

1992

Iron Tricarbonyl Derivatives of Ditertiary Phosphines

Xi Chen

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Iron Tricarbonyl Derivatives of Ditertiary Phosphines

(TITLE)

BY

Xi Chen

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

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IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1992

YEAR

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Date Submitted: October 14, 1992

By Xi Chen

Adviser: Dr. Richard L. Keiter

Approved by the Thesis Committee

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Abstract

In this work we have explored reactions of coordinated diphenylvinylphosphine with coordinated diphenylphosphine. Starting materials, $(OC)_4FePPh_2CH=CH_2$, *trans*- $(OC)_3Fe(PPh_2CH=CH_2)_2$, $(OC)_4FePPh_2H$, and *trans*- $(OC)_3Fe(PPh_2H)_2$ were successfully prepared from known procedures. The bimetallic complex, $(OC)_4FePPh_2CH_2CH_2PPh_2Fe(CO)_4$, was obtained in 69% yield from the reaction of $(OC)_4FePPh_2CH=CH_2$ with $(OC)_4FePPh_2H$. The trimetallic complex, $(OC)_4FePPh_2CH_2CH_2PPh_2Fe(CO)_3PPh_2CH_2CH_2PPh_2Fe(CO)_4$, was obtained from the reaction of $(OC)_4FePPh_2CH=CH_2$ with *trans*- $(OC)_3Fe(PPh_2H)_2$, in 51% yield. The bimetallic and trimetallic complexes were prepared in THF by employing potassium tert-butoxide as a base catalyst. All of these complexes were characterized by phosphorus-31 NMR and by IR spectroscopy.

It was not possible to prepared the trimetallic complex from *trans*- $(OC)_3Fe(PPh_2CH=CH_2)_2$ with $(OC)_4FePPh_2H$. Nor was it possible to induce polymerization from the reaction of *trans*- $(OC)_3Fe(PPh_2CH=CH_2)_2$ with *trans*- $(OC)_3Fe(PPh_2H)_2$. In each case the diphenylvinylphosphine complex was recovered

unchanged, but the diphenylphosphine complex decomposed to unidentified products. It became evident that whereas $(OC)_4FePPh_2CH=CH_2$ undergoes reaction with either $Fe(CO)_4PPh_2H$ or *trans*- $Fe(CO)_3(PPh_2H)_2$, *trans*- $Fe(CO)_3(PPh_2CH=CH_2)_2$ undergoes reaction with neither. It appears that the rate of decomposition of either diphenylphosphine complex is faster than the rate of addition to *trans*- $Fe(CO)_3(PPh_2CH=CH_2)_2$.

It was shown that phosphines react with *trans*- $Fe(CO)_3(AsPh_3)_2$ to displace triphenylarsine in stepwise fashion. This method was used to produce the mixed ligand complex, *trans*- $Fe(CO)_3(PPh_2H)(PPh_2CH=CH_2)$. It was not established whether this monomer can be polymerized in the presence of base.

Preliminary work also shows that $Ph_2PC\equiv CPh_2$ reacts with *trans*- $Fe(CO)_3(AsPh_3)_2$ by displacing triphenylarsine. This reaction shows promise as a means of producing polymers in which the $Fe(CO)_3$ units are bridged by $Ph_2PC\equiv CPh_2$.

Acknowledgments

I would like to thank Dr. Richard L. Keiter for his knowledgeable assistance and direction. His patience and guidance were very much appreciated.

I would also like to thank Dr. Ellen A. Keiter for obtaining all NMR spectra.

I also wish to express my appreciation to the faculty and staff of the Chemistry Department at Eastern Illinois University.

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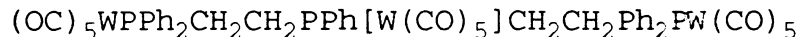
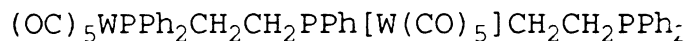
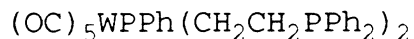
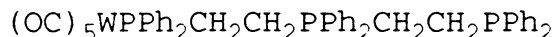
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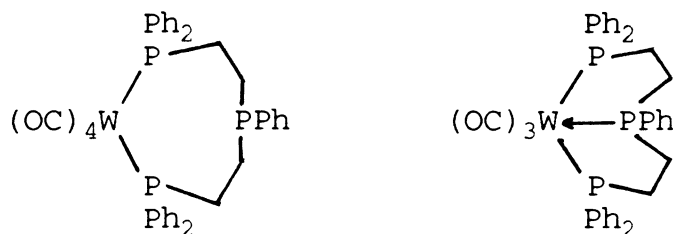
Introduction:

Organometallic chemistry has grown enormously over the past several decades. Studies in this field have led to new insights into bonding, structure, and reactivity of molecules. Many new synthetic techniques have been developed. It has become more possible than ever before for organometallic chemists to create new materials. In particular, organometallic polymers containing transition metals have a promising future.

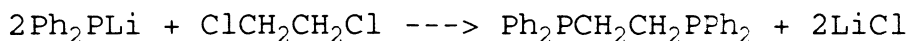
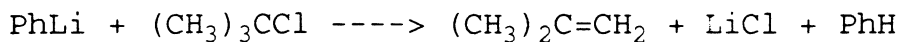
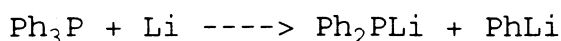
Organophosphines are among the most important ligands in organometallic chemistry because their complexes often have high stability. In particular, polytertiary phosphines have attracted much attention because of the following reasons: (1) they may function as multidentate chelating or bridging agents. (2) they provide more control than monodentate ligands of the coordination number, stereochemistry, and magnetic properties of complexes.¹ For example, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhCH}_2\text{CH}_2\text{PPh}_2$ can bind to one, two, or three metal atoms.²



In addition it can function as a bidentate ligand or a tridentate ligand.



Polytertiary phosphines, such as $\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$, have been known for nearly thirty years. The first ones were prepared by reaction of organic polyhalides with alkali metal diarylphosphides.³

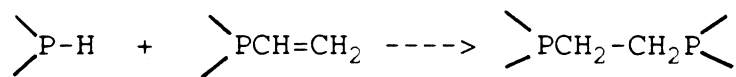


It was difficult to extend this synthetic method to more complex polytertiary phosphines because either the appropriate polyhalide was unavailable or it was difficult to obtain complete reaction with the phosphide reagent. The synthetic unavailability limited the utility of polytertiary phosphines.

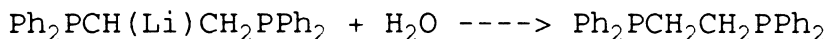
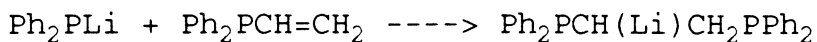
In the early 1970's, two different methods of high-yield syntheses were discovered independently by King⁴, Meek⁵, and Issleib⁶.

King utilized a base-catalyzed addition reaction of a phosphorus-hydrogen bond across the carbon-carbon double bond of vinylphosphines according to the

following general scheme:

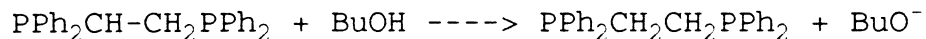
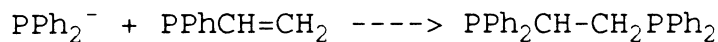
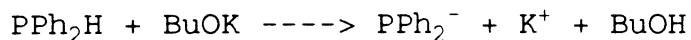


Actually, a version of King's work had been discovered prior to his work.⁷



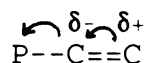
Meek and Issleib employed a free-radical addition reaction which also allowed addition of phosphorus-hydrogen bonds to the carbon-carbon double bonds of vinylphosphines in the presence of the free radical precursor, 2,2'-azobis(isobutyronitrile) (AIBN).

The base-catalyzed addition of phosphorus-hydrogen bonds across the carbon-carbon double bonds of vinylphosphines is a special case of a Michael addition reaction. Phosphorus-hydrogen derivatives such as Ph_2PH readily lose their protons in the presence of strong bases to form dialkylphosphide anions which react with vinylphosphine by nucleophilic attack at the terminal end of the carbon-carbon double bond.

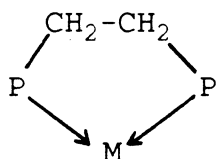


The reaction disobeys Markovnikov's rule because the base-catalyzed addition reactions involve nucleophilic addition (rather than electrophilic as in the case of

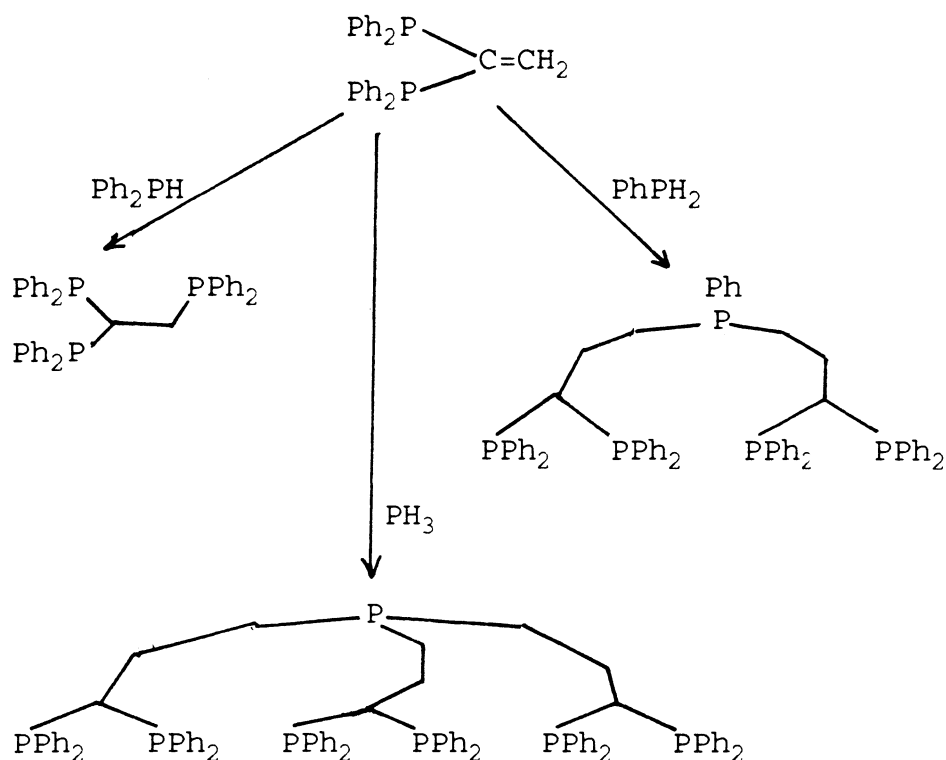
the addition of HX to an olefin) and the reaction intermediate is anionic. Phosphorus is sufficiently electronegative to withdraw electron density from the carbon-carbon double bond and leave the terminal carbon with a partial positive charge.



