B}$	$J_{A,C}$	$J_{B,CF_2}$	$J_{C,CF_2}$	$J_{A,CF_2}$
CF <sub>3</sub> CF <sub>2</sub> I (a)	65.2									
CF <sub>3</sub> CF <sub>2</sub> Co(CO) <sub>4</sub>	59.2									
(C <sub>2</sub> F <sub>5</sub> )CF <sub>2</sub> I	60.5									
(C <sub>2</sub> F <sub>5</sub> )CF <sub>2</sub> Co(CO) <sub>4</sub>	53.0									
(present work)										
CF <sub>2</sub> :CFCF <sub>2</sub> I	49.7 (c)	96	104.7	177.5	53.4	36.2	115	5.1	32.6	26.0
CF <sub>2</sub> :CFCF <sub>2</sub> Co(CO) <sub>4</sub>	41.6							5.2	32.2	24.0



(a)  $\delta$  values taken from ref (48) and ref (49)

(b)  $\delta$  values in ppm upfield from CFCI<sub>3</sub>, J values in Hz

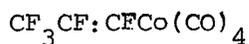
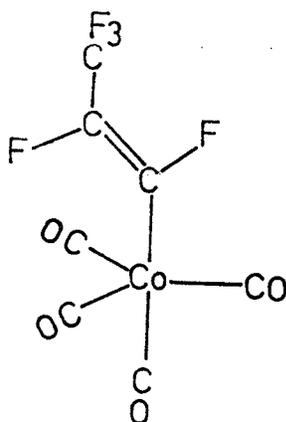
(c) In a paper by K. C. Ramsey and W. S. Brey, J. Chem. Phys., 40, 2349 (1964), this value was reported as 63.6 ppm. These workers were interested in the changing  $\delta_{CF_2}$  values for the series C<sub>3</sub>F<sub>5</sub>Cl, C<sub>3</sub>F<sub>5</sub>Br, C<sub>3</sub>F<sub>5</sub>I. Their reported value of 63.6 ppm did not fit the downward trend shown by the chloride and bromide derivatives. The value  $\delta = 49.7$  ppm (determined in the present work) fits this trend: C<sub>3</sub>F<sub>5</sub>Cl (62.0 ppm), C<sub>3</sub>F<sub>5</sub>Br (55.1 ppm), C<sub>3</sub>F<sub>5</sub>I (49.7 ppm). The coupling constants and values for the other fluorines of the allyl group were measured to be the same as those reported by Brey and Ramsey.

absorptions did not rise above the level of the noise.

This complex was reasoned to be  $\text{CF}_2\text{:CFCF}_2\text{Co(CO)}_4$  and the rearrangement or decarbonylation of this compound yields the two major products.

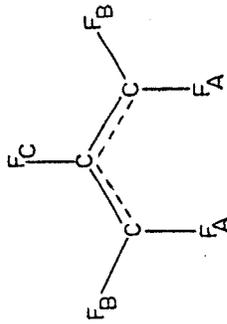
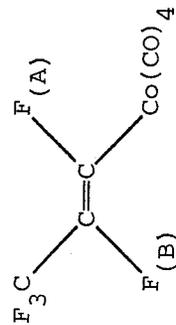
These two major products were separated by slow trap to trap distillations, (0.01 mm). The NMR and IR spectra of these two complexes are listed in Table III.

The lower melting, less stable compound was identified as  $\sigma$ -perfluoropropenylcobalt tetracarbonyl.



Although an elemental analysis was not possible because the compound was thermally unstable above  $0^\circ\text{C}$ , the NMR and IR spectra were sufficient to identify the complex. The  $^{19}\text{F}$  NMR spectrum shows the presence of a perfluoropropenyl group which has been observed in the previous section and the references therein. The coupling constant ( $J_{\text{A,B}} = 147 \text{ Hz}$ ) between the single fluorine atoms on the olefinic carbon atoms of the ligand indicates that the  $\text{CF}_3$  group and the  $\text{Co(CO)}_4$  group are trans to each other about the C;C bond.

TABLE III

IR and NMR Spectra (a) of  $\text{CF}_3\text{CF}_3\text{CFCo}(\text{CO})_4$  and  $\pi\text{-C}_3\text{F}_5\text{Co}(\text{CO})_3$ 

Complex	$\nu(\text{CO}) \text{ cm}^{-1}$	$\nu(\text{C:C}) \text{ cm}^{-1}$	$\delta_{\text{CF}_3}^{(c)}$	$\delta_{\text{A}}$	$\delta_{\text{B}}$	$J_{\text{A,CF}_3}$	$J_{\text{B,CF}_3}$	$J_{\text{A,B}}$
$\text{CF}_3\text{CF}_3\text{CFCo}(\text{CO})_4$	2130.0 (m)	1640 (w)	66.5	155	89.8	24	13	147
	2068.1 (s)							
	2059.8 (s)							
	2051.2 (s)							
$\pi\text{-C}_3\text{F}_5\text{Co}(\text{CO})_3$	2115 (m)	1425 (m)	81.5	92.7	195	74	118	18
	2064 (s)	( $\text{C}=\text{C}=\text{C}$ )						

(a) Pentane solution for IR;  $\text{CH}_2\text{Cl}_2$  solution for NMR (5%  $\text{CFCl}_3$ )

(b) Abbreviations: (s) strong, (m) medium, (w) weak

(c)  $\delta$  values in ppm upfield from  $\text{CFCl}_3$ , J values in Hz

The terminal C-O stretching region in the IR spectrum had four bands.

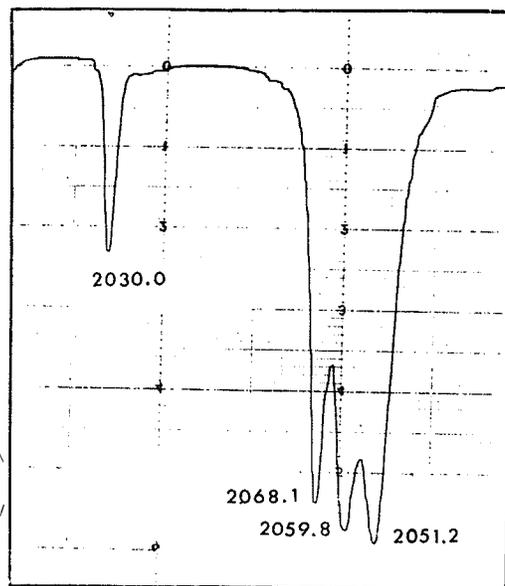
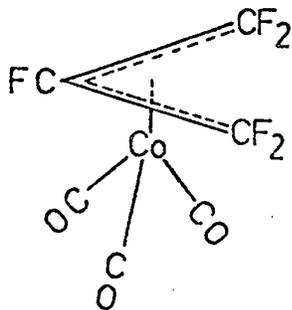


Figure 3 IR carbonyl absorption bands of  $\text{CF}_3\text{CF:CFCO}(\text{CO})_4$

The configuration for molecules of the type  $\text{R}_f\text{Co}(\text{CO})_4$ , (where  $\text{R}_f$  is a perfluoroalkyl group), has been studied by Hagen and MacDiarmid<sup>(50, 51)</sup> and the  $\text{R}_f$  group is assigned the axial position of a trigonal bipyramid due to bonding considerations. This configuration corresponds to the point group  $\text{C}_{3v}$  and three C-O active IR bands ( $2\text{A}_1 + \text{E}$ ) are predicted by group theory. Four bands are observed for  $\text{CF}_3\text{CF:CFCO}(\text{CO})_4$ , (Fig. 3). This fact was also reported by Wilford, Forster and Stone<sup>(25)</sup> for the complex  $\text{HCF}_2\text{CF}_2\text{Co}(\text{CO})_4$  and is ascribed to the lowering of the carbonyl group symmetry by the presence of a non-axially symmetric fluorocarbon-metal group. The E mode is split with the resulting extra band.

The main product was identified as:



$\pi$ - perfluoroallylcobalt tricarbonyl

The compound at room temperature was a yellow liquid, stable in vacuum but sensitive to air. The compound melted at  $+5^{\circ}\text{C}$  and had a volatility such that distillation in vacuo (0.01 mm) at room temperature was rapid.

The IR spectrum in the carbonyl region had two bands, (Fig.4). This is predicted for a molecule with three equivalent carbonyl groups and  $C_{3v}$  symmetry ( $A_1 + E$ ).

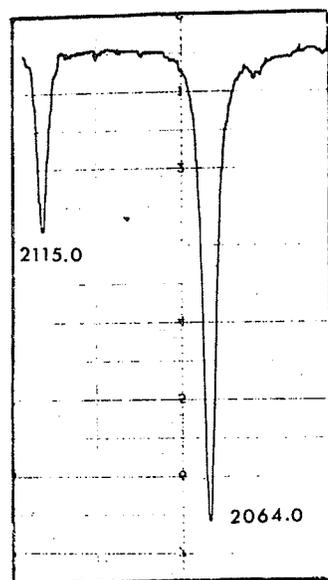


Figure 4 IR carbonyl absorption bands of  $\pi\text{-C}_3\text{F}_5\text{Co(CO)}_3$

This is also the pattern seen for  $\pi\text{-C}_3\text{H}_5\text{Co(CO)}_3$ , (2056 (m), 2001 (s)  $\text{cm}^{-1}$ ), except for the shift to higher frequency. (52)

The  $^{19}\text{F}$  NMR spectrum for  $\pi\text{-C}_3\text{F}_5\text{Co(CO)}_3$  was analyzed as being first order, although it was borderline to being second order. The spectrum is shown in Fig.5 and tabulated in Table III.

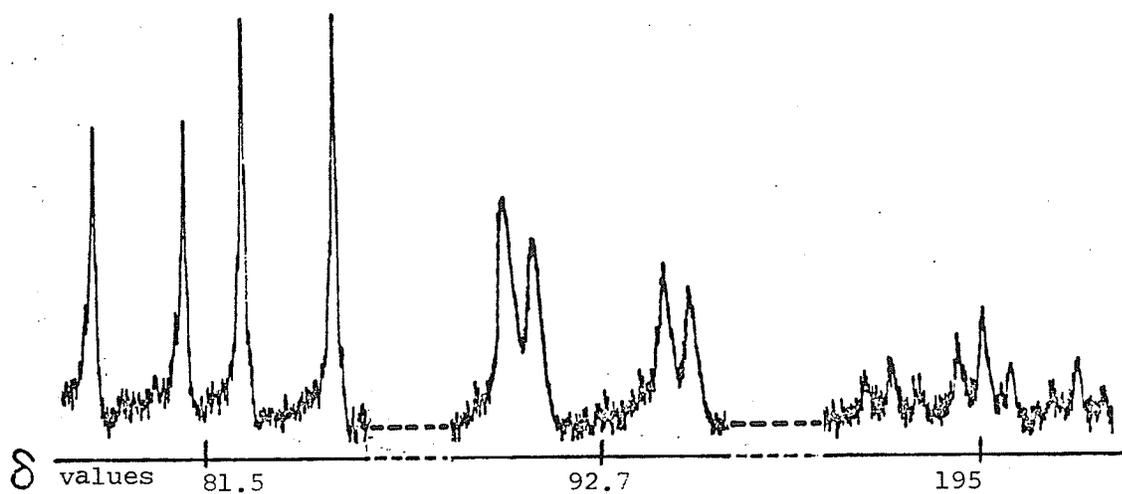
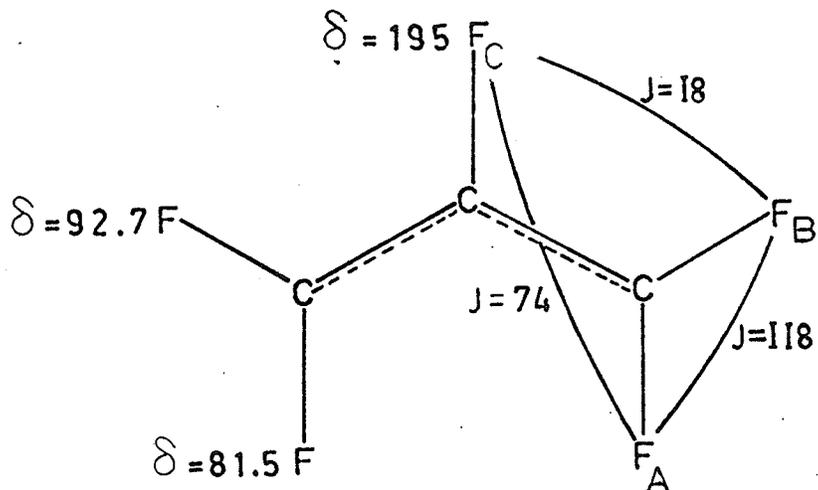


Figure 5  $^{19}\text{F}$  NMR spectrum of  $\pi\text{-C}_3\text{F}_5\text{Co(CO)}_3$

The chemical shifts, (ppm from  $\text{CFCl}_3$ ), and coupling constants are shown in Table III and are represented graphically below:



It was noted in the introduction to this section that carbonyl force constants were used in an attempt to determine whether  $\sigma$ -bonded fluorinated alkyl groups possessed any  $\pi$ -acceptor capacity. Many other studies have also been carried out to examine the  $\sigma$ -donor and  $\pi$ -acceptor properties of various ligands. A review by Haines and Stiddard<sup>(13)</sup> covers most of this work, particularly the attempts to separate the  $\sigma$  and  $\pi$  effects from the force constant (k) data.

A method proposed to separate the two effects follows the  $(k_{\text{equatorial}} - k_{\text{axial}})$  value where changing the ligand (R) in complexes of the types  $\text{RMn}(\text{CO})_5$  and  $\text{RCo}(\text{CO})_4$  will affect the carbonyl groups cis and trans to it in a different manner.<sup>(50)</sup> This may be valid in octahedral molecules, but not in trigonal bipyramidal systems because of the different bonding schemes in these two cases. Even for octahedral configurations, only large changes in force constants can be inter-

puted, and small changes must be neglected because of the approximate approach used.<sup>(13)</sup>

Therefore, force constant data can only give a qualitative estimate of the overall ( $\sigma$ - $\pi$ ) donation of charge from observing the net movement of charge toward or away from the carbonyl groups.

A comparison for similar olefinic  $\pi$ -complexes and fluoroolefinic  $\pi$ -complexes has not been examined previously. This is due to the lack of examples where the olefin and fluoroolefin bond to the metal in the same manner and the molecular structure is not changed significantly. This problem is overcome by a comparison of  $\pi$ -C<sub>3</sub>H<sub>5</sub>Co(CO)<sub>3</sub> with  $\pi$ -C<sub>3</sub>F<sub>5</sub>Co(CO)<sub>3</sub>. The force constants in Table IV have been calculated by the method of Cotton and Kraihanzel.<sup>(53)</sup> Some other calculations have been listed in Table IV for comparison.