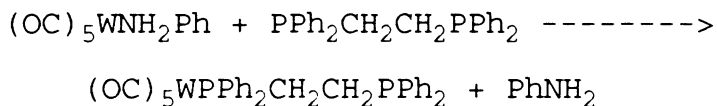
Polytertiary phosphines synthesized by base-catalyzed addition reactions contain an ethane bridge linking two phosphorus atoms. The $\text{PCH}_2\text{CH}_2\text{P}$ units are useful for synthesizing polytertiary phosphine complexes because five-membered chelating rings are quite stable (more stable than four- or six-membered rings).



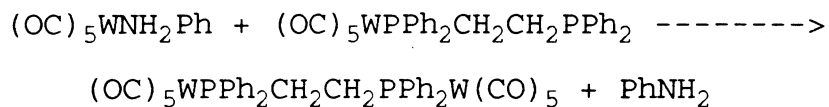
With these new synthetic methods, a number of polydentate phosphorus ligands have been designed and synthesized. For example, McFarlane has used 1,1-bisdiphenylphosphinoethene to prepare 1,1,2-tridiphenylphosphinoethane and other derivatives:⁸



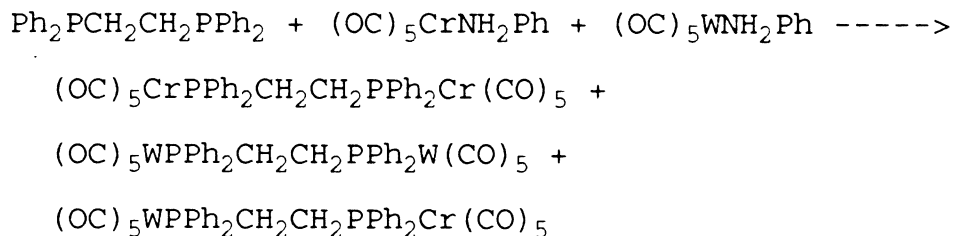
Early syntheses of transition metal complexes containing polytertiary phosphines typically involved substitution reactions, e.g.



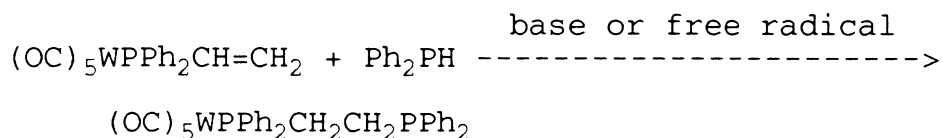
However, substitution reactions are in general inadequate because they are not selective, too often leading to mixtures of isomers and/or mixtures of mono- and bimetallic products that may not be easily separated. In the above reaction one also obtains $(\text{OC})_5\text{WPPH}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{W}(\text{CO})_5$ as a secondary product.



In addition, substitution reactions do not readily allow the incorporation of more than one kind of metal atom into the complex.

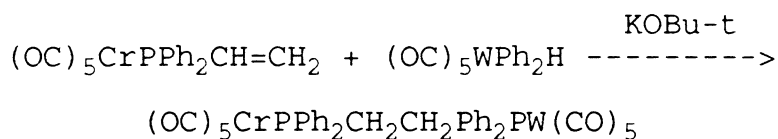


In 1977, Keiter found that the Michael type addition reactions are effective even when carried out between secondary and vinylphosphine that have been coordinated prior to reaction.⁹



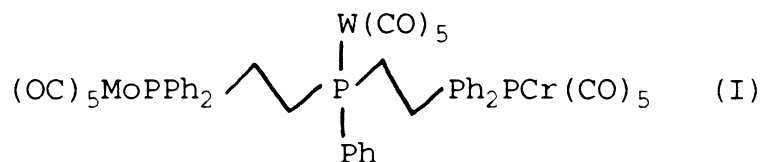
With this new approach, syntheses can be designed that lead to selective formation of products. In the above reaction there is no opportunity for chelation to occur, nor is there any chance for bimetallic complexes to form. This is because vacant coordination sites do not become available during the course of the reaction.

Two different metals can be easily incorporated into the complex, e.g.:

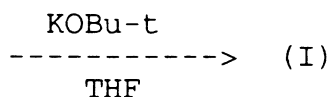
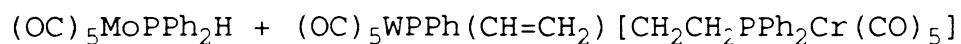
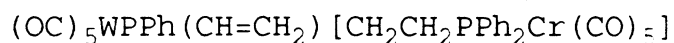
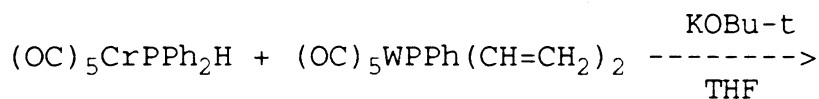


Perhaps the ultimate example is given by the synthesis

of a transition metal complex that contains all elements of Group 6:¹⁰

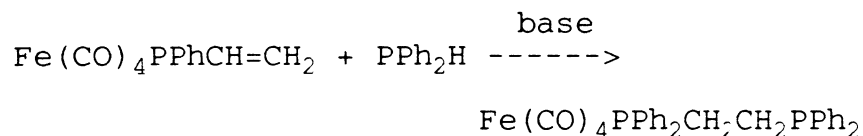


This complex was synthesized by the following reaction sequence:



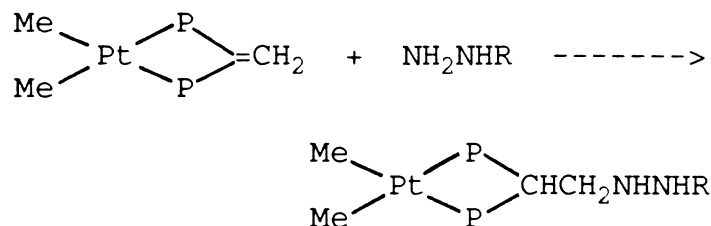
The tungsten derivatives mentioned on Page 1 and 2 were obtained from similar reactions.

Thus it is possible to synthesize transition metal complexes of polytertiary phosphine by design. In 1983, it was demonstrated that base-catalyzed addition reactions are also effective for the preparation of iron complexes.¹¹

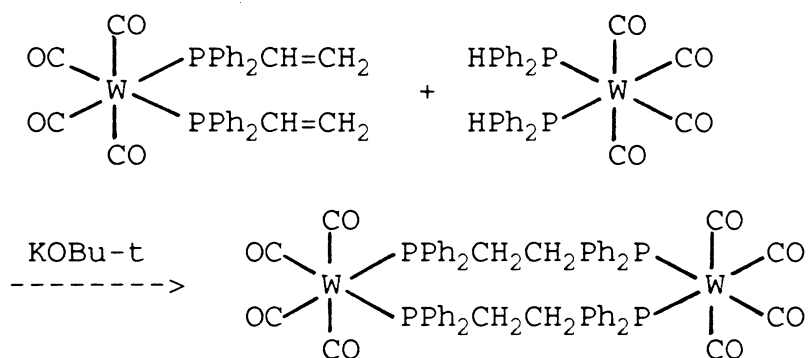


In 1985, Shaw reported that $(\text{Ph}_2\text{P})_2\text{CH=CH}_2$ is much

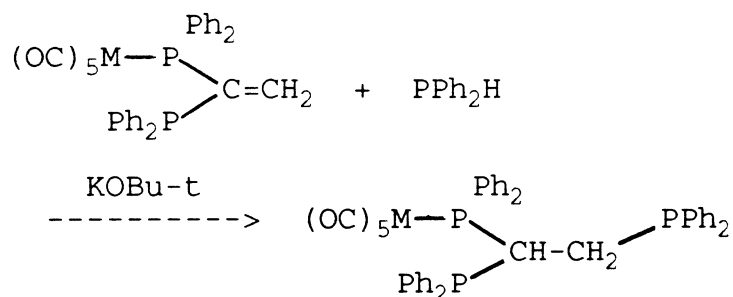
more reactive in a Michael addition reaction when it is complexed. Thus complexes of Pt(II) and Pt(IV) react readily with a variety of nucleophiles.¹²

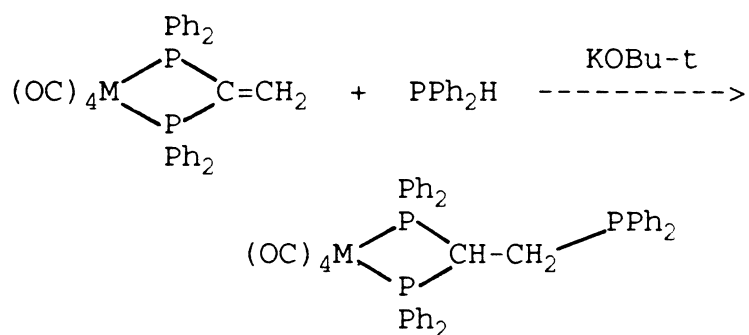


In the same year, Shaw introduced two bridges into Group 6 carbonyl complexes by using the base-catalyzed addition reaction.¹³



Following this work, McFarlane used the ligand to create a variety of complexes in which a tridentate phosphine molecule is bonding as a mono- or bidentate ligand.¹⁴

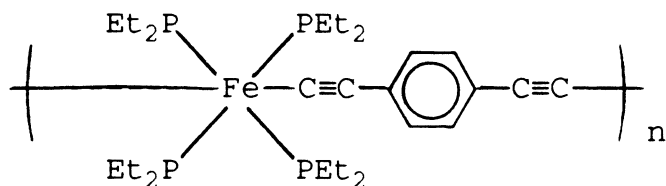




The field of inorganic macromolecules is entering a phase of rapid development and change. For the past 20 years this area has grown steadily, mainly through fundamental studies by a small number of academic, government, and industrial scientists. Today, the burgeoning interest in this field is driven by the search for new high-performance materials with special properties. For example, inorganic polymers with delocalized π systems can have unique physical and electronic properties and may have numerous technological applications. These include one-dimensional conductors, light-weight battery components, molecular transistors, photoconductors, non-linear optical materials and even high temperature superconductors.

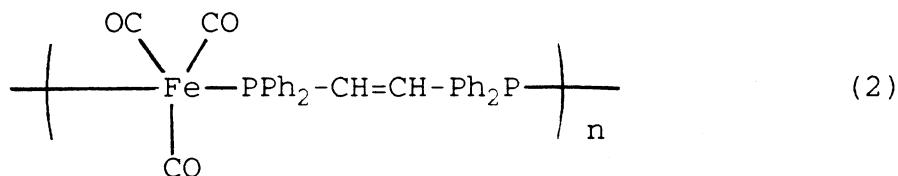
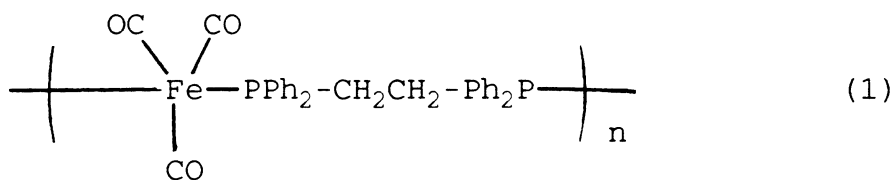
Inorganic polymers can be constructed by linking the metal centers with olefin or aromatic bridges. E.g. the following polymer has been reported by

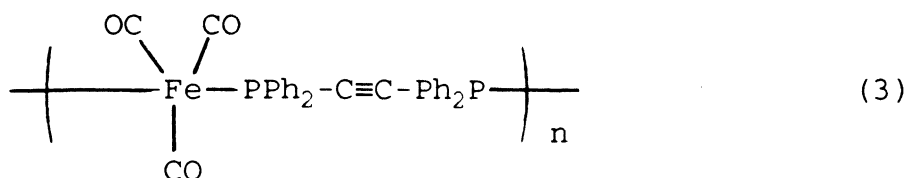
Lewis.¹⁵



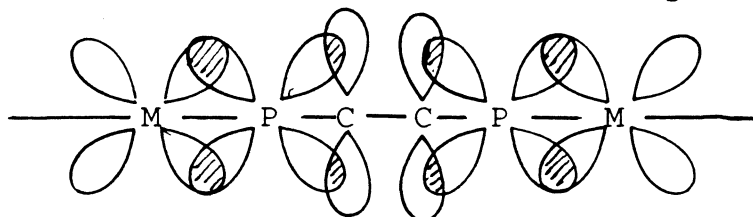
The electronic conjugation between the adjacent metal in such unsaturated bridges occurs primarily by π orbital interaction between the highest occupied molecular orbitals, HOMOs, (i.e., filled d orbitals) on the metal centers with the empty π^* orbitals on the bridging ligands.

Based on the previous work, we thought that it might be possible to construct organometallic polymers by using Michael-type addition reactions. Our long range goal was to synthesize the following three kinds of polymers:



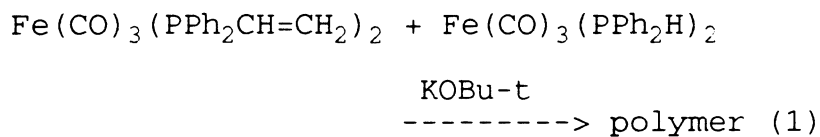


Polymer (2) and (3) might serve as one-dimensional conductors in which the filled d-orbital of the metal, the empty d-orbital of phosphorus, and the antibonding orbital of the unsaturated carbon bridge are involved.

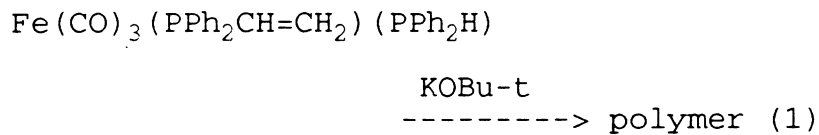


We hoped that polymers (1) and (2) could be obtained by using the following synthetic routes:

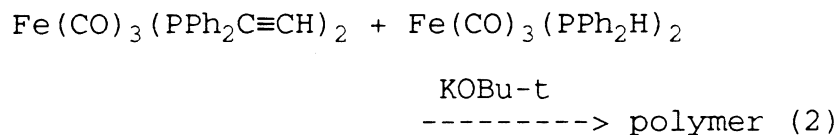
Method I:



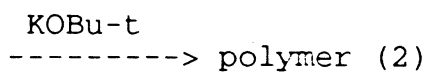
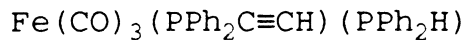
Method II:



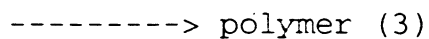
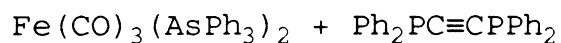
Method I:



Method II:



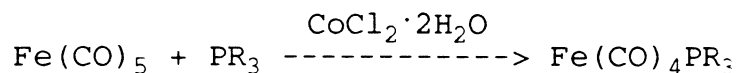
We proposed that polymer (3) could be built up by using a substitution reaction involving a triphenylarsine complex and $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$.



Although polymer (1) is not expected to be a one-dimensional conductor, we thought it would be useful to compare its rigidity, solubility and other properties with polymers (2) and (3).

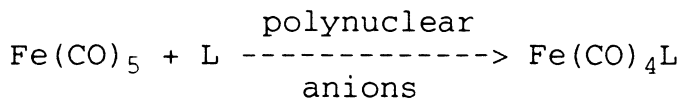
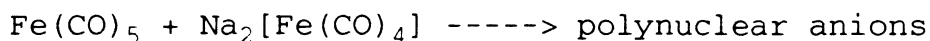
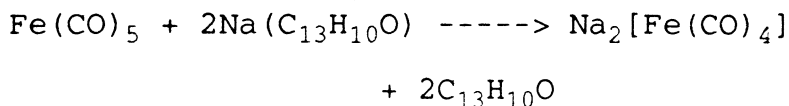
Results and Discussion

Three different synthetic methods were used for the preparation of mono-substituted iron carbonyl complexes, $\text{Fe}(\text{CO})_4\text{PR}_3$. The first was the so-called cobalt method¹⁶ which involves $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ as a catalyst.



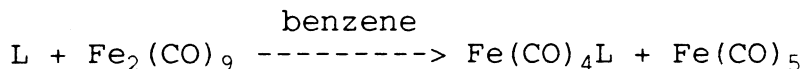
Although the mechanism for this reaction is not well understood, it has been speculated that CoCl_2 and PR_3 form a $\text{CoCl}_2(\text{PR}_3)_2$ complex as a first step. The formation of this complex can be detected by an instant color change of the reaction solution. Coville and coworkers¹⁶ have successfully synthesized a series of tertiary phosphine complexes of iron carbonyl by using this method. In our work a good yield of $\text{Fe}(\text{CO})_4\text{PPh}_3$ was obtained, but the cobalt method was not effective for the preparation of PPh_2H complexes. It is unclear why PPh_3 and PPh_2H react differently, but it may have something to do with the rather acidic hydrogen of the secondary phosphine.

The second method employed was reported by Butts and Shriver¹⁷ who used sodium benzophenone ketyl as a catalyst. They postulated that iron pentacarbonyl reacts with sodium benzophenone ketyl to form polynuclear iron carbonyl anions which can activate $\text{Fe}(\text{CO})_5$ toward substitution by phosphine.



In these reactions L is a phosphine and the polynuclear anions were $[\text{Fe(CO)}_4]^{2-}$, $[\text{Fe}_2(\text{CO})_8]^{2-}$, or $[\text{Fe}_3(\text{CO})_{11}]^-$. However, with this method we obtained very low yields (18%) of $\text{Fe(CO)}_4\text{PPh}_2\text{CH=CH}_2$ and no product at all for the PPh_2H reaction. The reason might be that the secondary phosphine cannot survive in the environment of such a strong reducing agent, sodium benzophenone ketyl.

The third method used for the production of $\text{Fe(CO)}_4\text{PR}_3$ complexes was first reported by Thompson¹⁸ and developed by Treichel¹⁹. Diiron nonacarbonyl reacts with secondary phosphine to afford the appropriate phosphine iron tetracarbonyl along with iron pentacarbonyl:



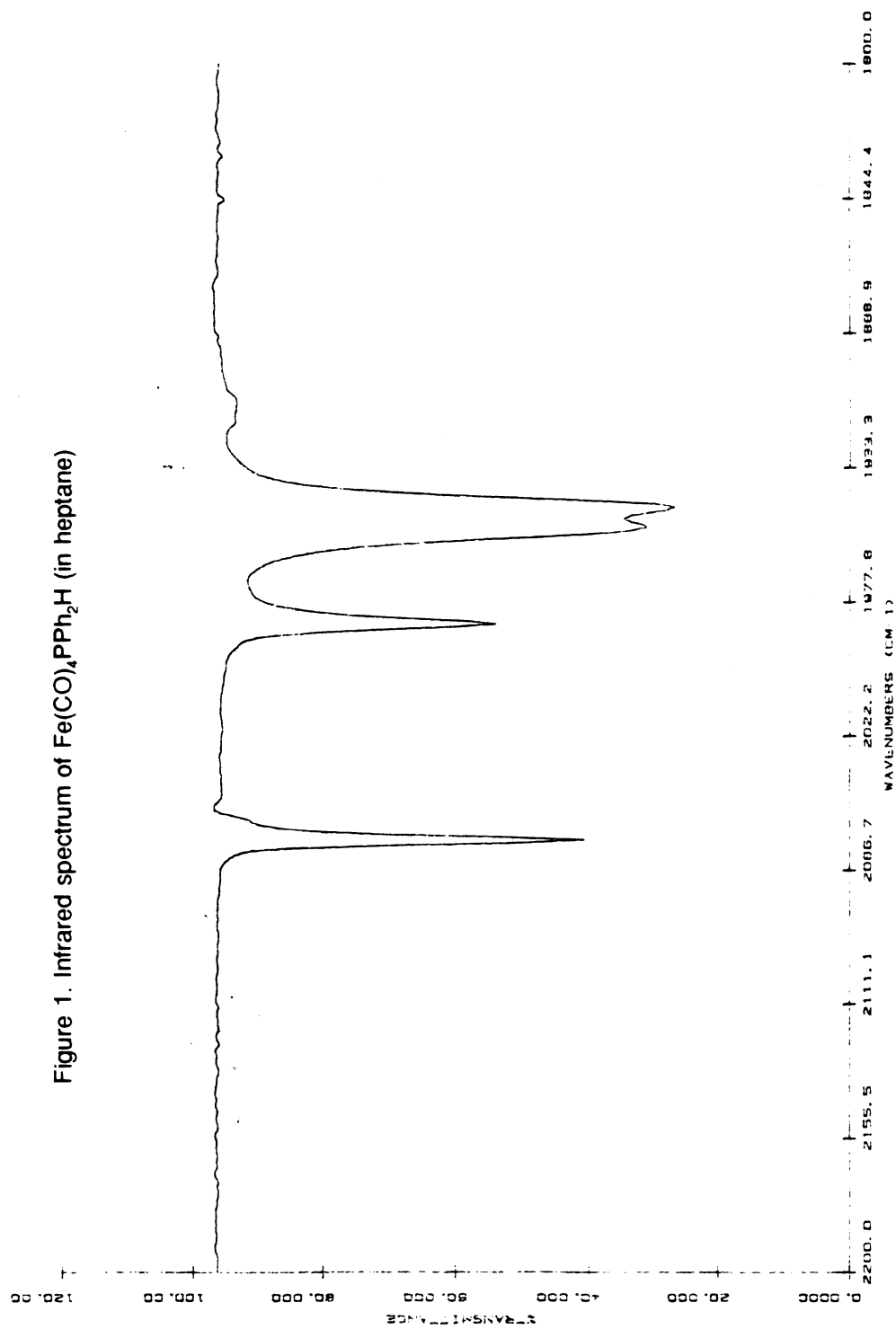
The reaction was carried out under moderate conditions: room temperature, no reducing agent, and no catalyst. The product was separated from other materials by column chromatography and purified by crystallization from heptane. This method proved to be very effective for a reactive ligand, such as PPh_2H . In this reaction