It is seen in Table IV that the force constant of the three equivalent carbonyl groups has increased considerably when all the protons of the  $\pi$ -allyl group are replaced by fluorine atoms. A net movement of electrons away from the carbonyl groups is evident. This is expected considering the predicted poor  $\sigma$ -donor and good  $\pi$ -acceptor properties of the  $\pi$ -C<sub>3</sub>F<sub>5</sub> group compared to the  $\pi$ -C<sub>3</sub>H<sub>5</sub> ligand. The  $\sigma$  and  $\pi$  effects cannot be separated, particularly in this case, where the three carbonyl groups are equivalent.

It is interesting to note the work of Noack et al<sup>(54)</sup> on a series of RMn(CO)<sub>5</sub> complexes, (where R = CH<sub>3</sub>, CH<sub>2</sub>F, CHF<sub>2</sub>, and CF<sub>3</sub>), where a replacement of one proton by a fluorine atom resulted in the increase of each C-O stretching frequency by  $\sim 10 \text{ cm}^{-1}$ . It is

TABLE IV

Carbonyl Force Constants

Compound	C-O Stretching Frequencies (cm <sup>-1</sup> )	Force Constants (e)
		k <sub>axial</sub> k <sub>equatorial</sub>
CH <sub>3</sub> Co(CO) <sub>4</sub> (a)	2111, 2046, 2031	16.86      17.09
HCF <sub>2</sub> CF <sub>2</sub> Co(CO) <sub>4</sub> (b)	2126, 2060, 2050	17.07      17.37
CH <sub>3</sub> Mn(CO) <sub>5</sub> (c)	2108, 1989, 2010	16.12      16.82
CF <sub>3</sub> CF <sub>2</sub> Mn(CO) <sub>5</sub>	2130, 2023, 2038	16.67      17.25
π-C <sub>3</sub> H <sub>5</sub> Co(CO) <sub>3</sub> (d)	2056 (A <sub>1</sub> ), 2001 (E)	k <sub>k</sub> 16.47
π-C <sub>3</sub> F <sub>5</sub> Co(CO) <sub>3</sub>	2115 (A <sub>1</sub> ), 2064 (E)	17.49

(a) IR data and calculations from ref (50) and ref (51)

(b) Calculation from ref (50) and IR data from ref (25)

(c) IR data and force constants for Mn compounds from ref (22)

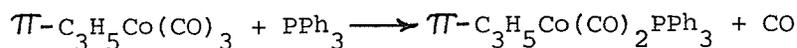
(d) For calculations of C-O force constants for molecules with C<sub>3v</sub> symmetry see ref (53)

(e) Force constants in mdynes/A

seen for the  $\pi$ -allyl complexes here that the substitution by five fluorine atoms leads to an increase of  $59 \text{ cm}^{-1}$  for the  $A_1$  mode absorption and  $63 \text{ cm}^{-1}$  for the E mode absorption.

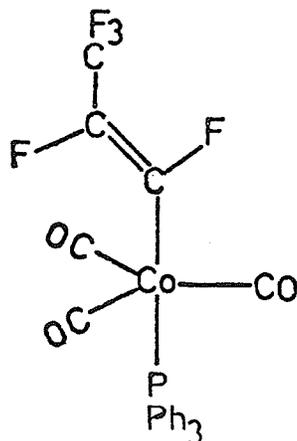
Reaction of  $\pi\text{-C}_3\text{F}_5\text{Co}(\text{CO})_3$  with  $\text{PPh}_3$

The reaction of  $\pi\text{-C}_3\text{F}_5\text{Co}(\text{CO})_3$  with triphenylphosphine was carried out with the intention of synthesizing a  $\pi$ -perfluoroallyl complex which would be more stable than the tricarbonyl derivative. It was thought that this would follow the reaction of the hydrocarbon analogue  $\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$ :<sup>(52)</sup>



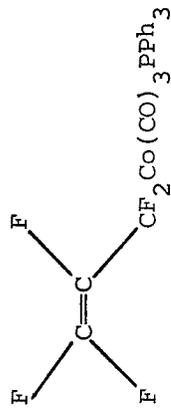
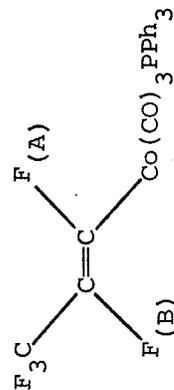
This however, did not occur. The reaction proceeded without the loss of carbon monoxide and two different products were isolated. The products were separated by fractional crystallization from methylcyclohexane. The spectral data for each compound are listed in Table V.

The more soluble compound, (initial crystallization at  $-80^\circ\text{C}$  from methylcyclohexane), was identified as trans- $\text{CF}_3\text{CF}:\text{CFCo}(\text{CO})_3\text{PPh}_3$  from the IR and NMR spectra. (Table V)



trans- $\text{CF}_3\text{CF}:\text{CFCo}(\text{CO})_3\text{PPh}_3$

TABLE V

IR and NMR Spectra (a) of  $\text{trans-CF}_3\text{CF:CFCo(CO)}_3\text{PPh}_3$  and  $\text{cis-CF}_2\text{:CFCF}_2\text{Co(CO)}_3\text{PPh}_3$ 

Complex	$\nu(\text{CO}) \text{ cm}^{-1}$	$\nu(\text{C:C}) \text{ cm}^{-1}$	$\delta_{\text{CF}_3}^{(\text{c})}$	$\delta_{\text{A}}$	$\delta_{\text{B}}$	$J_{\text{A,CF}_3}$	$J_{\text{B,CF}_3}$	$J_{\text{A,B}}$	$J_{\text{F-A}}$
$\text{trans-CF}_3\text{CF:CFCo(CO)}_3\text{PPh}_3$	2068.8 (w)	1640 (w)	66.5	161	89.9	24	13	146	30
	2005.7 (s)								
	2000.0 (s)								
$\text{cis-CF}_2\text{:CFCF}_2\text{Co(CO)}_3\text{PPh}_3$	2048.0 (s)	1750 (w)	43.1						
	1979.6 (sh)								
	1976.9 (s)								
	1963.2 (s)								

$\delta_{\text{CF}_2}$  J from  $-\text{CF}_2$ -resonance absorption pattern

$\delta_{\text{CF}_2}$  18, 5.5, 3.1

(a) Methylcyclohexane solution for IR; THF solution for NMR (5%  $\text{CFCl}_3$ )

(b) Abbreviations: (w) weak, (s) strong, (sh) shoulder

(c)  $\delta$  values in ppm upfield from  $\text{CFCl}_3$ , J values in Hz

The  $^{19}\text{F}$  NMR spectrum indicated a  $\sigma$ -perfluoropropenyl group with the  $\text{CF}_3$  and  $\text{Co}(\text{CO})_3\text{PPh}_3$  groups trans to each other about the C:C bond, ( $J_{\text{A,B}} = 146$  Hz). The configuration of the ligands about the Co atom was determined from the C-O stretching region of the IR spectrum. Group theory predicts, <sup>(25)</sup> for complexes of the type trans- $\text{R}_f\text{Co}(\text{CO})_3\text{PPh}_3$ , (symmetry  $\text{C}_{3v}$ ), one intense\* absorption, (E mode), and one weaker absorption, ( $\text{A}_1$  mode). The E mode absorption may be broad or split into two absorptions if the  $\text{R}_f$ -Co group is axially non-symmetric. Complexes of this type where  $\text{R}_f = \text{HCF}_2\text{CF}_2$  <sup>(25)</sup> or  $\text{C}_2\text{F}_5$  <sup>(55)</sup> have previously been characterized. The compound isolated shows this pattern, (Fig.6)

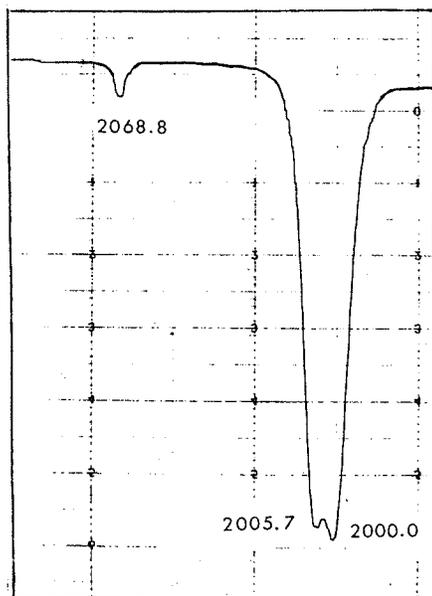
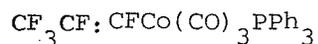


Figure 6 IR carbonyl absorption bands of trans-



\* - The relative intensities of the predicted bands are calculated by the method of local oscillating dipoles and are only approximate. (page 89 of ref.13)

The coupling constant between the  $^{31}\text{P}$  of the  $\text{PPh}_3$  group and the F-C-Co fluorine nucleus was measured to be 30 Hz. This is comparable to the coupling constants for similar perfluoroalkyl trans-complexes which have been reported, ( $J_{\text{F-P}} = 30.5 \text{ Hz}$ ).<sup>(25)</sup>

The less soluble product of the reaction was difficult to identify because of solubility and thermal stability problems and unusual IR and NMR spectra. It is, however, the more interesting product.

The IR spectrum showed a weak absorption at  $1750 \text{ cm}^{-1}$ . The C:C stretching frequency for  $\text{CF}_2:\text{CFCF}_2\text{I}$  and  $\text{CF}_2:\text{CFCF}_2\text{Cl}$  occurs at  $1750 \text{ cm}^{-1}$ , while  $\nu(\text{C:C})$  for a perfluoropropenyl group falls at  $1640 \text{ cm}^{-1}$ . From this observation, the fluorocarbon moiety was reasoned to be the  $\sigma$ -perfluoroallyl ligand.

The C-O stretching region of the spectrum showed the absorption pattern in Fig.7.

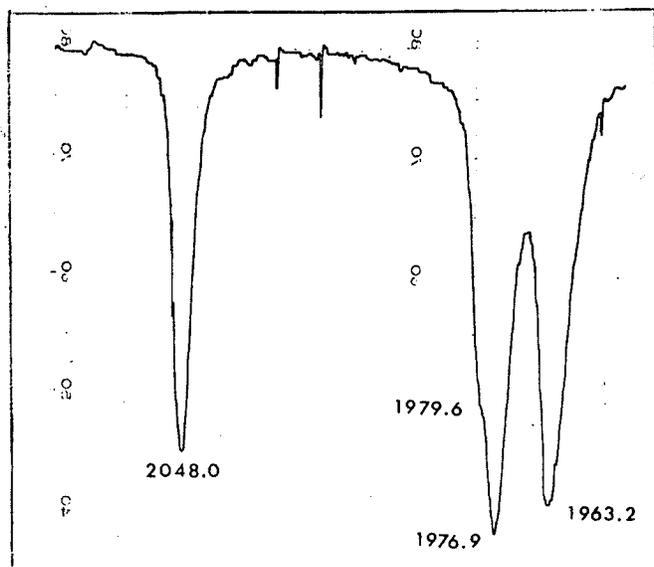


Figure 7 IR carbonyl absorption bands of  
 $\text{cis-CF}_2:\text{CFCF}_2\text{Co}(\text{CO})_3\text{PPh}_3$

There are two molecular structures possible for trigonal bipyramidal complexes of the type  $R_f\text{Co}(\text{CO})_3\text{PR}_3$ . The trans-configuration, ( $C_{3v}$ ), has been discussed, and the spectrum for trans- $\text{CF}_3\text{CF}:\text{CFCo}(\text{CO})_3\text{PPh}_3$  is shown in Fig. 6. The cis-configuration, (with the  $R_f$  group in the axial position,  $\text{PR}_3$  in an equatorial position), corresponds to the point group  $C_s$ , and group theory predicts three C-O absorption bands of equal intensity,  $(2A_1 + B)$ .<sup>(25)</sup> This is the pattern observed and shown in Fig. 7. The shoulder at  $1979.6\text{ cm}^{-1}$  does not conform exactly to this assignment, and an explanation of this will be proposed later.

The  $^{19}\text{F}$  NMR spectrum was expected to verify the structure of the fluorocarbon ligand and the configuration of the molecule. As was discussed previously, perfluoroallyl and perfluoropropenyl groups give rise to different  $^{19}\text{F}$  NMR spectra. Also, the  $^{31}\text{P}$  coupling constants to a fluorine nucleus on the carbon  $\alpha$  to the cobalt will vary depending on the geometry of the molecule. Udovich and Clark<sup>(56)</sup> studied the complex  $\text{CF}_3\text{Co}(\text{CO})_3\text{PF}_3$  where the cis-form and trans-form are in equilibrium. The P-F coupling constants across the cobalt were reported to be:  $J_{\text{F},\text{P}}(\text{trans}) = 80\text{ Hz}$  and  $J_{\text{F},\text{P}}(\text{cis}) = 38\text{ Hz}$ . For complexes of the type trans- $R_f\text{Co}(\text{CO})_3\text{PPh}_3$  it has already been noted that  $J_{\text{F},\text{P}}(\text{trans}) = 30\text{ Hz}$ . It would be expected, therefore, that cis- $R_f\text{Co}(\text{CO})_3\text{PPh}_3$  complexes would have  $J_{\text{F},\text{P}}(\text{cis}) \sim 15\text{ Hz}$ .

The  $^{19}\text{F}$  NMR spectrum had to be recorded at  $10^\circ\text{C}$  due to the thermal instability of the complex. At  $10^\circ\text{C}$ , however, the solubility of the compound in THF, (or any suitable solvent), was so low that only one resonance absorption could be observed. The C-1024 Varian Time Averaging Computer was necessary to record this absorption at

$\delta = 43.1$  ppm in Fig.8. The measured splitting of this resonance shows coupling constants 18, 5.5 and 3.1 Hz. The fluorine nuclei corresponding to this absorption are coupled to three different single nuclei of spin  $\frac{1}{2}$ .