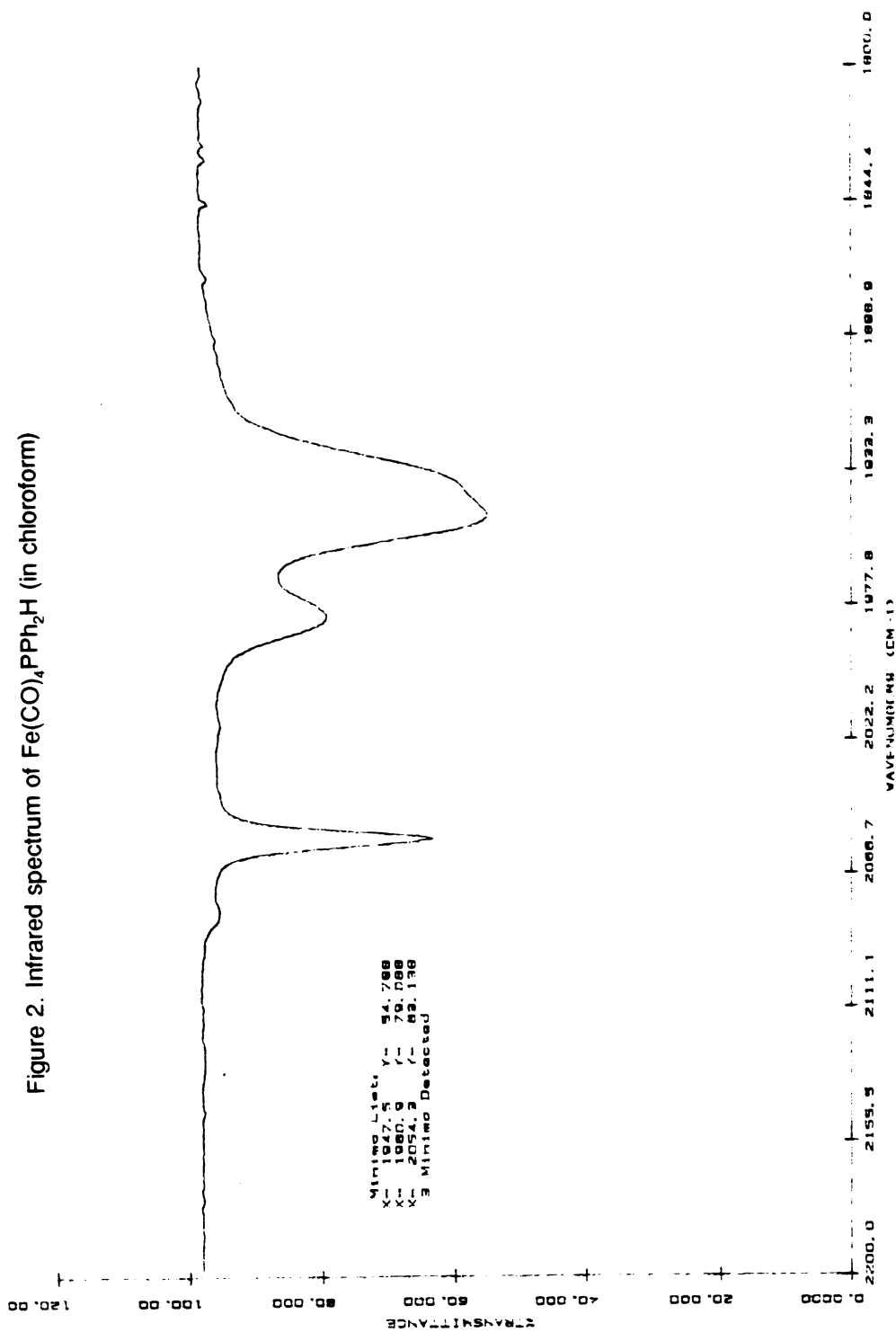
$\text{Fe}_2(\text{CO})_9$ is the source of $\text{Fe}(\text{CO})_4$, which has a vacant coordination site and can readily accept the lone electron pair from the phosphine.

The traditional synthetic methods for the preparation of $\text{Fe}(\text{CO})_4\text{PR}_3$ complexes (thermal and photochemical reactions) suffer from the following disadvantages: (a) long reaction times, (b) forcing conditions, (c) low yields, and (d) the formation of mixtures of $\text{Fe}(\text{CO})_4\text{PR}_3$ and $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$. Although in recent years some high-yield synthetic methods have been developed, there is none which works for all different types of ligands. In our work, the diiron nonacarbonyl method gives good yields of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$ and $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ complexes and is free of contamination from $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$.

Infrared spectra of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$ in the carbonyl region are shown in Figures 1 and 2. Phosphine substituted derivatives of iron pentacarbonyl are most conveniently identified by infrared spectroscopy. Coordinated carbon monoxide exhibits intense stretching vibrations in a region (2200 cm^{-1} to 1800 cm^{-1}) which is fairly well isolated from other types of vibrations that are likely to be present. The derivatives of iron pentacarbonyl of the type $\text{Fe}(\text{CO})_4\text{PR}_3$ are of C_{3v} symmetry. The phosphine ligand occupies the one axial position while one carbonyl ligand occupies the trans

Figure 1. Infrared spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$ (in heptane)



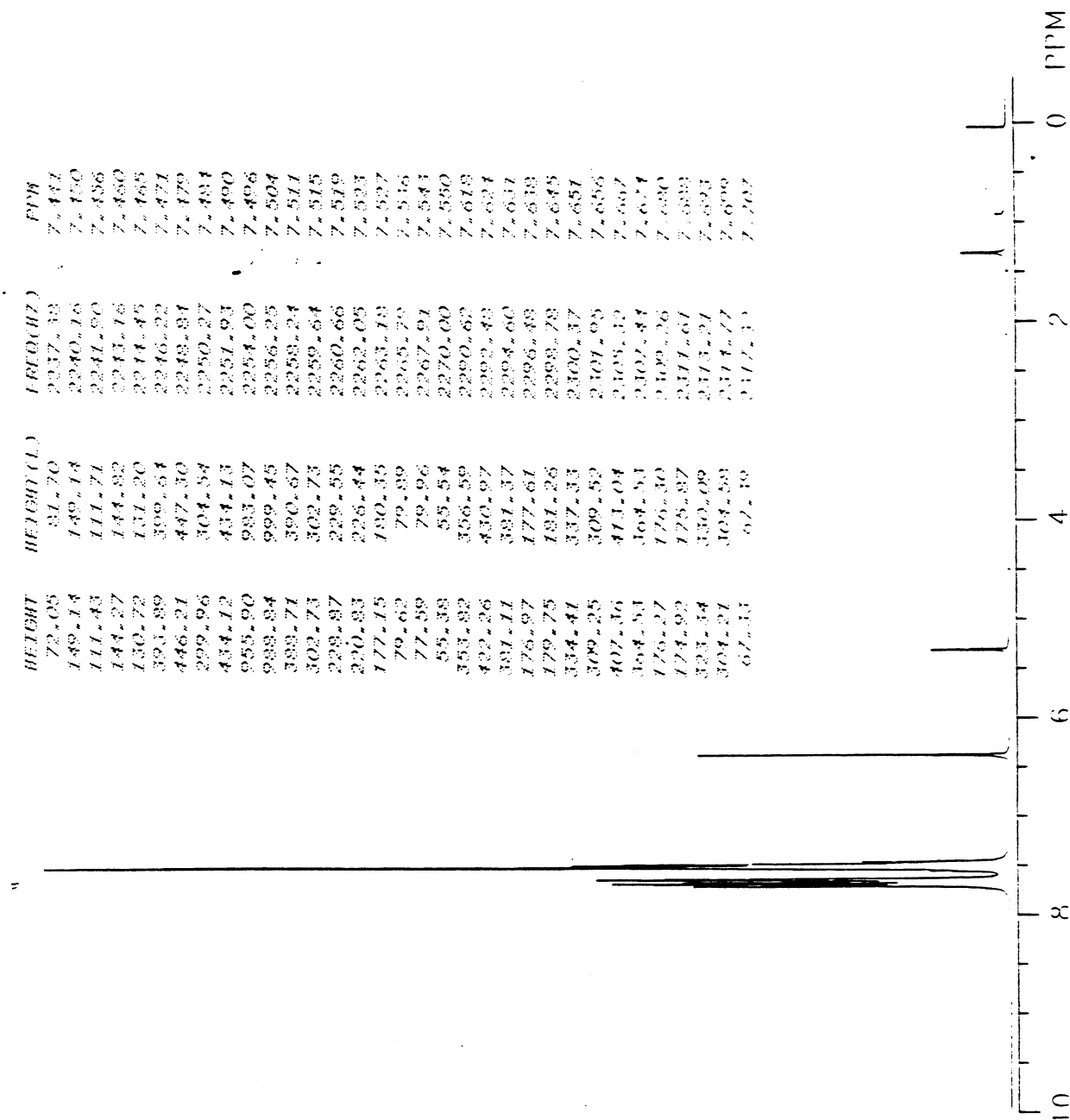


axial position and other three carbonyl ligands occupy the three equatorial positions. According to standard group theory, a molecule of C_{3v} symmetry has three vibrational modes: two bending modes (A_1) and one stretching mode (E).

In each of the spectra (Figure 1 and 2) a splitting or a broadening of the E stretching mode was observed. These observations can be attributed to one effect, namely the lowering of the symmetry of the complex to something less than C_{3v} . This deviation from the idealized point group of the molecule is caused by two factors, the bulkiness of the phosphine ligand and the interactions between the complex and the solvent in which the spectra were taken. In order to illustrate the above discussion the spectra of $Fe(CO)_4PPh_2H$ taken in heptane, a noninteractive solvent (Figure 1) and chloroform, an interactive solvent (Figure 2). Resolution is best in heptane, a solvent in which interaction between solvent and solute is minimized.

A 1H NMR spectrum of $Fe(CO)_4PPh_2H$ is shown in Figure 3. The signal at 5.3 ppm arises from CH_2Cl_2 in the CD_2Cl_2 solvent. The signal at 6.4 ppm arises from the hydrogen bound to phosphorus. Only one line of the expected doublet is observed because the second line overlaps with the phenyl region. The two phenyl groups appear as groups of signals shown in the spectrum from

Figure 3. Proton NMR spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$



7.4 ppm to 7.7 ppm. The signal at 1.3 ppm arises from an unknown impurity, perhaps vacuum grease.

Proton decoupled and coupled P-31 NMR spectra of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$ are shown in Figures 4 & 5, respectively. The single strong signal in the decoupled spectrum demonstrates the absence of disubstituted complex contamination. The satellites associated with the single signal may arise from the 2.1% abundant Fe-57 coupled to phosphorus. There is also some possibility that this is the result of the coupling of the C-13 to phosphorus. Two groups of signals are observed in the P-31 coupled spectrum. The separation of these two groups of signals gives the coupling constant ($J_{\text{PH}} = 377 \text{ Hz}$) between the ^{31}P nucleus and the ^1H nucleus of the P-H bond.

The proton decoupled P-31 NMR spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$, prepared by using sodium benzophenone ketyl method is shown in Figure 6. The major signal is consistent with that expected for $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ but a small signal at 76.2 ppm shows that there is a 20% $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$ contamination. As shown by Figure 7, the preparation of the same complex by the diiron nonacarbonyl method gives $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ free of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$.

The infrared spectrum (heptane) and ^1H NMR spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ are shown in Figures 8 and 9,

Figure 4. P-31 NMR spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$ (decoupled)

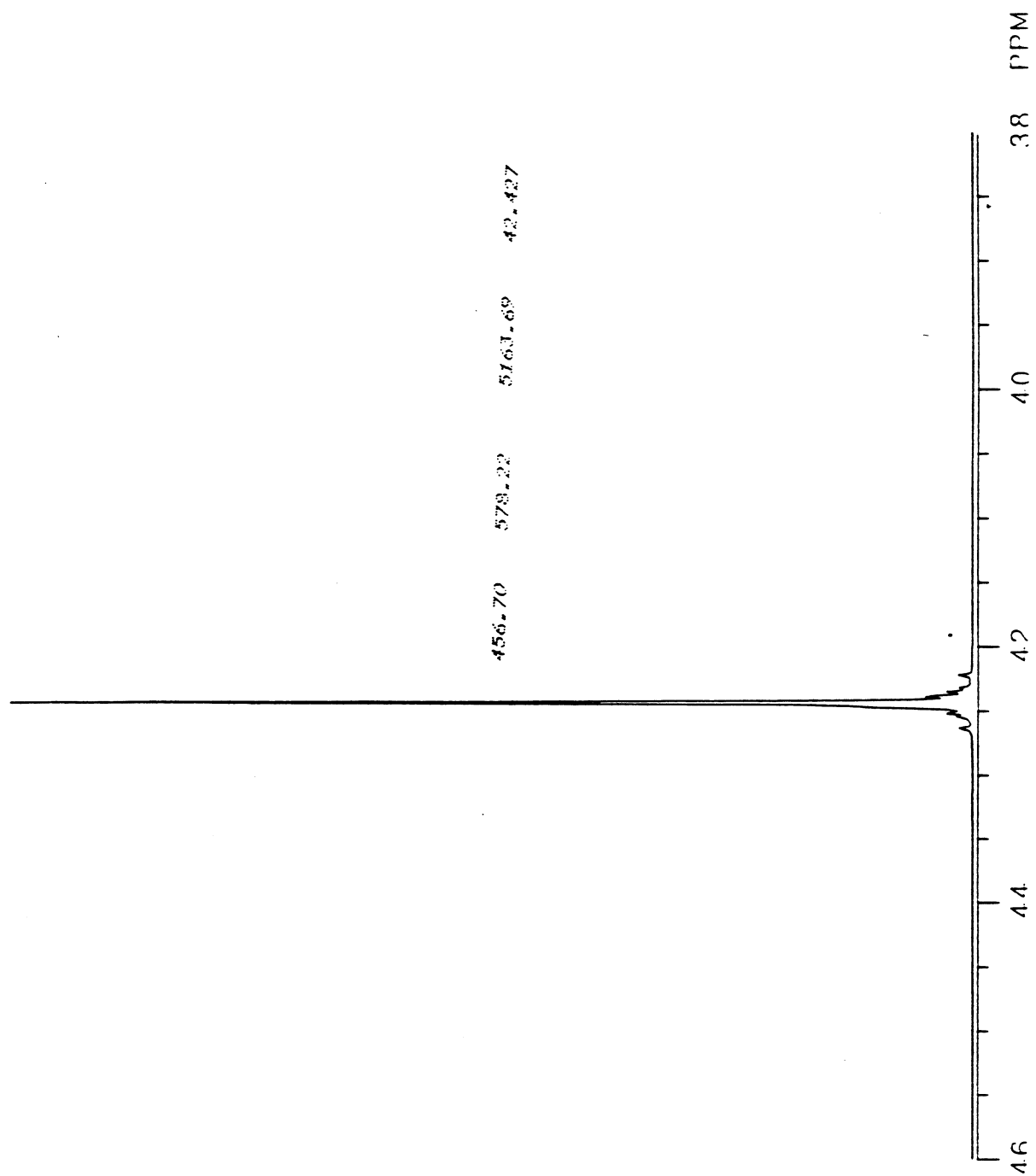


Figure 5. P-31 NMR spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$ (coupled)

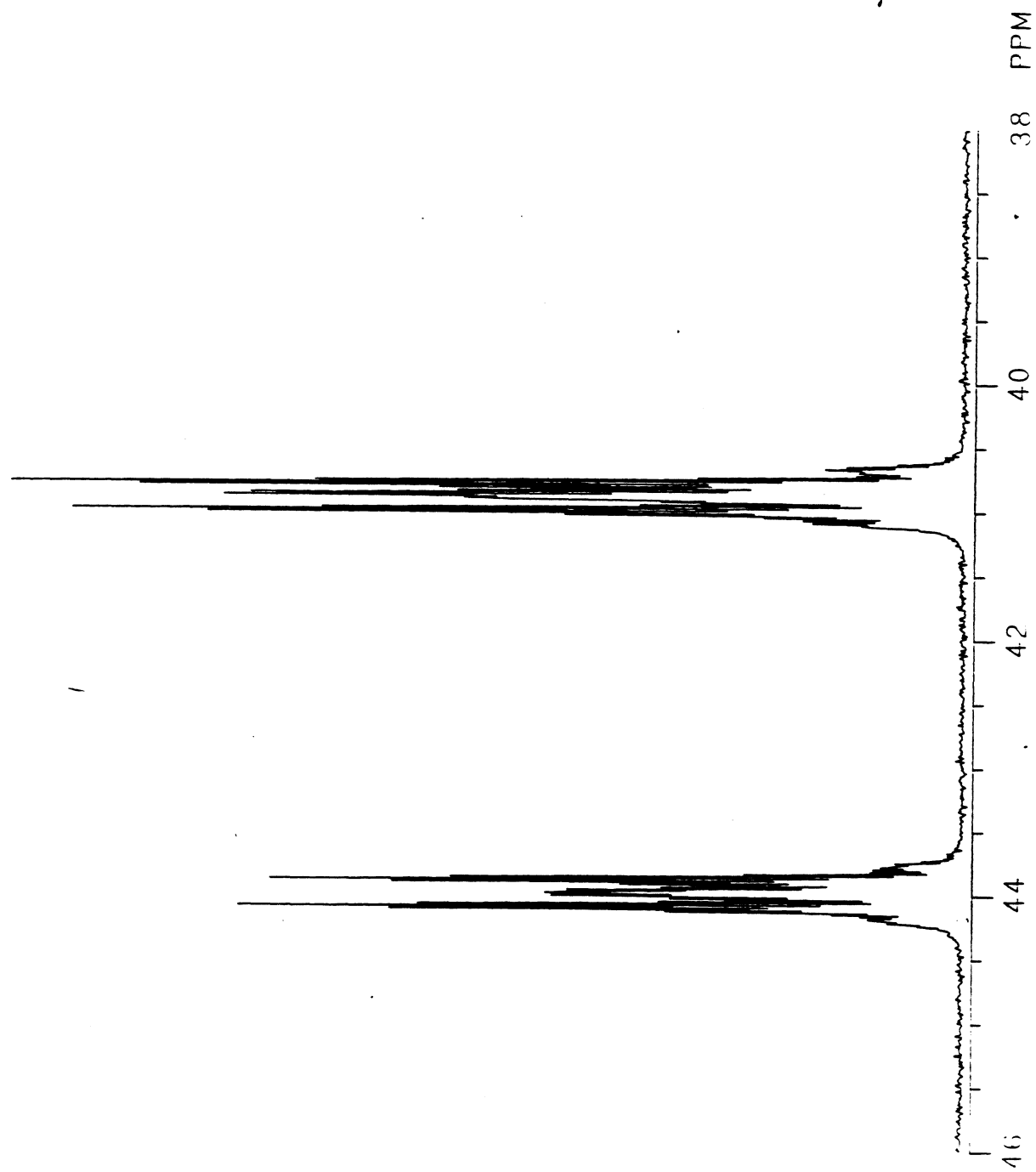


Figure 6. P-31 NMR spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ (method 1)