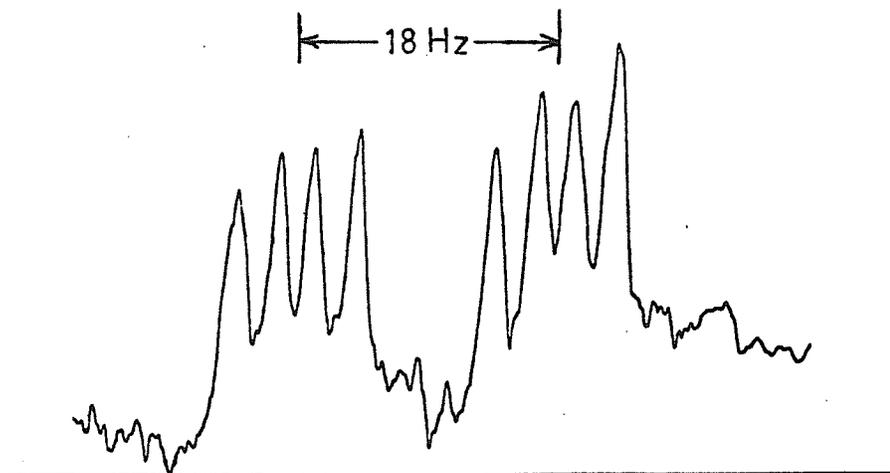
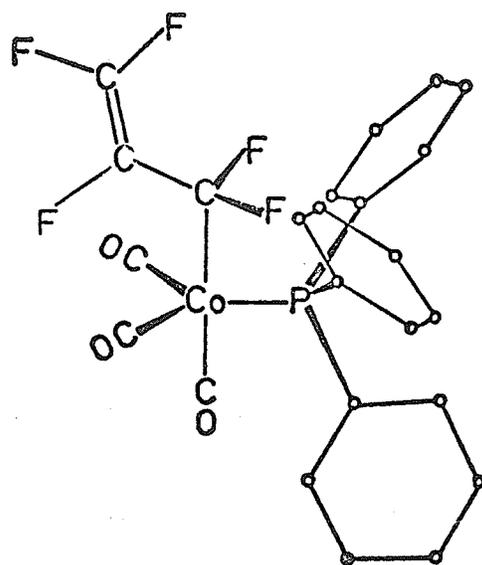


Figure 8 Partial  $^{19}\text{F}$  NMR spectrum of cis- $\text{CF}_2:\text{CFCF}_2\text{Co}(\text{CO})_3\text{PPh}_3$   
( $\delta = 43.1$  ppm)

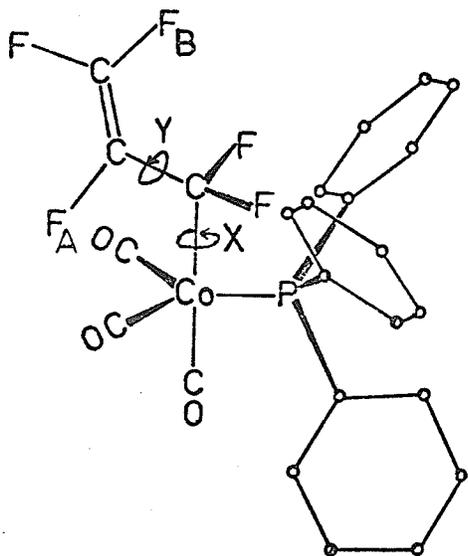
In spite of the incomplete spectrum, several things can be derived from the recorded resonance absorption. The chemical shift ( $\delta = 43.1$  ppm) is close to that seen for the  $-\text{CF}_2-\text{Co}$  group in  $\text{CF}_2:\text{CFCF}_2\text{Co}(\text{CO})_4$ , (see Table II). The measured coupling constant  $J = 18$  Hz can be attributed to the  $^{31}\text{P}$  nucleus and was expected if the molecule was in the cis-configuration.

In summarizing the spectral evidence: (a)  $\nu(\text{C:C}) = 1750 \text{ cm}^{-1}$  as in  $\text{CF}_2:\text{CFCF}_2\text{I}$ , (b) C-O absorption bands in a pattern predicted for a  $\text{C}_s$  symmetry, (c)  $\delta = 43.1$  ppm for the only resonance recorded in the  $^{19}\text{F}$  NMR spectrum, and (d) a splitting of 18 Hz for this resonance, it is reasoned that the compound is cis- $\sigma$ -perfluoroallyl-cobalt tricarbonyl triphenylphosphine.

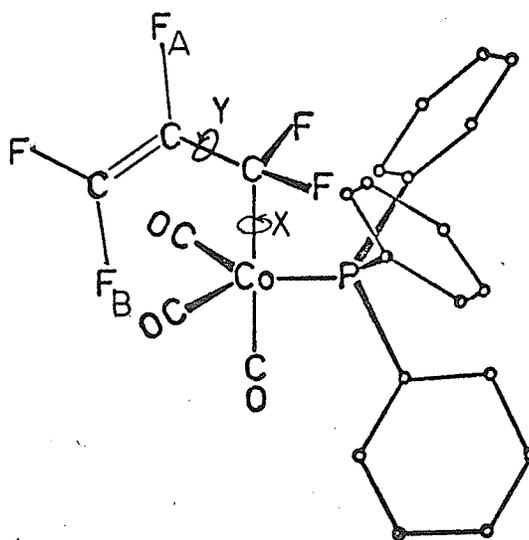


cis-σ-perfluoroallyl cobalt tricarbonyl triphenylphosphine

Only the  $\nu(\text{C:C})$  assignment can be considered unequivocal evidence for this structure. The shoulder at  $1979.6 \text{ cm}^{-1}$  in the IR spectrum and the splitting of the  $-\text{CF}_2-$  resonance in the NMR spectrum both must be explained. These features may be better understood by examining a molecular model of the cis- $\text{CF}_2:\text{CFCF}_2\text{Co}(\text{CO})_3\text{PPh}_3$  molecule. A pictorial representation of the model is shown below:



(a)



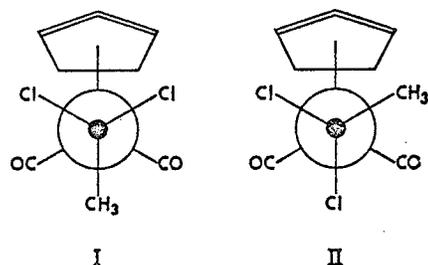
(b)

From the model, it can be seen that with the  $\text{CF}_2\text{:CFCF}_2$ -group and the  $\text{PPh}_3$ -group cis to each other, there is considerable steric hindrance encountered in the free rotation of the  $\text{CF}_2\text{:CFCF}_2\text{-Co}$  system. Rotation about the C-Co bond, (designated X), is prohibited because of the bulky  $\text{PPh}_3$  group. Looking at the C-C bond, (designated Y), it can be seen that the free rotation about this bond is also hindered because of the steric interaction between the carbonyl groups in the equatorial plane and the fluorine atoms of the allyl group, ( $\text{F}_\text{A}$  and  $\text{F}_\text{B}$ ). Several conformers are possible. The steric interaction is considerable when  $\text{F}_\text{A}$  is toward the equatorial plane (diag.a). With  $\text{F}_\text{B}$  towards the carbonyl groups (diag.b), the interaction is maximized. A third conformer is also possible. One of the fluorine atoms of the  $-\text{CF}_2$ -group could be eclipsed by  $\text{F}_\text{A}$ . It is difficult to say which of these conformers is most stable. In addition, any steric interaction between the  $-\text{CF}_2$ -fluorine atoms and the phenyl rings of the  $\text{PPh}_3$  group would lead to a greater steric interaction between  $\text{F}_\text{A}$  or  $\text{F}_\text{B}$  and the equatorial carbonyl groups.

A cis-configuration can also be drawn with the allyl and  $\text{PPh}_3$  groups in equatorial positions. This means the angle between the two ligands would be  $120^\circ$  instead of  $90^\circ$  for the axial-equatorial configuration. However, a molecular model of this structure shows that this rearrangement does little to alleviate the steric interactions.

Only a crystal structure determination could show the configuration of the molecule and the conformation of the allyl ligand.

The presence of conformers of the  $\sigma$ -perfluoroallyl ligand would be expected to alter the C-O absorption band pattern and would account for the shoulder at  $1979.6 \text{ cm}^{-1}$ . Examples of similar systems have been reported. The IR spectrum of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SiCl}_2\text{Me}$  shows four C-O bands where only two were predicted.<sup>(57)</sup> The presence of conformers I and II was used to explain the two extra bands.



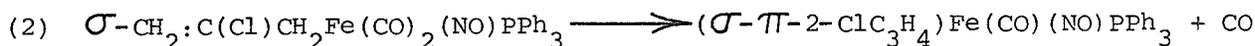
from  
ref. (57)

The IR spectrum of  $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\pi\text{-C}_3\text{H}_5)$  has been explained by the occurrence of conformers of the  $\pi$ -allyl group.<sup>(58)</sup> Some perfluoroalkyl complexes of the type  $(\text{R}_f)_2\text{Fe}(\text{CO})_4$  have given extra bands in the C-O stretching region of the IR spectrum. The extra bands can be explained by the presence of rotamers of the perfluoroalkyl ligands.<sup>(43)</sup>

The  $^{19}\text{F}$  NMR spectrum can be explained by the occurrence of hindered rotation about the C-C single bond. The splitting of the  $\text{CF}_2$  group resonance absorption in freely rotating  $\sigma$ -perfluoroallyl systems is listed in Table II. The spectrum of the hindered system is listed in Table V and shown in Fig. 8. The F-F coupling constants have changed dramatically. It has been shown that vicinal F-F coupling constants change considerably depending on the conformation of the molecule.<sup>(59)</sup> The splitting of the  $\text{CF}_2$  resonance shows this

change and is therefore consistent with some degree of hindered rotation in the perfluoroallyl ligand in cis-CF<sub>2</sub>:CFCF<sub>2</sub>Co(CO)<sub>3</sub>PPh<sub>3</sub>.

It is noteworthy that cis-CF<sub>2</sub>:CFCF<sub>2</sub>Co(CO)<sub>3</sub>PPh<sub>3</sub> did not decarbonylate to form a  $\pi$ -perfluoroallyl complex. Cardaci et al<sup>(60)</sup> have studied the phosphine substitution reaction for the  $\pi$ -allyl complex  $\pi$ -2-chloroallyliron nitrosyl dicarbonyl and have proposed a two step mechanism:



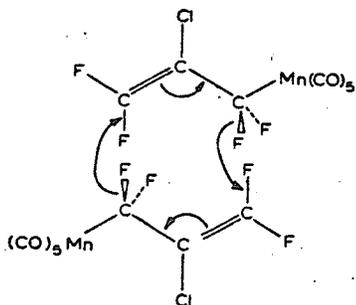
The  $\pi$ -allyl group is forced to reduce its coordination to a  $\sigma$ -bond by the addition of PPh<sub>3</sub> to the iron atom. Then, the  $\sigma$ - $\pi$ -linkage is formed by the nucleophilic attack by the allyl group with the concerted loss of the CO group.

The reaction of PPh<sub>3</sub> with  $\pi$ -C<sub>3</sub>F<sub>5</sub>Co(CO)<sub>3</sub> yielded cis-CF<sub>2</sub>:CFCF<sub>2</sub>Co(CO)<sub>3</sub>PPh<sub>3</sub> as the first step but the second step was not accomplished under moderate conditions. It was observed, however, that on melting the compound at 110°C, a gas, presumably carbon monoxide, was evolved. The resultant product, which probably contained the  $\pi$ -perfluoroallyl ligand, could not be isolated. It can be reasoned that the fluorinated  $\pi$ -allyl group does not possess the electron donating ability to displace a carbonyl group by nucleophilic attack

in a system that has been stabilized by a  $\text{PPh}_3$  group, except under extreme conditions.

This poor coordinating ability of fluoroolefins has been shown by Cramer<sup>(61)</sup> in the exchange of  $\text{CF}_2:\text{CF}_2$  and hydrocarbon olefins, (e.g., propene) with the  $\pi$ -bonded ethylene ligand of acetylacetonate- $\text{Rh}(\pi\text{-CH}_2:\text{CH}_2)_2$ . The hydrocarbon olefins exchange with the ethylene at moderate temperatures, but  $\text{CF}_2:\text{CF}_2$  only begins exchanging at  $100^\circ\text{C}$ . It was reasoned that the  $\sigma$ -donating ability of the incoming group is more important to the development of the transition state for the nucleophilic olefin exchange than is the  $\pi$ -bond formation. This would also be true in comparing the ability of a  $\sigma$ -allyl and  $\sigma$ -perfluoroallyl group to displace a CO group.

It was noted in the introduction that, with the exception of  $\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})\text{CF}_2\text{CF}:\text{CF}_2$ ,  $\sigma$ -perfluoroallyl transition metal complexes have been found to rearrange to  $\sigma$ -perfluoropropenyl derivatives.<sup>(37)</sup> The work of Goldwhite, Rowsell and Valdez<sup>(38)</sup> suggested a bimolecular nucleophilic reaction may be responsible for this rearrangement.



from

ref. (38)

rearrangement transition state

If this is the case, then it could account for the  $\sigma$ -perfluoropropenyl group in trans- $\text{CF}_3\text{CF}:\text{CFCo}(\text{CO})_3\text{PPh}_3$  and the  $\sigma$ -perfluoroallyl group in cis- $\text{CF}_2:\text{CFCF}_2\text{Co}(\text{CO})_3\text{PPh}_3$ . If the phosphine addition reaction to  $\pi\text{-C}_3\text{F}_5\text{Co}(\text{CO})_3$  initially yields a  $\sigma$ -perfluoroallyl group in both the cis and trans complexes, this transition state would only be possible if the  $\sigma$ -allyl group were open to attack. This would be possible in the trans-form. But in the cis-configuration, the bulky  $\text{PPh}_3$  group would prevent the transition state from being attained.

Why the phosphine addition reaction yields both the cis- and trans-configurations is very interesting, but no answer to this question can be given from the experiments carried out here.