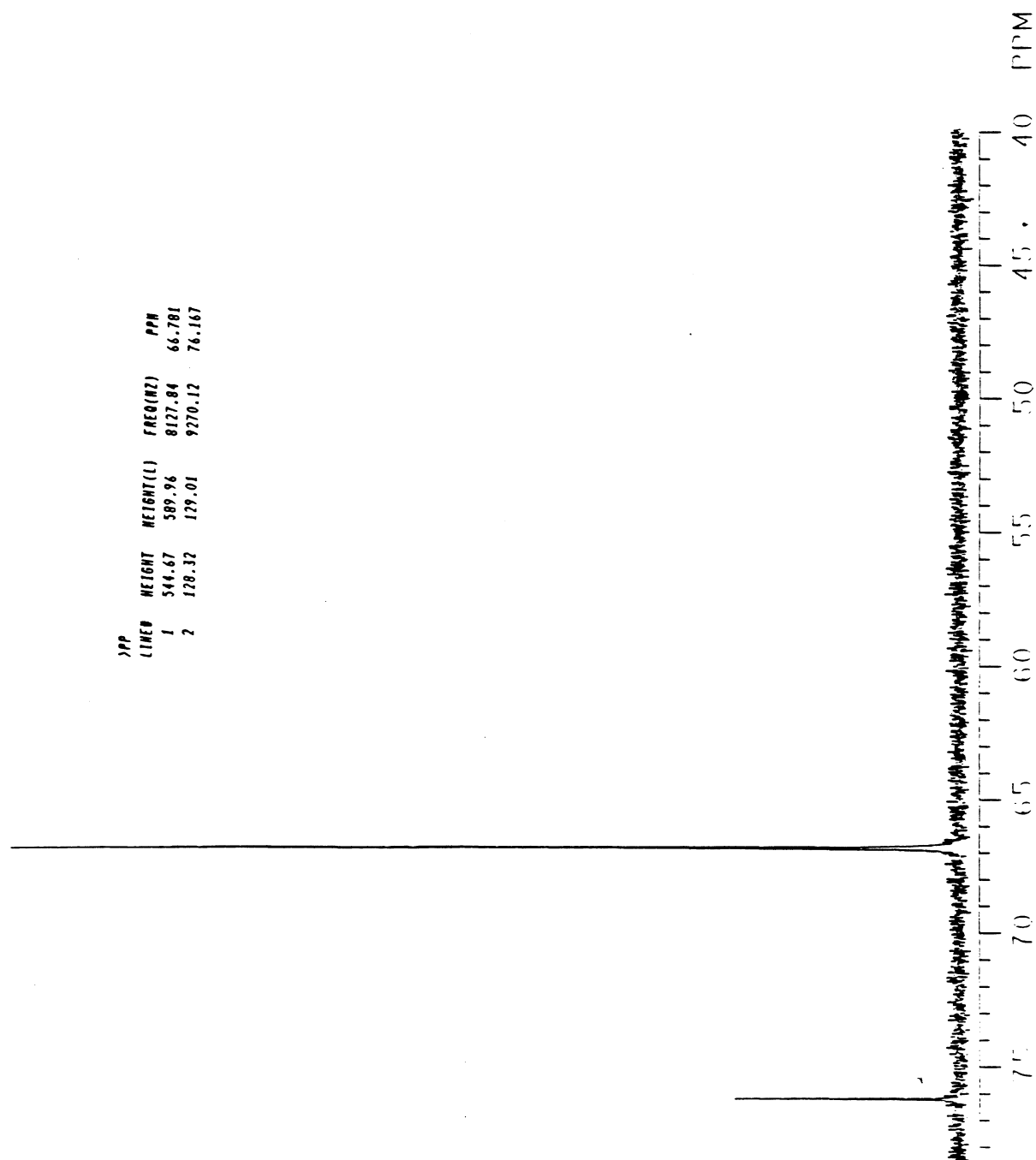


Figure 7. P-31 NMR spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ (method 2)

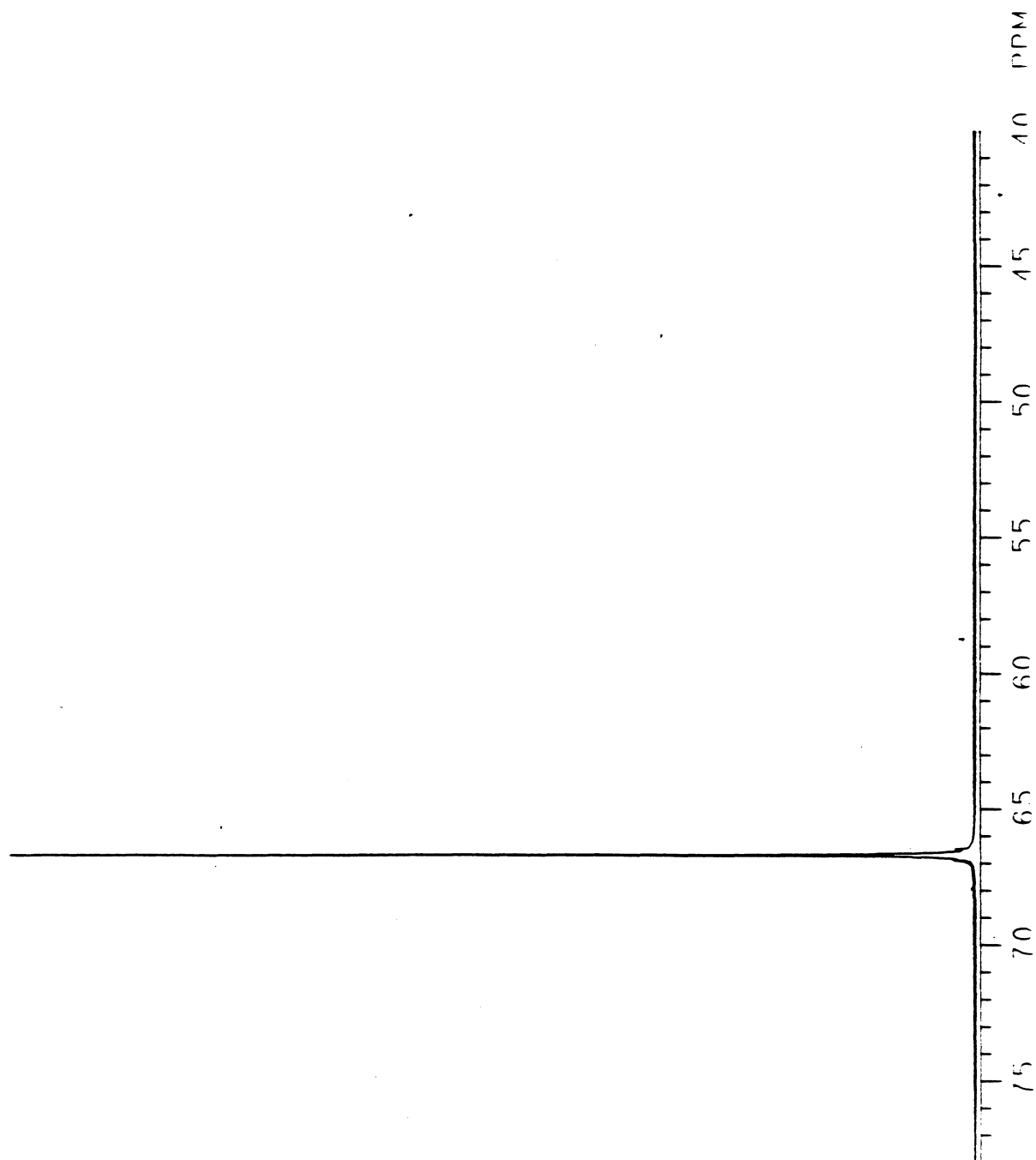


Figure 8. Infrared spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH=CH}_2$ (in chloroform)

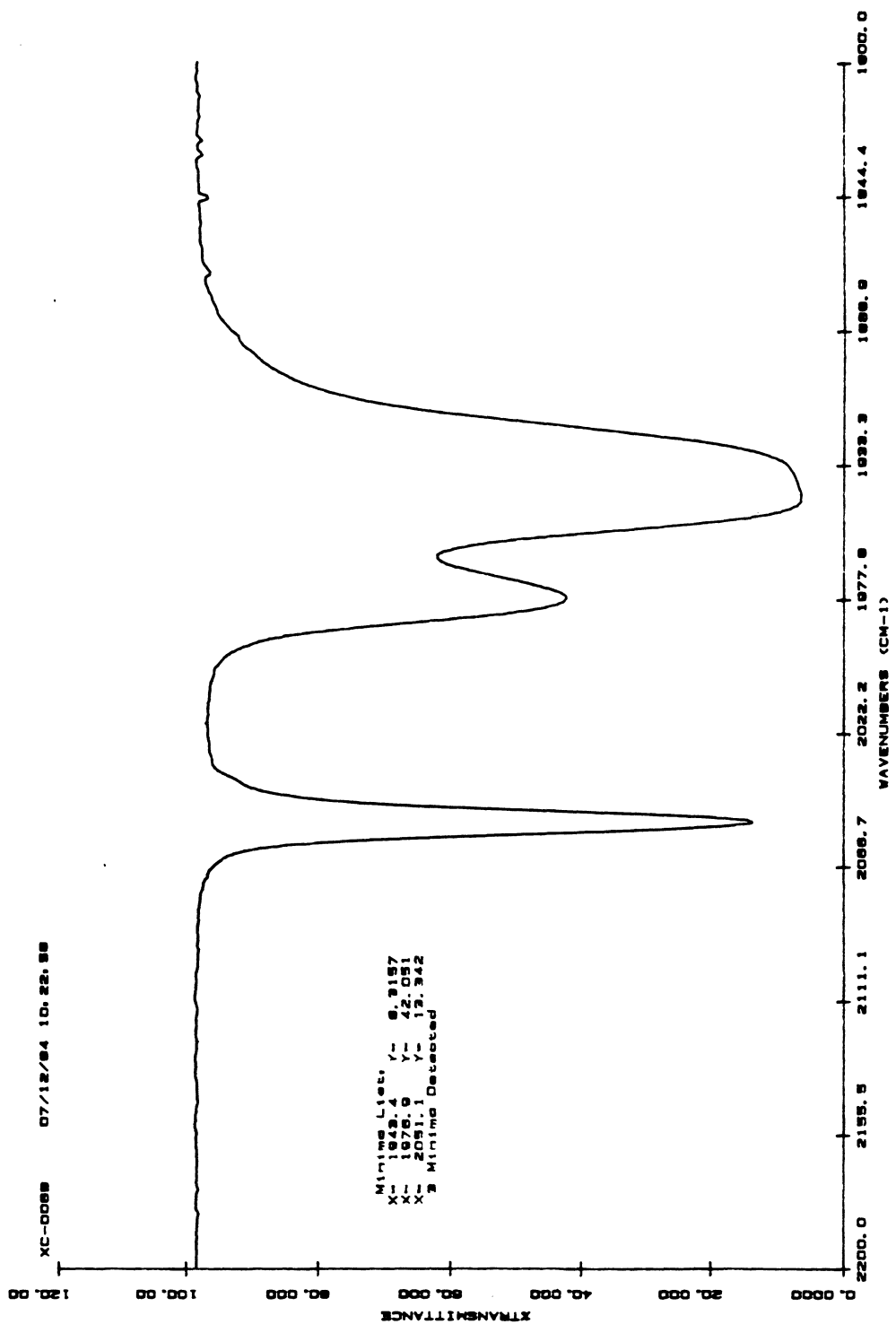
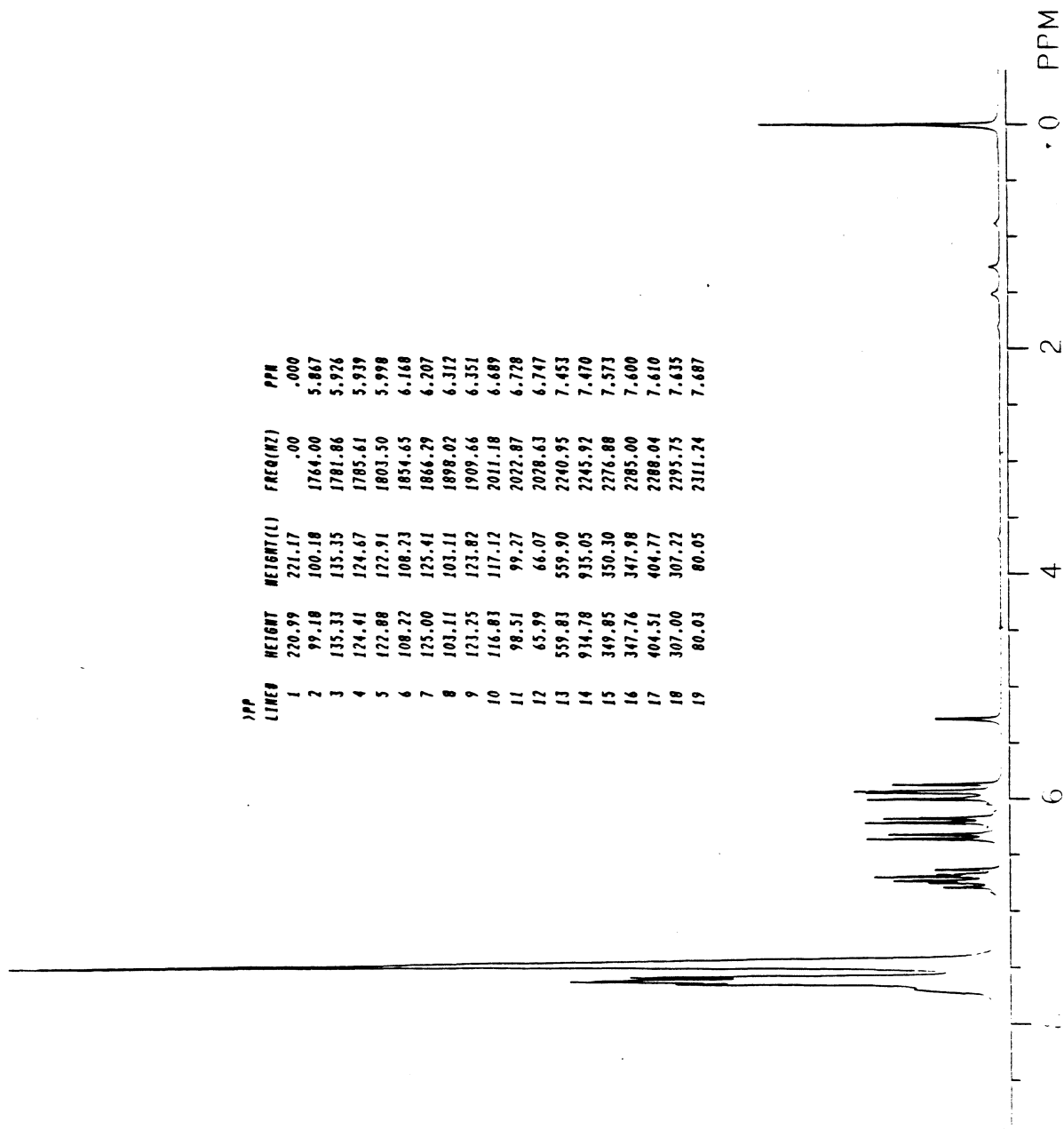
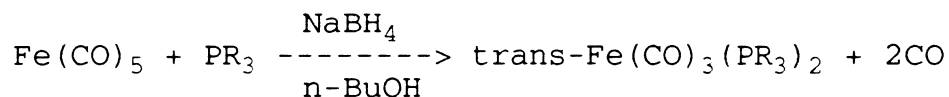


Figure 9. Proton NMR spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$



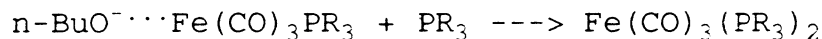
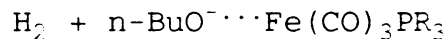
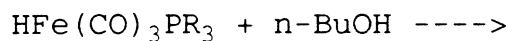
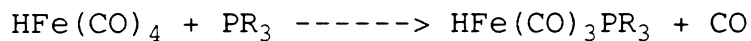
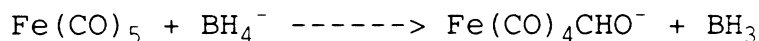
respectively. The infrared spectrum of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ is very similar to that for $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$, shown in Figure 2. As these complexes have the same symmetry, this is an expected result. The proton spectrum (Figure 9) shows, in addition to the phenyl region a very complex set of signals from 5.8 to 6.7 ppm that arise from the phosphorus coupled vinyl protons.

Keiter's method¹⁹ was used for the preparation of $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$ complexes. Iron pentacarbonyl reacts with alkyl and arylphosphine and NaBH_4 in refluxing 1-butanol to give $\text{trans-Fe}(\text{CO})_3(\text{PR}_3)_2$ without contamination from $\text{Fe}(\text{CO})_4\text{PR}_3$.



where PR_3 is PPh_2H or $\text{PPh}_2\text{CH}=\text{CH}_2$.

Keiter²⁰ has postulated a mechanism of this reaction:



The principal intermediate during the reaction is likely to be $[\text{HFe}(\text{CO})_3\text{PR}_3]^-$ since $[\text{Et}_4\text{N}]^+[\text{HFe}(\text{CO})_3\text{PR}_3]^-$,

prepared independently, rapidly reacts with 1 equivalent of PPh_3 in refluxing 1-butanol to yield selectively $\text{trans-Fe(CO)}_3(\text{PR}_3)_2$ (67%). More recently Brunet²¹ has confirmed most of the steps shown in the reaction sequence.

Two derivatives of iron pentacarbonyl of the type $\text{trans-Fe(CO)}_3(\text{PR}_3)_2$ are of D_{3h} symmetry. The two phosphine ligands occupy the two axial positions while the carbonyl ligands occupy the three equatorial positions. The number of infrared active modes in the carbonyl region of the infrared spectrum can be derived by standard symmetry procedures. Only one stretching mode (E') is infrared active, while two bands, which are due to stretching modes, are expected to be observed in the Raman spectrum. Furthermore, there are two bending modes (A_2'', E') which are infrared active. However, these vibrational modes appear below 700 wavenumbers in the infrared spectrum and were not used in the identification of the compound.

The infrared spectrum of $\text{Fe(CO)}_3(\text{PPh}_2\text{H}_2)$ is shown in Figure 10. An intense broad signal is observed along with a very weak one. The broadening of the intense signal and the appearance of the weak one is the result of the complex having lower symmetry than the expected D_{3h} .

The proton coupled and decoupled P-31 NMR spectra

Figure 10. Infrared spectrum of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$ (in chloroform)

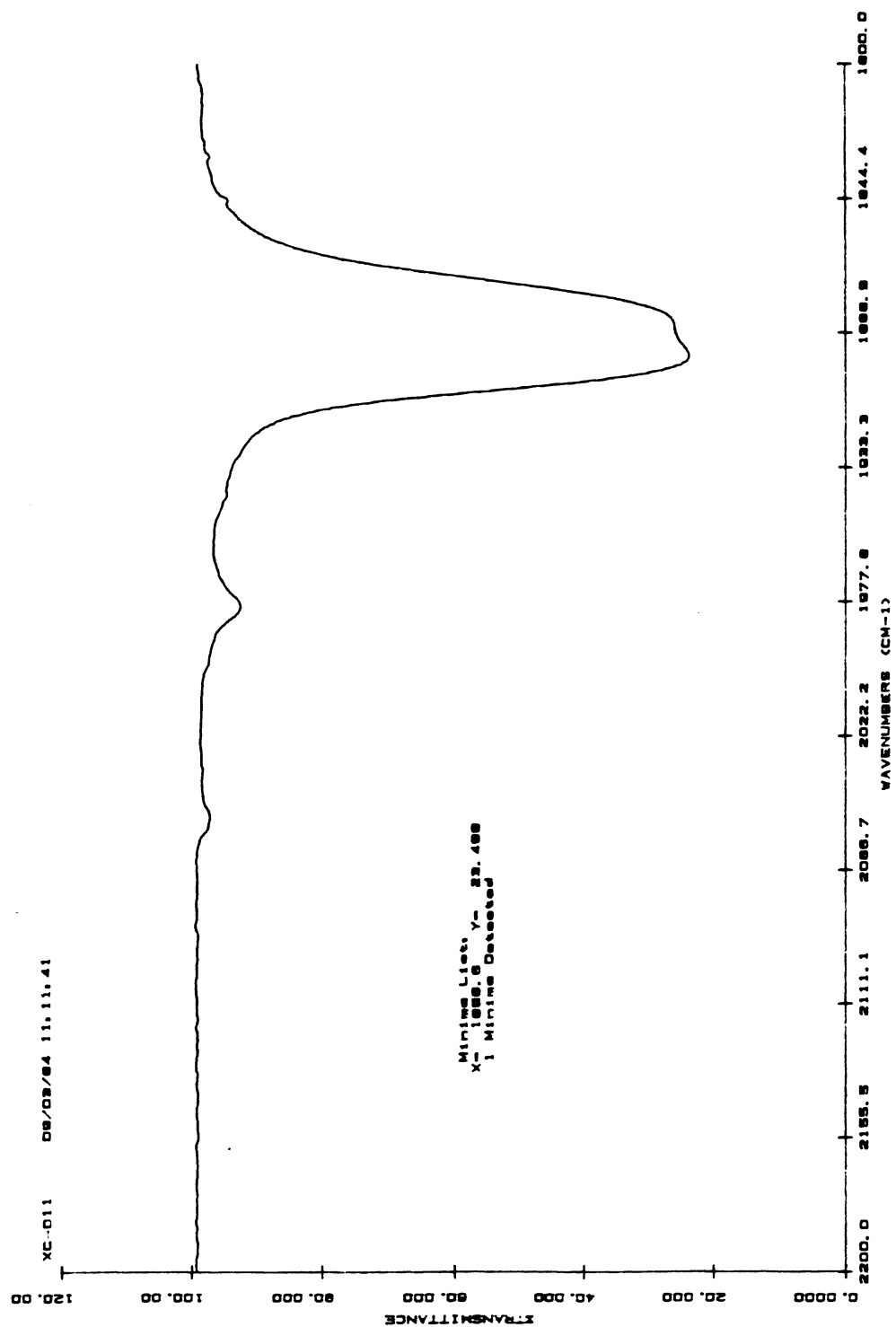


Figure 11. P-31 NMR spectrum of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$ (coupled)