SECTION B

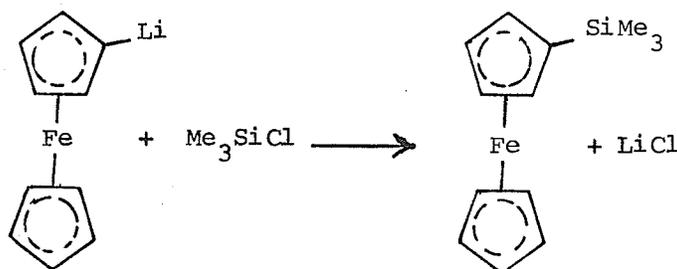
Synthesis of  $\pi$ -2-trimethylsilylallyl Complexes

## Introduction

Group IVB metals, (Si, Ge, Sn and Pb), have been incorporated into many organometallic transition metal complexes with the main emphasis being on the synthesis of metal-metal bonds<sup>(62)</sup> and characterization of the subsequent effects that this bond has on the molecule. An example of this type of complex is:

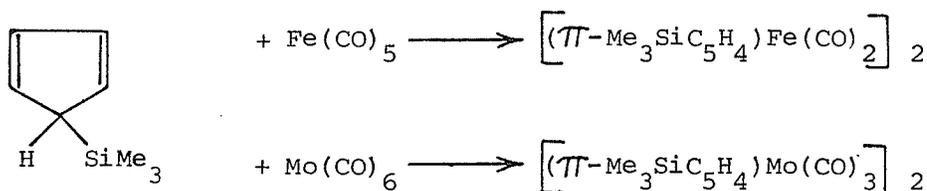
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{ER}_3$ , where E = Si, Ge, Sn or Pb, and R = alkyl, aryl or halogen. At the same time, organic ligands with Group IVB substituents have also received some attention. It was noted by Wozniak et al<sup>(63)</sup> that the complex  $\text{Me}_3\text{SiCH}_2\text{Mn}(\text{CO})_5$  was more thermally stable than the corresponding alkyl complex, due to the inhibition of alkene elimination reactions. Likewise, a series of  $\pi\text{-C}_5\text{H}_5\text{MCH}_2\text{SiMe}_3$  derivatives were synthesized and found to be more stable than the alkyl analogues.<sup>(64)</sup>

Several groups have prepared substituted  $\pi$ -cyclopentadienyl complexes replacing one of the ring protons with an  $\text{ER}_3$  group. Mono and disubstituted ferrocenes were the first to be synthesized.<sup>(65)</sup>



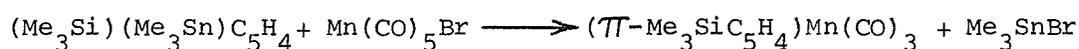
A similar reaction was used to produce the corresponding trialkylgermane compounds. (66)

Recently, more direct methods for preparing some of these substituted cyclopentadienyl complexes have been reported. Kraihanzel and Conville used 5-(trimethylsilyl)cyclopentadiene. (67)



This reaction was later extended to prepare complexes of W, Mn, Re and Co. (68)

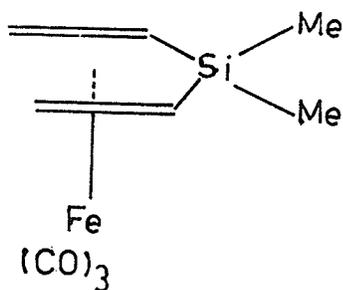
Abel and Moorhouse (69) reacted (trimethylsilyl)(trimethylstannyl)cyclopentadiene with transition metal carbonyl halides to give  $\pi\text{-Me}_3\text{SiC}_5\text{H}_4$  complexes by cleavage of the  $\text{C}_5\text{H}_4\text{-Sn}$  bond, i.e.,



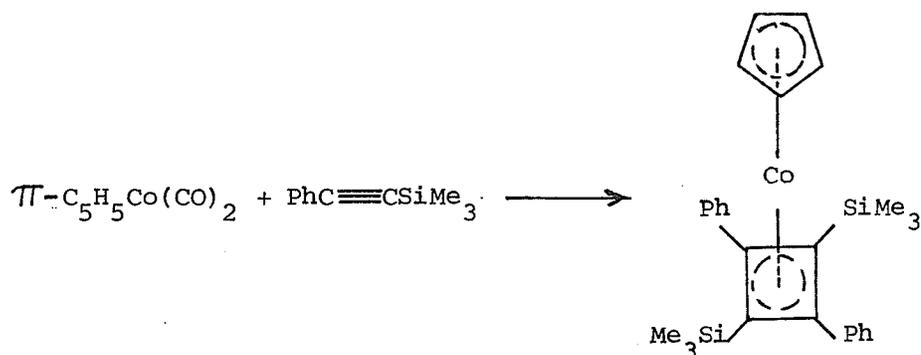
A  $\pi$ -arene complex has also been prepared with a Group IVB substituent. (70)



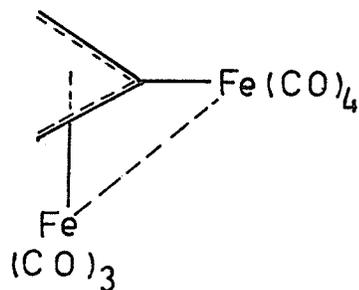
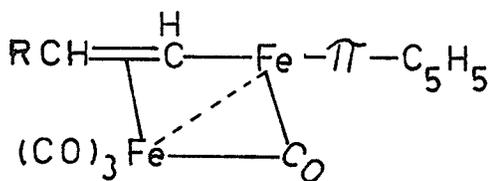
The reactions of vinylmetallics such as  $\text{Me}_3\text{SiCH:CH}_2$  and  $\text{Me}_2\text{Sn}(\text{CH:CH}_2)_2$  have been reported to react with  $\text{CuCl}$  to yield  $\pi$ -complexes.<sup>(71)</sup> Similarly,  $\text{Me}_2\text{Si}(\text{CH:CH}_2)_2$  reacts with  $\text{Fe}_3(\text{CO})_{12}$  to give:<sup>(72)</sup>



Metallated acetylenes also give some substituted  $\pi$ -complexes.<sup>(73)</sup>

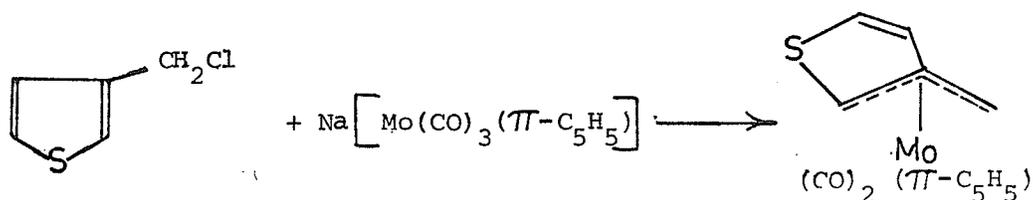
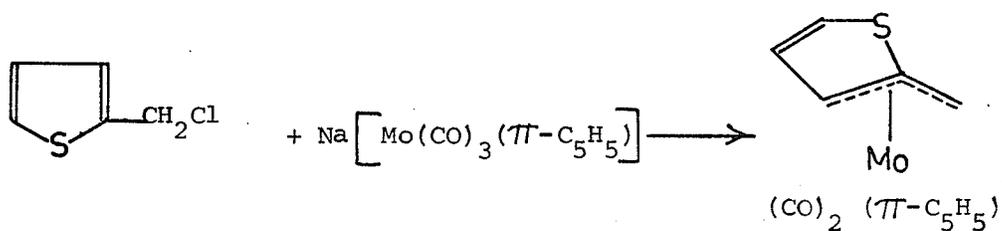


The occurrence of transition metals as substituents in  $\pi$ -complexes has been reported for the compounds:<sup>(74, 75, 76)</sup>



The metallated  $\pi$ -allyl complex above and the general interest in Group IVB metals prompted the research here of trimethylsilyl substituted  $\pi$ -allyl complexes. The synthesis of organo- or halo-substituted  $\pi$ -allyl complexes has been an active field for some time. Substituents such as Cl, Br,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  and  $\text{C}_6\text{H}_5$  have been incorporated into the  $\pi$ -allyl ligand. More recently, allyl complexes containing the substituents hydroxyl, benzoyl, methoxy and acetate have been prepared. The occurrence of syn- and anti-isomers for complexes substituted at the terminal carbon atoms have been studied by NMR. The bulkiness of the substituent often prohibits formation of the anti-isomer, although a complex with the bulky tertiary-butyl group in the anti-position was recently isolated. (77)

King and Kapoor have isolated some sulphur-substituted  $\pi$ -allyl complexes from the reactions: (78)



The work presented here details the preparation of several  $\pi$ -allyl complexes where the proton on the central carbon atom has been substituted by a trimethylsilyl group.

Experimental

Propargyl chloride ( $\text{CH}\equiv\text{CCH}_2\text{Cl}$ ),  $\text{Fe}(\text{CO})_5$  and  $\text{Ni}(\text{CO})_4$  were obtained from commercial sources and were used without further purification.  $\text{Hg}\left[\text{Co}(\text{CO})_4\right]_2$  was prepared by the method described by Brauer.<sup>(41)</sup>

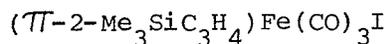
2-Trimethylsilyl-3-chloropropene,  $(\text{CH}_2:\text{C}(\text{SiMe}_3)\text{CH}_2\text{Cl})$ 

Following the procedure reported by Miranov,<sup>(79)</sup> 15 g, (0.21 mol) propargyl chloride, and 17 g, (0.23 mol) trimethylsilane, ( $\text{Me}_3\text{SiH}$ ), were mixed at  $-80^\circ\text{C}$  under  $\text{N}_2$  in a 100 ml flask equipped with a magnetic stirrer and a dry ice condenser. The catalyst,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , (0.2 g in 1 ml isopropanol), was added and the mixture was allowed to warm slowly at a rate that produced gentle refluxing. After 20 minutes the contents reached room temperature, at which time the dry ice condenser was replaced by a water cooled condenser. The flask was warmed until the contents reached a temperature of  $130^\circ\text{C}$  and then allowed to cool. The mixture was fractionally distilled, and the  $142^\circ\text{C}$  fraction collected. The yield was 95%. The mass spectrum showed the molecular ion at  $m/e$  148 ( $\text{CH}_2:\text{C}(\text{SiMe}_3)\text{CH}_2^{35}\text{Cl}$ ) and  $m/e$  150 ( $\text{CH}_2:\text{C}(\text{SiMe}_3)\text{CH}_2^{37}\text{Cl}$ ).

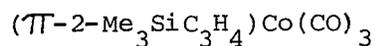
2-Trimethylsilyl-3-iodopropene,  $\text{CH}_2:\text{C}(\text{SiMe}_3)\text{CH}_2\text{I}$ 

$\text{CH}_2:\text{C}(\text{SiMe}_3)\text{CH}_2\text{Cl}$ , (20 g, 0.13 mol), was added to an excess of  $\text{NaI}$  (40 g, 0.26 mol), in dry acetone (200 ml), and stirred occasionally for a period of one week. The precipitated  $\text{NaCl}$  was filtered off and the solution was added to 1500 ml  $\text{H}_2\text{O}$ . The product

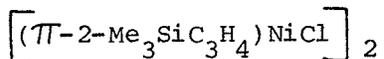
separated from the H<sub>2</sub>O-acetone mixture and was fractionally distilled at reduced pressure (1 mm). The yield was 50%. The mass spectrum showed the parent ion at m/e 240.



CH<sub>2</sub>:C(SiMe<sub>3</sub>)CH<sub>2</sub>I, (5 g, 21 mmol), and Fe(CO)<sub>5</sub> (7g, 36 mmol) were heated in 40 ml hexane for 48 hours at 40°C under N<sub>2</sub>. The hexane and unreacted Fe(CO)<sub>5</sub> were removed in vacuo and the non-volatile solid crystallized from boiling hexane. Gold-brown crystals with mp 103°C (decomposition) were isolated in 60% yield.

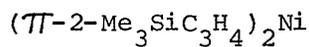


CH<sub>2</sub>:C(SiMe<sub>3</sub>)CH<sub>2</sub>Cl, (0.9 g, 6 mmol), was added to NaCo(CO)<sub>4</sub> (6 mmol) (prepared by stirring 1.5 g Hg [Co(CO)<sub>4</sub>]<sub>2</sub> in 100 ml THF with excess Na/Hg) under N<sub>2</sub>. After stirring for one hour the THF was removed in vacuo at -30°C, and the product was distilled into the vacuum trapping system. After several trap to trap fractional distillations, the yield was 55%. The melting point of the product was 5°C. Pure samples for spectral analysis were prepared by crystallization from pentane at -80°C.



Ni(CO)<sub>4</sub>, (4 g, 25 mmol), and CH<sub>2</sub>:C(SiMe<sub>3</sub>)CH<sub>2</sub>Cl (3.2 g, 21 mmol), were refluxed under N<sub>2</sub> in 40 ml hexane until CO evolution

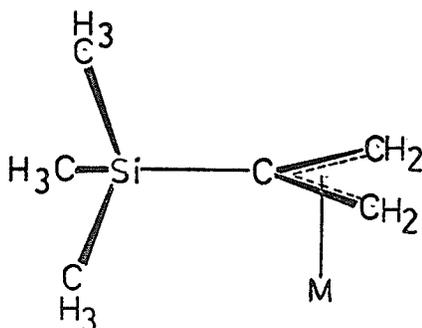
had ceased. Cooling the solution to  $-80^{\circ}\text{C}$  yielded dark orange crystals from the deep red solution. After three recrystallizations from pentane at  $-80^{\circ}\text{C}$ , pure product was obtained. The product was extremely air sensitive in solution; moderately so in the crystalline form.



To 1 g  $\left[(\pi\text{-}2\text{-Me}_3\text{SiC}_3\text{H}_4)\text{NiCl}\right]_2$  was added an excess of  $\text{C}_3\text{H}_5\text{MgCl}$  in ether at  $-20^{\circ}\text{C}$  under  $\text{N}_2$ . After stirring for one hour, the solution was warmed to room temperature and the ether removed in vacuo. Extraction with pentane yielded a yellow solution. The pentane was removed in vacuo at  $-80^{\circ}\text{C}$ . The products were distilled into the trapping network at  $50^{\circ}\text{C}$ . Repeated distillation at 0.1 mm separated a very volatile component, (which was identified as  $(\pi\text{-C}_3\text{H}_5)_2\text{Ni}$  by NMR and mass spectra), from the less volatile product. The latter compound was a yellow solid which melted at  $45^{\circ}\text{C}$  and was moderately air-stable. Conventional analysis was not possible due to partial decomposition to a white powder after one or two days under vacuum. A high resolution mass spectrum of the molecular ion  $m/e$  284 showed elemental composition  $\text{C}_{12}\text{H}_{26}\text{Si}_2\text{Ni}$ , (measured  $m/e$  284.0912 calculated  $m/e$  284.0919). Yield 15%

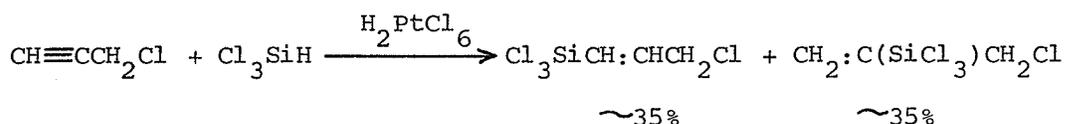
## Results and Discussion

The compounds synthesized here constitute the first  $\pi$ -allyl complexes where one of the protons has been replaced with a Group IVB metal substituent.



$\pi$ -2-trimethylsilylallyl ligand ( $\pi$ -2-Me<sub>3</sub>SiC<sub>3</sub>H<sub>4</sub>)

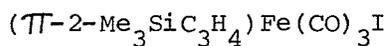
The preparation of the starting compound, CH<sub>2</sub>:C(SiMe<sub>3</sub>)CH<sub>2</sub>Cl, was carried out following the method of Miranov.<sup>(79)</sup> Miranov reported that the addition of Cl<sub>3</sub>SiH or MeCl<sub>2</sub>SiH to propargyl chloride resulted in two isomers being produced in approximately equal yields:



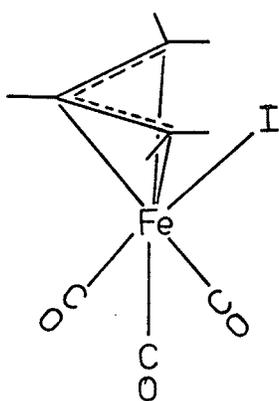
In the reaction performed here, Me<sub>3</sub>SiH was added to propargyl chloride to give only the 2-substituted product identified by the <sup>1</sup>H NMR spectrum (TMS standard):  $\delta_{\text{CH}_3} = 0.28$  (singlet),  $\delta_{\text{CH}_2\text{Cl}} = 4.09$  (doublet with  $J = 1$  Hz),  $\delta_{\text{CH}_2} = 5.43$  (doublet with  $J = 2$  Hz), and 5.90 (multiplet), integration 9:2:1:1. The compound was identical to that prepared by Miranov:<sup>(79)</sup>



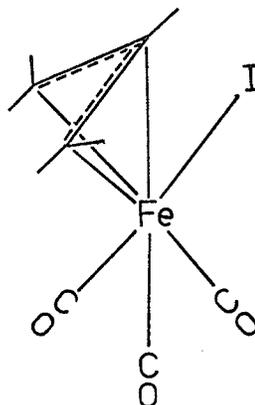
All the reactions described in the Experimental section are similar to the methods reported for the syntheses of the unsubstituted  $\pi$ -allyl derivatives. Elemental analyses were not performed on the new compounds because of the low stability but the identification by IR, NMR and mass spectra was definitive, (Table VI).



The IR and NMR spectra are easily interpreted and do not show the existence of rotamers due to the  $\pi$ -allyl group as was proposed by Nesmeyanov et al<sup>(15)</sup> for  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$ .



(a)

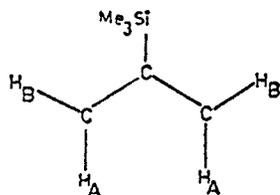


(b)

The silylated derivative probably exists in the (a)-form, (less steric hindrance), as was proposed for the 2-methyl and 2-bromo derivatives.

In an attempt to synthesize the mixed  $\pi$ -allyl complex  $(\pi\text{-}2\text{-Me}_3\text{SiC}_3\text{H}_4)(\pi\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_2$ , the two reactions below were performed. The only product isolated was the well characterized  $(\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_2$ .

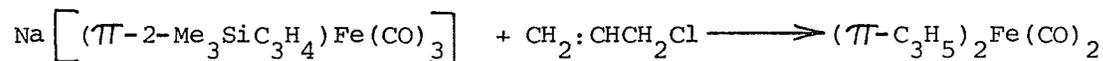
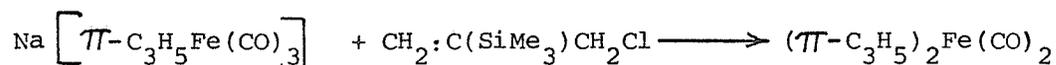
TABLE VI

IR and NMR Spectra<sup>(a)</sup> for  $\pi$ -2-trimethylsilylallyl Complexes

Complex	$\nu(\text{CO}) \text{ cm}^{-1}$	$\delta^{(b)}_{\text{SiMe}_3}$	$\delta_{\text{A}}$	$\delta_{\text{B}}$
$(\pi\text{-2-Me}_3\text{SiC}_3\text{H}_4)\text{Fe}(\text{CO})_3\text{I}$	2074 (s) <sup>(c)</sup>	-0.08	3.57	3.92
	2028 (s)			
	1993 (m)			
$(\pi\text{-2-Me}_3\text{SiC}_3\text{H}_4)\text{Co}(\text{CO})_3$	2067 (m)	0.21	2.19	3.01
	2002 (s)			
	2000 (s)			
$[(\pi\text{-2-Me}_3\text{SiC}_3\text{H}_4)\text{NiCl}]_2$		0.45	2.10	2.98
$(\pi\text{-2-Me}_3\text{SiC}_3\text{H}_4)_2\text{Ni}$		0.02	1.74	3.84

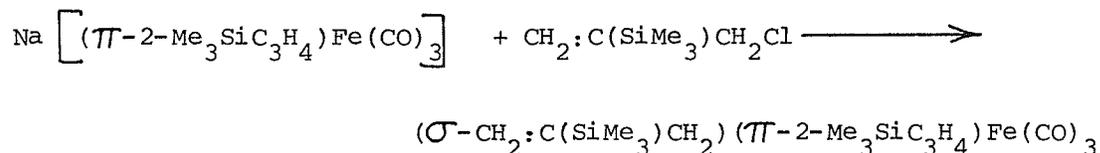
(a) Pentane solutions for IR;  $\text{CDCl}_3$  solutions for NMR (5% TMS)(b)  $\delta$  values in ppm downfield from TMS; all resonance absorptions were singlets

(c) Abbreviations: (s) strong, (m) medium

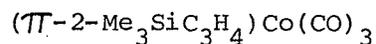


The sodium salt of  $(\pi\text{-2-Me}_3\text{SiC}_3\text{H}_4)\text{Fe}(\text{CO})_3^-$  was prepared in THF by stirring with excess sodium amalgam. The reaction went smoothly to a green-coloured solution, but no attempt was made to characterize the anion.

The reaction below was performed in an attempt to synthesize  $(\pi\text{-2-Me}_3\text{SiC}_3\text{H}_4)_2\text{Fe}(\text{CO})_2$ . The product, however, would not decarbonylate to the desired compound.



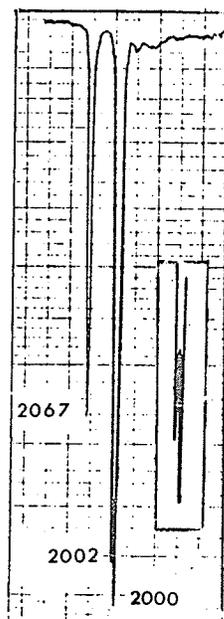
The product was isolated by sublimation, (0.01 mm), in 5% yield. The mass spectrum showed the parent ion at  $m/e$  253 with the successive loss of three CO groups. The IR spectrum showed three C-O absorption bands, ( $\text{cm}^{-1}$ ): 1959 (s), 1975 (vs) and 2040 (s), (in pentane). An elemental analysis or NMR were not possible because of the small amount of product obtained. Without these, the identification could not be considered conclusive.



The volatility and thermal stability of this complex are similar to those of  $\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$ . The IR spectrum, (Table VI), however, shows 3 C-O absorption bands while  $\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$  shows

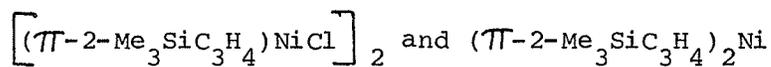
only two at  $2056\text{ cm}^{-1}$ , ( $A_1$  mode), and  $2001\text{ cm}^{-1}$ , (E mode).<sup>(52)</sup>

The  $\text{Me}_3\text{Si}$ -group with the methyl groups pointing towards the carbonyl groups causes the E mode to be split, (see Fig.9), due to the reduced local symmetry of the carbonyl groups.



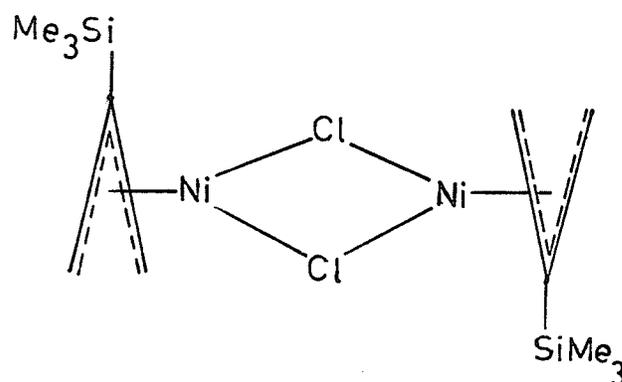
**Figure 9** IR carbonyl absorption bands of  $(\pi\text{-}2\text{-Me}_3\text{SiC}_3\text{H}_4)\text{Co}(\text{CO})_3$   
(insert showing E mode splitting)

In the reported spectra of other 2-substituted  $\pi$ -allyl cobalt tri-carbonyl complexes, it is seen that not even the bulky phenyl group causes this splitting.<sup>(81)</sup> Also, the compounds  $(\pi\text{-R}_3\text{SnC}_6\text{H}_5)\text{Mo}(\text{CO})_3$ <sup>(70)</sup> and  $(\pi\text{-SiR}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ <sup>(69)</sup> do not show any splitting of the E mode.

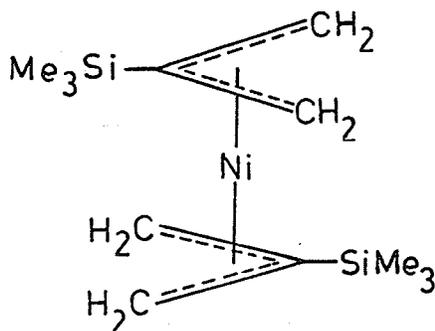


These complexes can exist as cis- and trans-isomers as has been seen in their  $\pi$ -allyl analogues.<sup>(2, 16)</sup> The NMR spectra, however, show that only one isomer is present. No changes in the spectra were

observed from  $-65^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$  and isomerization would seem to be prohibited by the bulky substituent. The configuration of the chlorine-bridged dimer can either be cis or trans because in both cases the steric interactions between the two  $\pi$ -allyl groups would be small, and at  $-65^{\circ}\text{C}$  the interconversion could still be occurring. However, in the crystal, the trans-configuration would be preferred as in trans  $[\pi\text{-C}_3\text{H}_5\text{PdCl}]_2$ .<sup>(82)</sup>



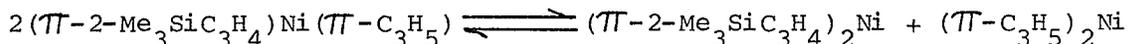
For  $(\pi\text{-2-Me}_3\text{SiC}_3\text{H}_4)_2\text{Ni}$ , the arrangement is most surely trans, (as in  $(\pi\text{-2-MeC}_3\text{H}_4)_2\text{Ni}$ <sup>(83)</sup>), because of the extreme steric interaction expected for the cis-configuration.



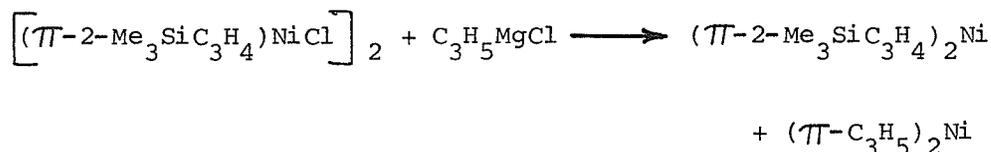
The stability of  $(\pi\text{-C}_3\text{H}_5)_2\text{Ni}$  is such that the compound decomposes completely in vacuum at room temperature in a few hours. It ignites in air.  $(\pi\text{-2-Me}_3\text{SiC}_3\text{H}_4)_2\text{Ni}$ , however, is stable for several days in vacuo but eventually decomposes to a white powder. It is stable in air for several hours.

The attempt to synthesize the mixed complex  $(\pi\text{-2-Me}_3\text{SiC}_3\text{H}_4)\text{Ni}(\pi\text{-C}_3\text{H}_5)$  was not successful, and only the two isoleptic complexes were isolated,  $(\pi\text{-C}_3\text{H}_5)_2\text{Ni}$  and  $(\pi\text{-2-Me}_3\text{SiC}_3\text{H}_4)_2\text{Ni}$ . Some evidence that the mixed complex was present in the product mixture was observed when the products were distilled in vacuo.

$(\pi\text{-C}_3\text{H}_5)_2\text{Ni}$  was very volatile at room temperature, while  $(\pi\text{-2-Me}_3\text{SiC}_3\text{H}_4)_2\text{Ni}$  was sublimed at  $+50^\circ\text{C}$ . But in the distillation of the mixture at room temperature, a considerable amount of the heavier product co-distilled with the lighter compound. This suggests that the heavy compound was carried along by the more volatile component, or that an equilibrium reaction was occurring in the mixture:



This follows from the experimental observations:



It seems likely that the mixed complex would be sufficiently volatile to move easily in the trapping system at 0.01 mm. The mixed complex was not observed in the NMR or mass spectra of the product mixture and must exist in small concentration.

### Mass Spectra

In Tables VII to X are listed the mass spectra of the  $\pi$ -2-trimethylsilylallyl complexes prepared. The spectra were recorded initially to observe the parent ion. The mass spectra of  $\pi$ -allyl complexes has been studied by Nesmeyanov et al (84) and reviewed briefly by Bruce. (85) The important feature of the mass spectra of these complexes is the migration of the  $\text{Me}_3\text{Si}$ -group from the allyl moiety to the metal with the loss of the  $\text{C}_3\text{H}_4$ , (allene), fragment. The migration of a  $\text{Me}_3\text{Si}$ - group has been discussed by Bruce for organic compounds. (85) For transition metal complexes, it was reported that  $(\pi\text{-Me}_3\text{SnC}_6\text{H}_8)\text{Cr}(\text{CO})_3$  shows a  $\text{SnCr}^+$  fragment. (70)

Of the four complexes studied here, only the cobalt derivative does not show the  $\text{Me}_3\text{Si}$  migration. Also, the parent ion is not observed and  $[\text{P-CO}]^+$  was the highest mass ion recorded.

The  $m/e$  values of fragments containing nickel, chlorine and silicon are spread over several mass numbers because of the naturally occurring isotopes of these elements. This is an advantage, because the fragments containing one or more of these elements have a very characteristic pattern. The  $m/e$  values quoted are based on  $^{58}\text{Ni}$ , (67.9% natural isotopic abundance),  $^{35}\text{Cl}$ , (75.4% natural isotopic abundance), and  $^{28}\text{Si}$ , (92.2% natural isotopic abundance.)

TABLE VIIMass Spectrum of  $(\pi\text{-}2\text{-Me}_3\text{SiC}_3\text{H}_4)\text{Fe}(\text{CO})_3\text{I}$ 

m/e	Intensity	Ion Fragment
380	0.3	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Fe}(\text{CO})_3\text{I}$
252	0.1	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Fe}(\text{CO})_2\text{I}$
324	3.7	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Fe}(\text{CO})\text{I}$
309	0.3	$\text{Me}_2\text{SiC}_3\text{H}_4\text{Fe}(\text{CO})\text{I}$
296	7.0	$\text{Me}_3\text{SiC}_3\text{H}_4\text{FeI}$
281	0.5	$\text{Me}_2\text{SiC}_3\text{H}_4\text{FeI}$
256	5.5	$\text{Me}_3\text{SiFeI}$
241	0.7	$\text{Me}_2\text{SiFeI}$
225	3.7	$\text{CH}_2\text{SiFeI}$
211	2.3	$\text{SiFeI}$
197	5.5	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Fe}(\text{CO})$
193	9.3	$\text{Fe-I}$
169	17.1	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Fe}$
73	100.0	$\text{Me}_3\text{Si}$

TABLE VIII

Mass Spectrum of  $(\pi\text{-}2\text{-Me}_3\text{SiC}_3\text{H}_4)\text{Co}(\text{CO})_3$ 

m/e	Intensity	Ion Fragment
228	2.69	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Co}(\text{CO})_2$
200	4.2	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Co}(\text{CO})$
185	0.9	$\text{Me}_2\text{SiC}_3\text{H}_4\text{Co}(\text{CO})$
172	9.1	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Co}$
113	21.0	$\text{Me}_3\text{SiC}_3\text{H}_4$
73	100.0	$\text{Me}_3\text{Si}$
59	28.0	Co

TABLE IX

Mass Spectrum of  $[(\pi\text{-}2\text{-Me}_3\text{SiC}_3\text{H}_4)\text{NiCl}]_2$ 

m/e	Intensity	Ion Fragment
412	0.36	$[\text{Me}_3\text{SiC}_3\text{H}_4\text{NiCl}]_2$
372	0.04	$\text{Me}_3\text{SiC}_3\text{H}_4\text{NiCl}_2\text{NiSiMe}_3$
304	1.0	$\text{Me}_3\text{SiC}_3\text{H}_4\text{NiClNiC}_3\text{H}_4$
264	5.3	$\text{Me}_3\text{SiC}_3\text{H}_4\text{NiClNi}$
113	20.5	$\text{Me}_3\text{SiC}_3\text{H}_4$
73	100.0	$\text{Me}_3\text{Si}$

TABLE X

Mass Spectrum of  $(\pi\text{-}2\text{-Me}_3\text{SiC}_3\text{H}_4)_2\text{Ni}$

m/e	Intensity	Ion Fragment
284	10.3	$(\text{Me}_3\text{SiC}_3\text{H}_4)_2\text{Ni}$
244	7.9	$\text{Me}_3\text{SiC}_3\text{H}_4\text{NiSiMe}_3$
228	3.8	$\text{CH}_2\text{MeSiC}_3\text{H}_4\text{NiSiMe}_3^*$
186	16.4	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Ni-Me}$
170	17.8	$\text{CH}_2\text{MeSiC}_3\text{H}_4\text{Ni-Me}^*$
156	12.3	$\text{MeSiC}_3\text{H}_4\text{NiMe}^*$
130	100.0	$\text{CH}_2\text{MeSiNi-Me}^*$
116	24.6	$\text{MeSiNiMe}^*$
73	43.8	$\text{Me}_3\text{Si}$

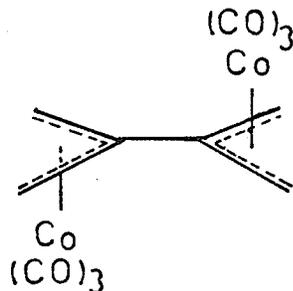
\* - These formulae are not necessarily meant to be ion structures but only represent the elemental composition.

SECTION C

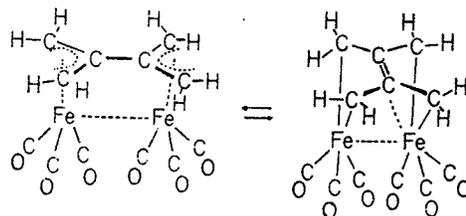
Synthesis and Reactions of (bi- $\pi$ -allyl)dicobalt Hexacarbonyl.

## Introduction

In the attempt to study the reactivity of the chlorine atom in  $\pi$ -2-chloro-allylcobalt tricarbonyl, the new compound (bi- $\pi$ -allyl)-dicobalt hexacarbonyl was prepared.



Only a few compounds with the bi- $\pi$ -allyl ligand have been reported. The first compound to incorporate this ligand was  $(C_3H_4)_2Fe_2(CO)_6$  in which valence tautomers were postulated to explain the NMR spectrum. (86)

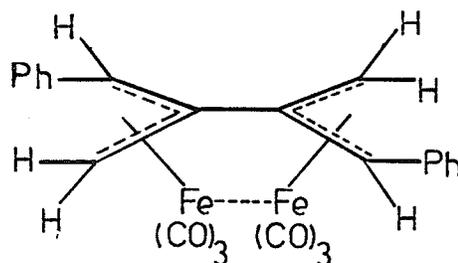


from

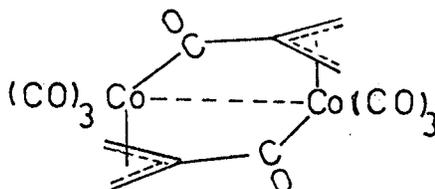
Ref. (86)

This compound was prepared later in greater yield by Pettit and Ben-Shoshan in the reaction of allene with  $Fe_2(CO)_9$ . (75) The

reaction between 1-phenylallene and  $\text{Fe}_2(\text{CO})_9$  was reported to give a substituted bi- $\pi$ -allyl complex.<sup>(87)</sup>



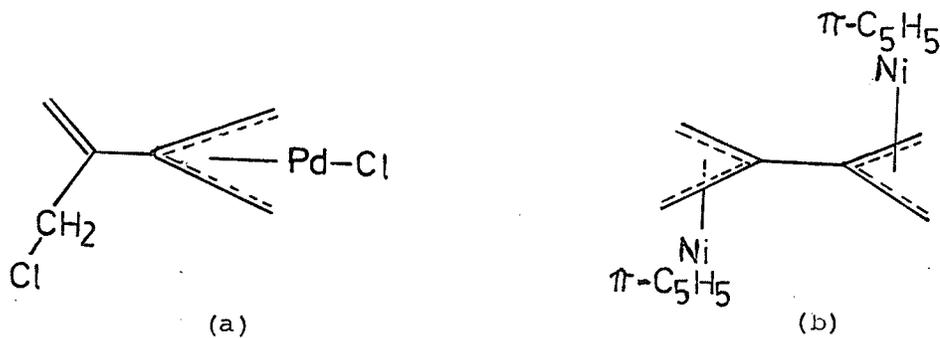
In a reaction, analogous to the bi- $\pi$ -allyl iron complex syntheses, gaseous allene was reacted with  $\text{Co}_2(\text{CO})_8$ , (in benzene), to give a complex reported as:<sup>(88)</sup>



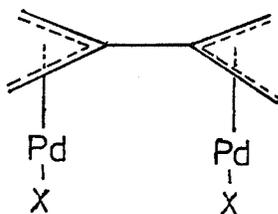
This complex was reported to react with triphenylphosphine to yield a stable compound, but the spectral details of the product were not given.

The reaction of the  $\pi$ -allyl palladium complex, (diagram a), with bis(1,5-cyclooctadiene)nickel followed by reaction with  $\text{NaC}_5\text{H}_5$

yielded a complex<sup>(89)</sup> which was identified by an x-ray crystal structure analysis<sup>(90)</sup> to be:  $(\text{bi-}\pi\text{-allyl})(\text{Ni-}\pi\text{-C}_5\text{H}_5)_2$ ,  
(diagram b).



Hughes and Powell prepared a series of bi- $\pi$ -allyl palladium complexes.<sup>(91)</sup>

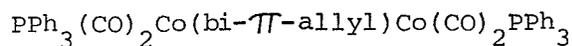


where X = acetylacetonate, Cl or  $\pi\text{-C}_5\text{H}_5$ .

## Experimental

### Synthesis of (2,2'-bi- $\pi$ -allyl)dicobalt Hexacarbonyl

Equimolar amounts (1.9 mmol) of  $\text{NaCo}(\text{CO})_4$  and 2,3-dichloropropene,  $(\text{CH}_2:\text{CClCH}_2\text{Cl})$  were reacted in refluxing THF under  $\text{N}_2$  for three hours. THF and the major product  $(\pi\text{-}2\text{-ClC}_3\text{H}_4)\text{Co}(\text{CO})_3$ , (synthesized previously by McClellan *et al*<sup>(92)</sup>), were removed in vacuo, (0.01 mm). The remaining solid was extracted with pentane and chromatographed on Florisil. Some unidentified products and  $\text{Co}_4(\text{CO})_{12}$ , (identified by IR and mass spectra), were eluted with pentane. A yellow band which did not move with pentane was eluted with methylene chloride. This fraction was collected under  $\text{N}_2$ . The  $\text{CH}_2\text{Cl}_2$  was removed in vacuo and the product was recrystallized several times from pentane at  $-80^\circ\text{C}$ . The pentane was removed from the crystals at  $-80^\circ\text{C}$  in vacuo and the product sealed in a tube under vacuum, (yield 10%). In this state, the product was stable indefinitely. In a dynamic vacuum, at  $25^\circ\text{C}$ , decomposition was complete in two to three hours. The product in solid form or in solution was unstable to air. Sublimation at  $75^\circ\text{C}$  (0.01 mm), was accompanied by extensive decomposition. A high resolution mass spectrum indicated the formula to be  $\text{C}_{12}\text{H}_8\text{O}_6\text{Co}_2$ , measured m/e 365.8996, calculated m/e 365.8984. Conventional elemental analysis was not possible due to impurities incurred during the isolation.

Synthesis of(2,2'-bi- $\pi$ -allyl)dicobalt Tetracarbonyl Bis(triphenylphosphine)

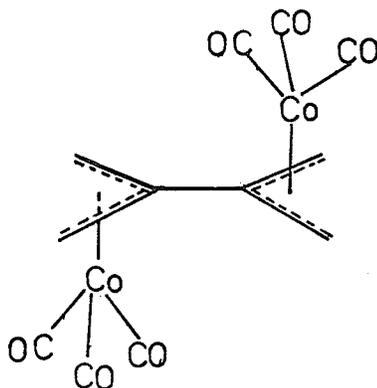
Approximately 2 mmol (bi- $\pi$ -allyl) $\text{Co}_2(\text{CO})_6$  and 4 mmol  $\text{PPh}_3$  were stirred in  $\text{CH}_2\text{Cl}_2$  under  $\text{N}_2$  at room temperature until CO evolution had ceased. On removal of the solvent, an orange, air stable solid was recovered and crystallized from benzene-hexane, (mp (decomposition) 140-143°C). Yield 98%. Elemental analysis calculated for  $\text{C}_{16}\text{H}_{18}\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$ : C 66.22%, H 4.55%, P 7.42% found: C 66.24%, H 4.54%, P 7.27%.

Reaction of (bi- $\pi$ -allyl)Cobalt Compounds with Bromine

The bi- $\pi$ -allyl complex was added to a large excess of bromine in carbon tetrachloride. Carbon monoxide was evolved and the solution turned green. The  $\text{CCl}_4$  and unreacted  $\text{Br}_2$  were removed under vacuum, (0.1 mm). Pentane was added to the solid and the insoluble material filtered off. The pentane was removed in vacuo, leaving a yellowish solid which was recrystallized twice from boiling hexane. A white, air stable, crystalline solid was isolated with mp 132-134°C. Elemental analysis calculated for  $\text{C}_7\text{H}_8\text{Br}_6\text{O}$ : C 14.31%, H 1.37%, Br 81.59%, found: C 14.45%, H 1.40%, Br 81.65%. Both bi- $\pi$ -allyl  $\text{Co}_2(\text{CO})_6$  and the phosphine derivative gave the same product upon bromination in this manner.

## Results and Discussion

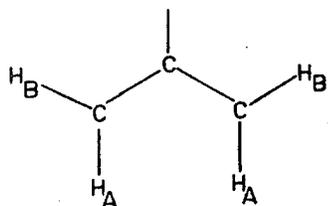
The minor product of the reaction of  $\text{CH}_2:\text{CClCH}_2\text{Cl}$  with  $\text{Na}[\text{Co}(\text{CO})_4]$  was determined by IR, NMR and mass spectra, (Table XI), to be the bi- $\pi$ -allyl complex:



An elemental analysis was not possible for this compound because of the unstable nature of the molecule in vacuum at a temperature high enough to ensure complete removal of the solvent used for recrystallization. The high resolution mass spectrum showed the molecular ion at  $m/e$  365.8996, (calculated for  $\text{C}_6\text{H}_8\text{Co}_2(\text{CO})_6$   $m/e$  365.8984), which corresponds to the structure proposed.

The IR spectrum (Fig. 10) shows three strong C-O absorption bands. This pattern corresponds to a lowering of the carbonyl symmetry ( $\text{C}_{3v}$ ) so that the E mode is split. This was shown for  $(\pi\text{-}2\text{-Me}_3\text{SiC}_3\text{H}_4)\text{Co}(\text{CO})_3$  but to a smaller degree.

TABLE XI

IR and NMR Spectra <sup>(a)</sup> of bi- $\pi$ -allyl Complexes

Complex	$\nu(\text{CO}) \text{ cm}^{-1}$	$\delta_A^{(b)}$	$\delta_B$			
$\pi\text{-C}_6\text{H}_8\text{Co}_2(\text{CO})_6$	2012 (vs) <sup>(c)</sup>	2.35	3.65			
	2023 (vs)					
	2072 (vs)					
$\pi\text{-C}_6\text{H}_8\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$	1949 (vs)	1.52 (d)	3.09 (d)	$\delta_{\text{Ph}}$ 7.37 (m)	$J_{A,P}$ 5 Hz	$J_{B,P}$ 3.5 Hz
	2001 (s)					

(a) Pentane solution for IR;  $\text{CDCl}_3$  solution for NMR, (5% TMS)(b)  $\delta$  values in ppm downfield from TMS

(c) Abbreviations: (vs) very strong, (s) strong, (d) doublet, (m) multiplet

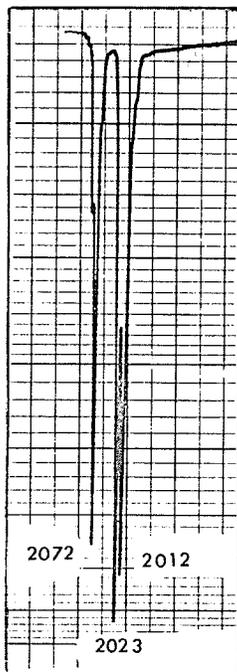


Figure 10 IR carbonyl absorption bands of  $(\text{bi-}\pi\text{-allyl})\text{Co}_2(\text{CO})_6$

The  $^1\text{H}$  NMR spectrum, (Table XI), shows only two resonance absorptions with no syn-anti coupling ( $J_{\text{A,B}}$ ) being observed. The NMR spectrum was not temperature-dependent in the range  $-50^\circ\text{C}$  to  $+60^\circ\text{C}$ . From the NMR, therefore, it is not possible to say whether or not there is free rotation about the  $\text{C}_2\text{-C}_2$  bond. The crystal structures of  $(\text{bi-}\pi\text{-allyl})\text{Ni}_2(\pi\text{-C}_5\text{H}_5)_2$ <sup>(90)</sup> and  $(\text{biphenyl})\text{Cr}_2(\text{CO})_6$ <sup>(93)</sup> show that the trans-configuration is preferred for these molecules in the crystalline state, where metal-metal or ligand-metal bonding does not constrain the molecule to the cis-configuration. At present, however, it is not possible to estimate the degree of rotation about the  $\text{C}_2\text{-C}_2$  bond for the molecule in solution.

The mass spectrum, (Table XII), shows an interesting feature that has been observed previously by Lupin and Cais<sup>(94)</sup> for some  $\pi$ -allyl complexes of rhodium and palladium. After the loss of

the fifth and sixth carbonyl groups, the presence of relatively intense peaks at  $m/e$  224 and 196 indicates the cyclopropenyl group attached to the cobalt. The loss of two hydrogens from one of the  $\pi$ -allyl groups gives the 2,2'-allyl-cyclopropenyl ligand, or the loss of one hydrogen from each  $\pi$ -allyl group would give the bi-cyclopropene ligand. It cannot be determined which of these two fragmentations occurs.

TABLE XII

Mass spectrum of (bi- $\pi$ -allyl) $\text{Co}_2(\text{CO})_6$

$m/e$	intensity	Ion Fragment
366	8	$\text{C}_6\text{H}_8\text{Co}_2(\text{CO})_6$
338	12	$\text{C}_6\text{H}_8\text{Co}_2(\text{CO})_5$
310	18	$\text{C}_6\text{H}_8\text{Co}_2(\text{CO})_4$
282	9	$\text{C}_6\text{H}_8\text{Co}_2(\text{CO})_3$
254	27	$\text{C}_6\text{H}_8\text{Co}_2(\text{CO})_2$
226	100	$\text{C}_6\text{H}_8\text{Co}_2(\text{CO})$
224	15	$\text{C}_6\text{H}_6\text{Co}_2(\text{CO})^*$
198	12	$\text{C}_6\text{H}_8\text{Co}_2$
196	25	$\text{C}_6\text{H}_6\text{Co}_2^*$
137	35	$\text{C}_6\text{H}_6\text{Co}$
118	100	$\text{Co}_2$
87	34	$\text{Co}(\text{CO})$
59	60	$\text{Co}$

\* - ion formula of the fragment containing the allyl-cyclopropenyl or bi-cyclopropene ligand

### Phosphine Substitution

The reaction of triphenylphosphine with (bi- $\pi$ -allyl)dicobalt hexacarbonyl leaves the bi- $\pi$ -allyl ligand intact and two carbonyl groups, (one from each cobalt), are replaced by two  $\text{PPh}_3$  groups to give the complex  $(\text{PPh}_3)_2(\text{CO})_2\text{Co}(\text{bi-}\pi\text{-allyl})\text{Co}(\text{CO})_2(\text{PPh}_3)_2$ . Carbon monoxide is evolved and no acyl or bridging C-O absorptions are observed in the IR spectrum. The C-O stretching region of the spectrum, (Fig. 11), shows two main absorption bands with two weak bands. The weak bands may indicate the presence of isomers or rotamers but this was not investigated further. Recrystallization of the compound did not change the IR spectrum.

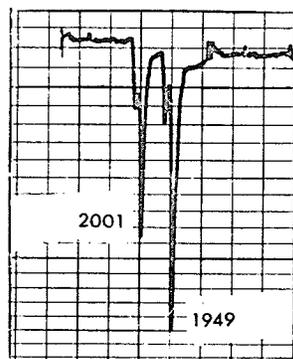
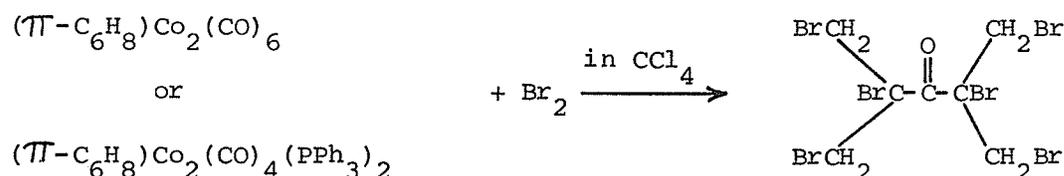


Figure 11 IR carbonyl absorption bands of  $(\text{bi-}\pi\text{-allyl})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$

### Bromination

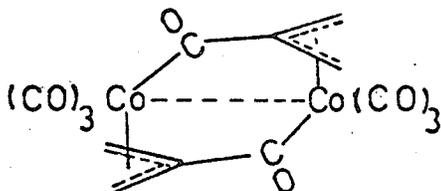
The reaction of excess bromine (in  $\text{CCl}_4$ ) with (bi- $\pi$ -allyl)-dicobalt hexacarbonyl or the phosphine-substituted complex gave a highly brominated ketone.



The bromination was initially performed in order to show the structure of the bi- $\pi$ -allyl ligand as was done with (bi- $\pi$ -allyl)- $\text{Fe}_2(\text{CO})_6$ .<sup>(86)</sup> The ketonic product, however, was unexpected. The product was a white crystalline solid which shows a very intense ketonic carbonyl absorption at  $1710 \text{ cm}^{-1}$  in the IR spectrum. The NMR spectrum ( $\text{CCl}_4$  solution) shows an AB system (quartet 1:3:3:1) centered at  $\delta = 4.25 \text{ ppm}$ . The methylene protons are magnetically non-equivalent because of the intrinsically asymmetric environment of the two protons<sup>(113)</sup>. An analysis of the AB system gives  $J = 11.4 \text{ Hz}$ . and  $\Delta\delta = 0.35 \text{ ppm}$ . for the two different protons. The mass spectrum had a parent ion at  $m/e$  582, (based on  $^{79}\text{Br}$ , 50.57% natural isotopic abundance), with the correct isotopic abundance pattern for six bromine atoms. The main fragmentation ions are  $(\text{CH}_2\text{Br})_2\text{CBr}^+$  and  $(\text{CH}_2\text{Br})_2\text{C}(\text{Br})\text{CO}^+$  in almost equal intensity.

The mechanism by which the carbonyl group is inserted into the 2,2'-carbon-carbon bond of the bi- $\pi$ -allyl group is only speculative at this point. It must involve an acyl intermediate with a  $\text{C}_{(2)}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Co}$  system as bromine adds to the terminal allylic carbon atoms or the cobalt.

To better understand this  $\pi$ -allyl-acyl-cobalt system, an attempt was made to prepare the complex:



which was reported by Nakamura.<sup>(88)</sup> It was thought that the reaction of this compound with triphenylphosphine may yield a bi- $\pi$ -allyl complex by loss of carbon monoxide and rearrangement of the acyl linkage.

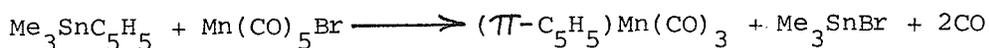
In the method by Nakamura,<sup>(88)</sup> allene gas was passed over a benzene solution of  $\text{Co}_2(\text{CO})_8$ . The compound was isolated by sublimation of the product mixture. In a preparation similar to this, a dilute solution of allene in benzene was added very slowly to a benzene solution of  $\text{Co}_2(\text{CO})_8$  at  $0^\circ\text{C}$ . However, no acyl-carbonyl absorption (reported to be at  $1620 \text{ (s) cm}^{-1}$ ) was observed in the IR spectrum of the reaction mixture, or of the products separated by column chromatography on Florisil, (pentane and pentane-benzene mixture). Instead, the major product was identified as (bi- $\pi$ -allyl)- $\text{Co}_2(\text{CO})_6$ . In addition, two minor complexes were separated, but neither showed an acyl absorption band in the IR spectrum and were not investigated further. The reaction was tried several times at  $0^\circ\text{C}$  and  $25^\circ\text{C}$  but Nakamura's results could not be reproduced. Perhaps the addition of gaseous allene is very important to the reaction mechanism, but it is surprising that it would be so. In the light of these results, the  $\text{PPh}_3$  substitution reaction could not be carried out.

SECTION D

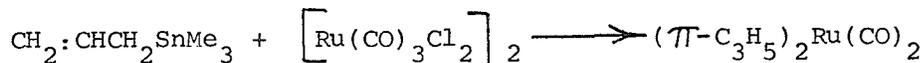
Synthesis of  $\pi$ -allyl Compounds of Fe, Co, and Ni, from Bridging  
Carbonyl Complexes and Tetraallyltin

## Introduction

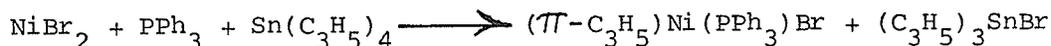
In the search for new and easier ways to synthesize  $\pi$ -allyl complexes from easily accessible starting materials, the use of tetraallyltin was considered to be an obvious source of the allyl ligand. Upon investigation, it was found that other research groups had considered allyl and cyclopentadiene-Group IVB compounds in this same light. Abel and Moorhouse<sup>(69, 95)</sup> found that ( $\sigma$ -cyclopentadienyl)trimethyltin with a metal halide yields the corresponding  $\pi$ -cyclopentadienyl complex, i.e.,



They also found that ( $\sigma$ -allyl)trimethyltin with carbonyl metal halides gave  $\pi$ -allyl complexes, and used this to synthesize a large number of complexes of Mn, Re and Ru:<sup>(95)</sup>



Maxfield<sup>(96)</sup> used tetraallyltin with Fe, Ru, Ni and Pd halide complexes to synthesize  $\pi$ -allyl complexes, i.e.,



The common feature in all these reactions was the use of a

metal halide. In these reactions, the M-X bond was cleaved and the halide eliminated as a trialkyl tin halide. Alternatives not employing a metal halide seemed feasible in the light of work performed by Abel et al<sup>(97)</sup> with  $(\sigma\text{-C}_5\text{H}_5)\text{SnMe}_3$  and bridging carbonyl complexes of Mn, Re, Fe, Co and Ni. A typical reaction in this series was:



The success of these reactions indicated that a halogen atom was not necessary for the transfer of the cyclopentadienyl group from the tin to the transition metal. This prompted the study presented here on the reactions of tetraallyltin with bridging carbonyl complexes of Fe, Co and Ni to yield  $\pi$ -allyl compounds.

## Experimental

Tetraallyltin was prepared from  $\text{SnCl}_4$  and excess allylmagnesium chloride.<sup>(98)</sup> It was fractionally distilled at reduced pressure and the NMR, IR and mass spectra agreed with published results. Storage at  $0^\circ\text{C}$  was necessary to prevent decomposition.

$\left[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})\right]_2$  was prepared from  $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}$  and  $\text{Ni}(\text{CO})_4$  as described by King.<sup>(99)</sup>  $\text{Co}_2(\text{CO})_8$  was from Alfa Inorganics and used directly.  $\text{Fe}_2(\text{CO})_9$  was prepared from  $\text{Fe}(\text{CO})_5$  in bright sunlight in a pyrex flask. The solid  $\text{Fe}_2(\text{CO})_9$  was washed with petroleum ether and dried in vacuo.  $\left[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\right]_2$  was prepared following the method of King.<sup>(100)</sup>

Reaction conditions and products are shown in Table XIII. The products were identified by NMR, IR and mass spectra by comparison to authentic samples or literature reports. The products were isolated by removing the solvent in vacuo (0.01 mm) at  $-30^\circ\text{C}$  and distilling or subliming the product into the trapping system at  $+50^\circ\text{C}$ .

TABLE XIII

## Reactions of Tetraallyltin with Bridging Carbonyl Complexes

Metal Carbonyl	Reaction Conditions (a)	Products	Yield %
$\text{Fe}_2(\text{CO})_9$	Reflux (2 hr) in petroleum	$(\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_2$	25%
	ether	$[(\pi\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3]_2$	5%
$[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$	In hexane at 150°C in stainless steel bomb (4 hr)	$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\pi\text{-C}_3\text{H}_5)$	(b)
$\text{Co}_2(\text{CO})_8$	Reflux pentane (1 hr)	$\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$	35%
		$(\text{C}_3\text{H}_5)_3\text{SnCo}(\text{CO})_4$	(c)
$[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$	Reflux hexane (2.5 hr)	$(\pi\text{-C}_5\text{H}_5)\text{Ni}(\pi\text{-C}_3\text{H}_5)$	42%

(a) Reactions were performed under  $\text{N}_2$ .

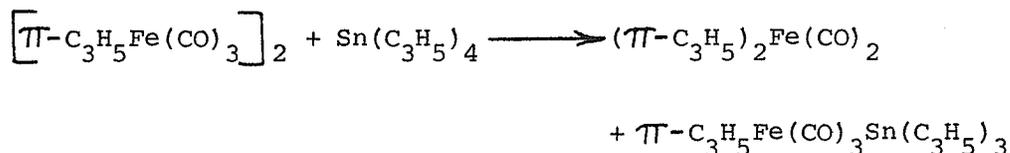
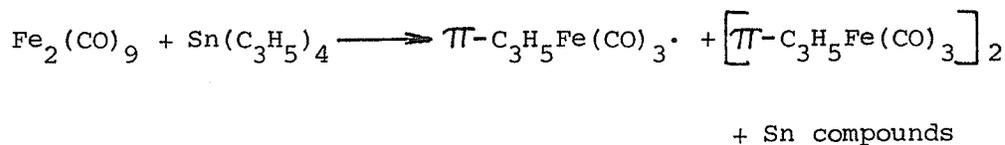
(b) Small amount isolated and only IR and mass spectra used in identification

(c) Only IR spectrum used in identification

## Results and Discussion

The reactions of tetraallyltin with bridging carbonyl complexes (listed in Table XIII) gave  $\pi$ -allyl complexes in good yield. In some reactions, the low volatility of unreacted  $\text{Sn}(\text{C}_3\text{H}_5)_4$  made the quantitative separation of the product difficult by vacuum distillation. In these cases column chromatography could not accomplish the separation.

The major product of the  $\text{Fe}_2(\text{CO})_9$  reaction was  $(\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_2$ . In the isolation of this product by trap to trap distillations (0.01 mm), a red liquid co-distilled in about 5% yield. This was decomposed to a yellow non-volatile compound on the addition of small amounts of air to the vacuum trapping system. This did not affect the major product yield appreciably. Only when this red liquid was absent could the  $^1\text{H}$  NMR spectrum of  $(\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_2$  be recorded. The red liquid was presumed to be  $[\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3]_2$  from a previously reported description of the compound.<sup>(101)</sup> If this is correct, then the reaction to prepare  $(\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_2$  can be written:



The oxidative cleavage products containing a Sn-Fe bond were not identified or isolated.

The reaction with  $\left[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\right]_2$  did not proceed in refluxing benzene but IR evidence for the product  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\pi\text{-C}_3\text{H}_5)$  was obtained when the reaction was carried out in refluxing diglyme, (bp 162°C). The product could not be isolated because of the low volatility of the solvent. Conducting the reaction at 160°C, (hexane solution), in a stainless steel bomb was more successful, and while the IR spectrum of the reaction solution indicated a large amount of product, only a small amount of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\pi\text{-C}_3\text{H}_5)$  was isolated by sublimation. The IR and mass spectra were used to identify the compound, (molecular ion at m/e 190).

The  $\text{Co}_2(\text{CO})_8$  reaction yielded  $\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$  and  $(\text{C}_3\text{H}_5)_3\text{SnCo}(\text{CO})_4$ . The latter could not be isolated from the unreacted  $\text{Sn}(\text{C}_3\text{H}_5)_4$  but was identified by the C-O absorption bands in the IR spectrum (2079 (s), 2017 (m), 1990 (vs)  $\text{cm}^{-1}$ ) by comparison to the IR spectra reported for  $\text{Me}_3\text{SnCo}(\text{CO})_4$  and  $\text{Ph}_3\text{SnCo}(\text{CO})_4$ .<sup>(102)</sup>

From this reaction and the proposed pathway for analogous  $\pi\text{-C}_5\text{H}_5\text{SnMe}_3$  reactions,<sup>(97)</sup> the mechanism for the  $\text{Sn}(\text{C}_3\text{H}_5)_4$  reactions can be described in terms of an oxidative cleavage of the bridging carbonyl complex. Although evidence for this was found in only one of the reactions carried out, it is likely to be the case for the other three reactions.



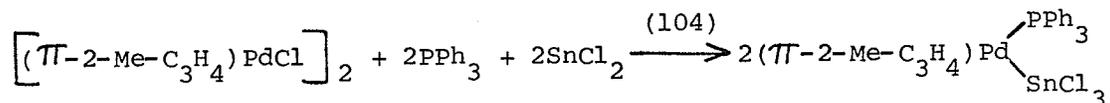
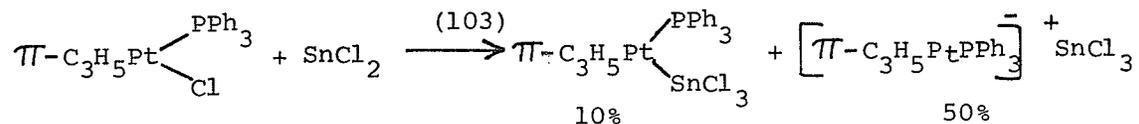
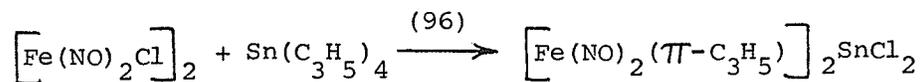
Where R, R' and R'' represent the CO or  $\pi\text{-C}_5\text{H}_5$  ligands.

SECTION E

Preparation of  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{SnPh}_3$

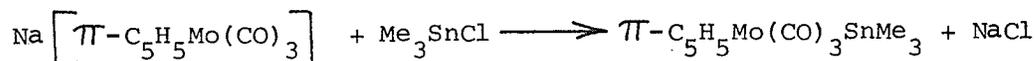
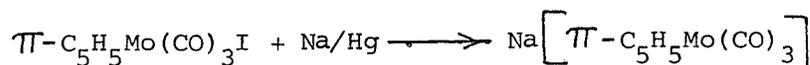
### Introduction

In the reaction of tetraallyltin with  $\text{Fe}_2(\text{CO})_9$ , the possibility of one of the products being  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Sn}(\text{C}_3\text{H}_5)_3$  was considered. On looking through the literature for a report concerning complexes of this type, it was found that none had been prepared. In fact, only three reports concerning  $\pi$ -allyl-metal- $\text{SnR}_3$  systems were found and these did not pertain to the complex in question.

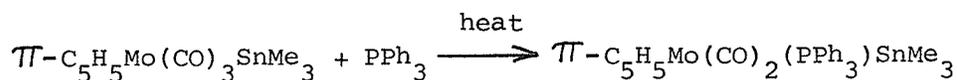


The lack of  $\pi$ -allyl complexes of this type was unusual because of the known existence of  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$  for several years, and the extensive research conducted by several groups into the chemistry and spectral characteristics of a variety of  $\pi$ -cyclopentadienyl complexes of the general type  $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{ER}_3$ , (where  $\text{M} = \text{Mo}, \text{Cr}$  or  $\text{W}$ , and  $\text{E} = \text{Si}, \text{Ge}$  or  $\text{Sn}$ , and  $\text{R} = \text{alkyl}, \text{aryl}$  or  $\text{halogen}$ ).<sup>(62)</sup> These complexes have also been studied by phosphine substitution reactions where one carbonyl group has been replaced by a trialkyl or triaryl

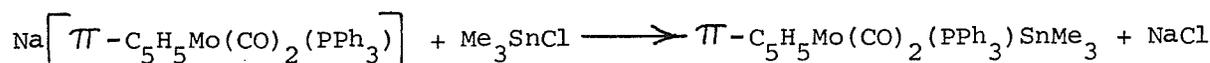
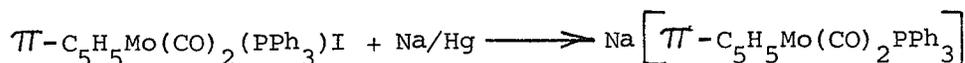
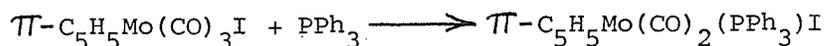
phosphine group. The general method of preparation for these complexes is shown by this example. <sup>(105)</sup>



The phosphine substitution can be carried out directly.

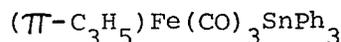


or by an indirect method which in this case was the more successful.

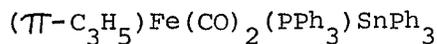


Cullen et al <sup>(106)</sup> prepared a series of ligand-substituted iron complexes of the type:  $\pi\text{-C}_5\text{H}_5\text{Fe(CO)}(\text{L})\text{SnR}_3$ , (where R = Me, Ph or Cl and L = CO, triphenylarsine, stibine or phosphine). The complexes were prepared from  $\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{SnR}_3$  by reaction with the ligand in the presence of ultra violet light. NMR, IR and Mossbauer spectra of the derivatives were reported.

The work presented here is the first step in extending the previous studies in  $\pi$ -cyclopentadienyl complexes to  $\pi$ -allyl complexes.

Experimental

The sodium salt of  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3^-$  was prepared by stirring  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$  (5 g) with excess sodium amalgam in THF for 45 minutes under  $\text{N}_2$ . An excess of  $\text{Ph}_3\text{SnCl}$  (6 g) was added to the solution at room temperature after the removal of the amalgam. The solution was stirred for one hour. The THF was removed in vacuo and benzene distilled into the flask (0.1 mm). The insoluble material was filtered off under  $\text{N}_2$  and the crude product isolated by removing the benzene in vacuo. The resulting solid was dissolved in a minimum amount of boiling hexane and the solution cooled slowly to  $0^\circ\text{C}$ . Large yellow crystals were separated mechanically from the unreacted, white  $\text{Ph}_3\text{SnCl}$ . Recrystallization gave an air-stable yellow solid, (mp  $70^\circ\text{C}$ ), in 70% yield. Elemental analysis calculated for  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{SnPh}_3$ : C 54.29%, H 3.77%, and Sn 22.39%, found: C 54.94%, H 3.98% and Sn 21.90%.



$\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{SnPh}_3$ , (1.2 g, 2.2 mmol), and triphenylphosphine, (0.9 g, 3.3 mmol), were reacted in 50 ml benzene at reflux under  $\text{N}_2$  for two hours. Then 50 ml hexane was added. The solution was refluxed briefly, filtered and allowed to cool at room temperature. Fine, light yellow, air-stable crystals in 90% yield were obtained. Recrystallization from 1:1 benzene-hexane

gave the pure product, (mp 185°C - 189°C (decomposition)) .

Elemental analysis calculated for  $C_3H_5Fe(CO)_2(PPh_3)SnPh_3$ :

C 64.34%, H 4.62%, Fe 7.30%, Sn 15.51%, found: C 64.35%,

H 4.60%, Fe 7.03%, Sn 15.37%.

Results and Discussion

The reaction of  $\text{Na} \left[ \pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3 \right]$  with  $\text{Ph}_3\text{SnCl}$  went smoothly to yield the complex  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{SnPh}_3$ . The mass spectrum showed the parent ion at  $m/e$  532, (based on  $^{120}\text{Sn}$ , 32.85% natural isotopic abundance), with the successive loss of three carbonyl groups. The IR and NMR spectra (Table XIV) are easily interpreted and do not show the presence of rotameric isomers for the compound in solution as does  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$ .<sup>(15)</sup>

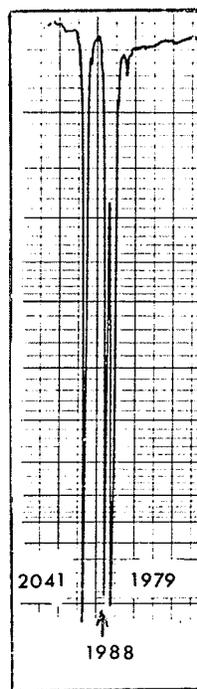
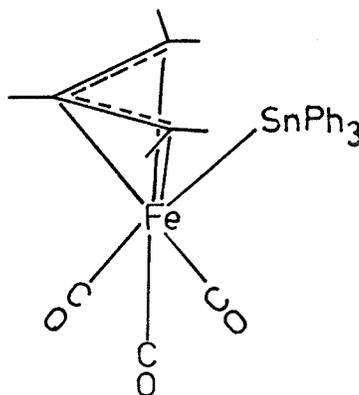


Figure 12 IR carbonyl absorption bands of  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{SnPh}_3$

The IR spectrum of  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$  shows four C-O absorption bands and the NMR spectrum shows a complicated number of resonance absorptions at 40°C which can only be interpreted at -65°C. To explain the spectral data, Nesmayanov et al<sup>(15)</sup> proposed the existence of two conformers of the  $\pi$ -allyl group, due to the hindered

rotation of the  $\pi$ -allyl group about the  $\pi$ -allyl-iron bond. One conformation has the  $C_2$  carbon of the  $\pi$ -allyl ligand directed towards the iodine atom, the other with the  $C_2$  carbon directed away from the iodine atom, (see Section B, p.70). For  $\pi$ - $C_3H_5Fe(CO)_3SnPh_3$ , the spectral data can be interpreted as indicating either free rotation or completely restricted rotation about the  $\pi$ -allyl-iron bond. Because of the size of the  $SnPh_3$  group, it is more likely this rotation is completely restricted and the  $\pi$ -allyl group stays in the conformation in which the  $C_2$  carbon is directed away from the  $SnPh_3$  group.



Whether or not the molecule is essentially octahedral as was shown for  $\pi$ - $C_3H_5Fe(CO)_3I$ <sup>(107)</sup> can only be determined by an x-ray crystal structure analysis.

The reaction of  $\pi$ - $C_3H_5Fe(CO)_3SnPh_3$  with  $PPh_3$  proceeded in refluxing benzene to give  $\pi$ - $C_3H_5Fe(CO)_2(PPh_3)SnPh_3$  in good yield. This reaction is interesting because of the possibility of cis- and trans-isomers being produced. There has been considerable study<sup>(108, 109)</sup> done on the cis- and trans-isomers of  $\pi$ - $C_5H_5Mo(CO)_2LR$ , where  $L = PPh_3, P(n-but)_3, P(OMe)_3$  and  $P(OPh)_3$ ;  $R = H, PhCH_2, Cl, Br$ , I. Manning<sup>(105, 108)</sup> observed the cis- and trans-isomers of  $\pi$ - $C_5H_5Mo(CO)_2PR_3I$  complexes but could only identify the trans-form

of  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{PR}_3)\text{SnPh}_3$  complexes.

The cis- and trans-isomers of  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{PR}_3)\text{I}$  complexes were identified by IR and NMR. In the IR spectrum, two C-O bands were observed for both isomers. The band at higher frequency was the more intense of the two for the cis-isomer but weaker for the trans-isomer. The NMR spectrum showed the resonance absorption due to the cyclopentadienyl protons of the cis-isomer to be a singlet, but a 1:1 doublet for the trans-derivative, (split by the  $^{31}\text{P}$  of the phosphine group).

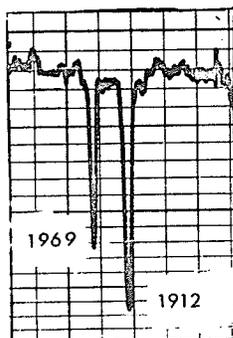


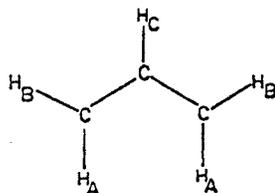
Figure 13 IR carbonyl absorption bands of  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2(\text{PPh}_3)\text{SnPh}_3$

From the C-O absorption band intensities, (higher frequency band less intense), in the IR spectrum, (Fig. 11), and the splitting of the allylic protons by the phosphorus nucleus, (2 Hz for the syn-protons and 11 Hz for the anti-protons), in the NMR spectrum, (Table XIV), it is concluded that the compound  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2(\text{PPh}_3)\text{SnPh}_3$  was isolated in the trans-form.

As it was concluded that the trans-form was prepared, it has not been determined whether the cis-form would give rise to different IR and NMR spectra. It must be remembered that crystal structure

analyses of  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{X}$ , (where  $\text{X} = \text{Cl}, \text{SnPh}_3$ ), (110, 111) show these molecules to have a tetragonal pyramidal structure, while  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$  has been shown to have a distorted octahedral structure<sup>(107)</sup> which does not approach a tetragonal pyramidal arrangement of the ligands. The complex  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2(\text{PPh}_3)\text{I}$  was synthesized by Heck and Boss<sup>(112)</sup> and Nesmeyanov et al<sup>(80)</sup>, but the configuration of the ligands was not discussed.

TABLE XIV

IR and NMR Spectra <sup>(a)</sup> of  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{SnPh}_3$  and  $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2(\text{PPh}_3)\text{SnPh}_3$ 

Complex	$\nu(\text{CO}) \text{ cm}^{-1}$	$\delta_{\text{A}}^{(\text{b})}$	$\delta_{\text{B}}$	$\delta_{\text{C}}$	$\delta_{\text{Ph}}$	$J_{\text{A,C}}$	$J_{\text{B,C}}$
$\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{SnPh}_3$	1979 (s)	1.59 (d) <sup>(c)</sup>	2.27 (d)	4.67 (m)	7.1 (m)	11	6
	1988 (s)						
	2041 (s)						
$\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2(\text{PPh}_3)\text{SnPh}_3$	1912 (vs)	1.36 (t)	2.44 (q)	*	7.5 (m)	11	7
	1969 (s)	$J_{\text{A,P}} = 11$	$J_{\text{B,P}} = 2$				

(a) Pentane solutions for IR;  $\text{CDCl}_3$  solutions for NMR, (5% TMS)(b)  $\delta$  values in ppm downfield from TMS, J values in Hz

(c) Abbreviations: (s) strong, (vs) very strong, (d) doublet, (m) multiplet, (t) triplet, (q) quartet

\* Solution too dilute to observe resonance absorption of  $\text{H}_{\text{C}}$ .

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