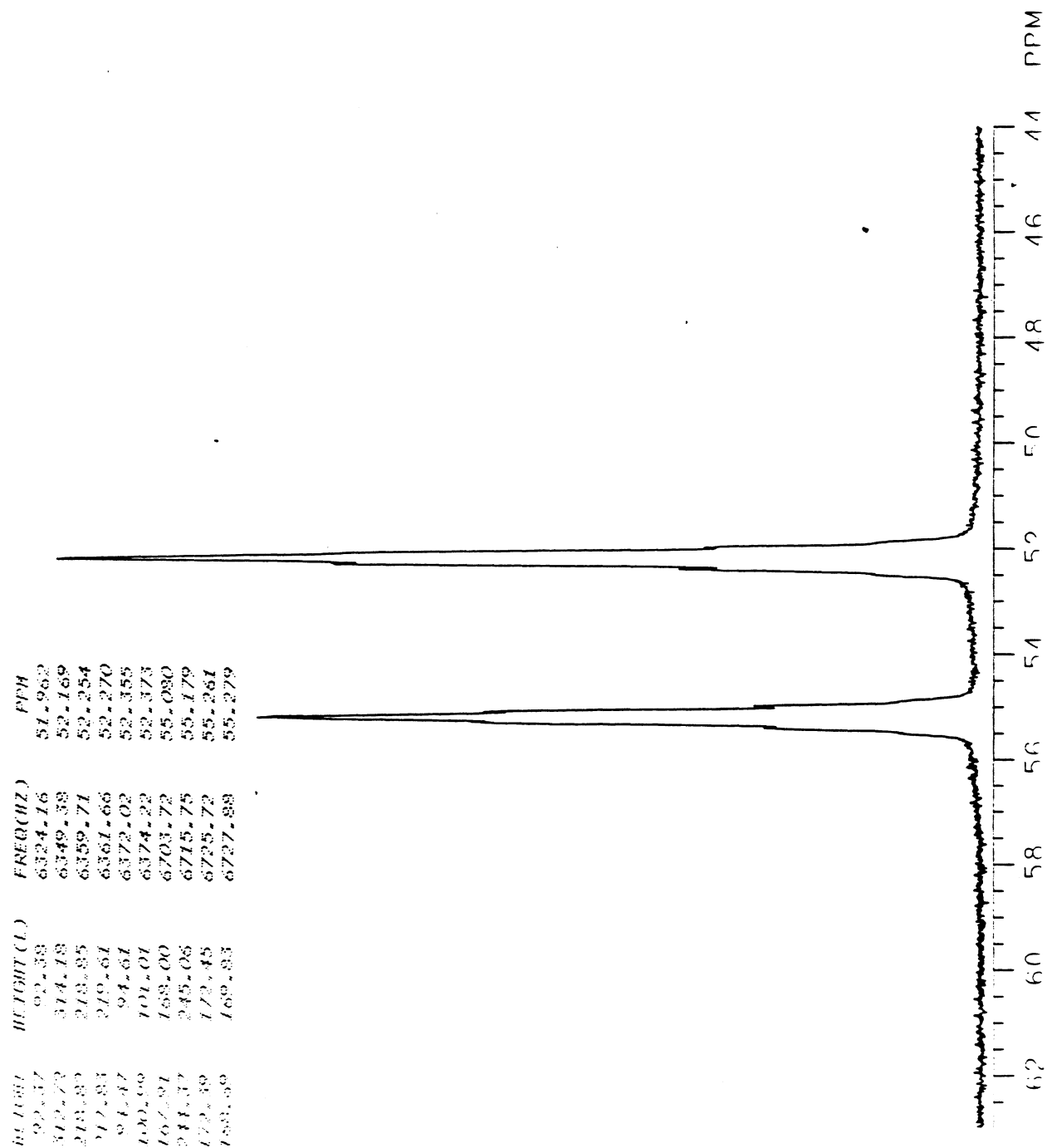


Figure 12. P-31 NMR spectrum of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$ (decoupled)

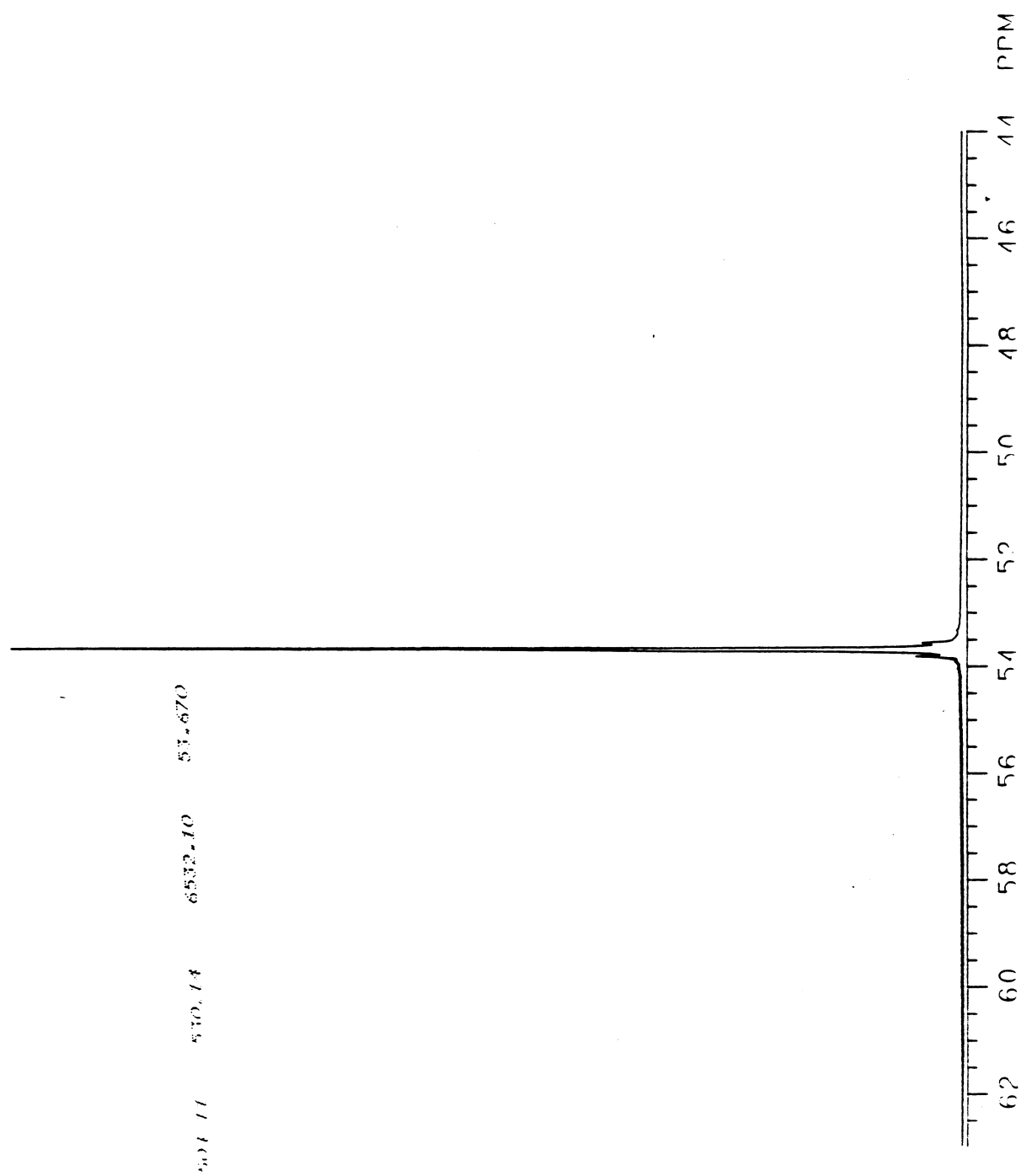


Figure 13. Proton NMR spectrum of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$

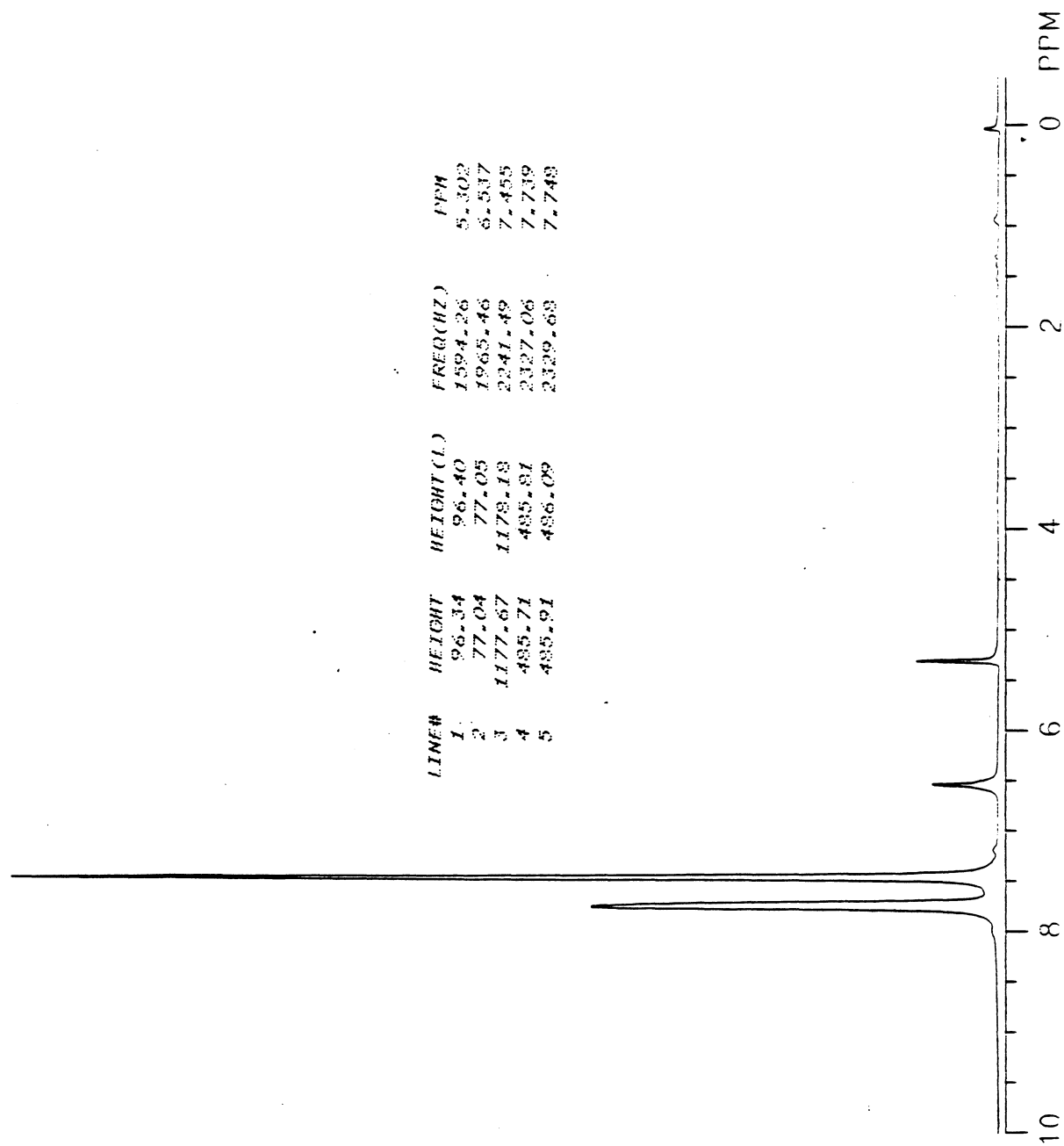
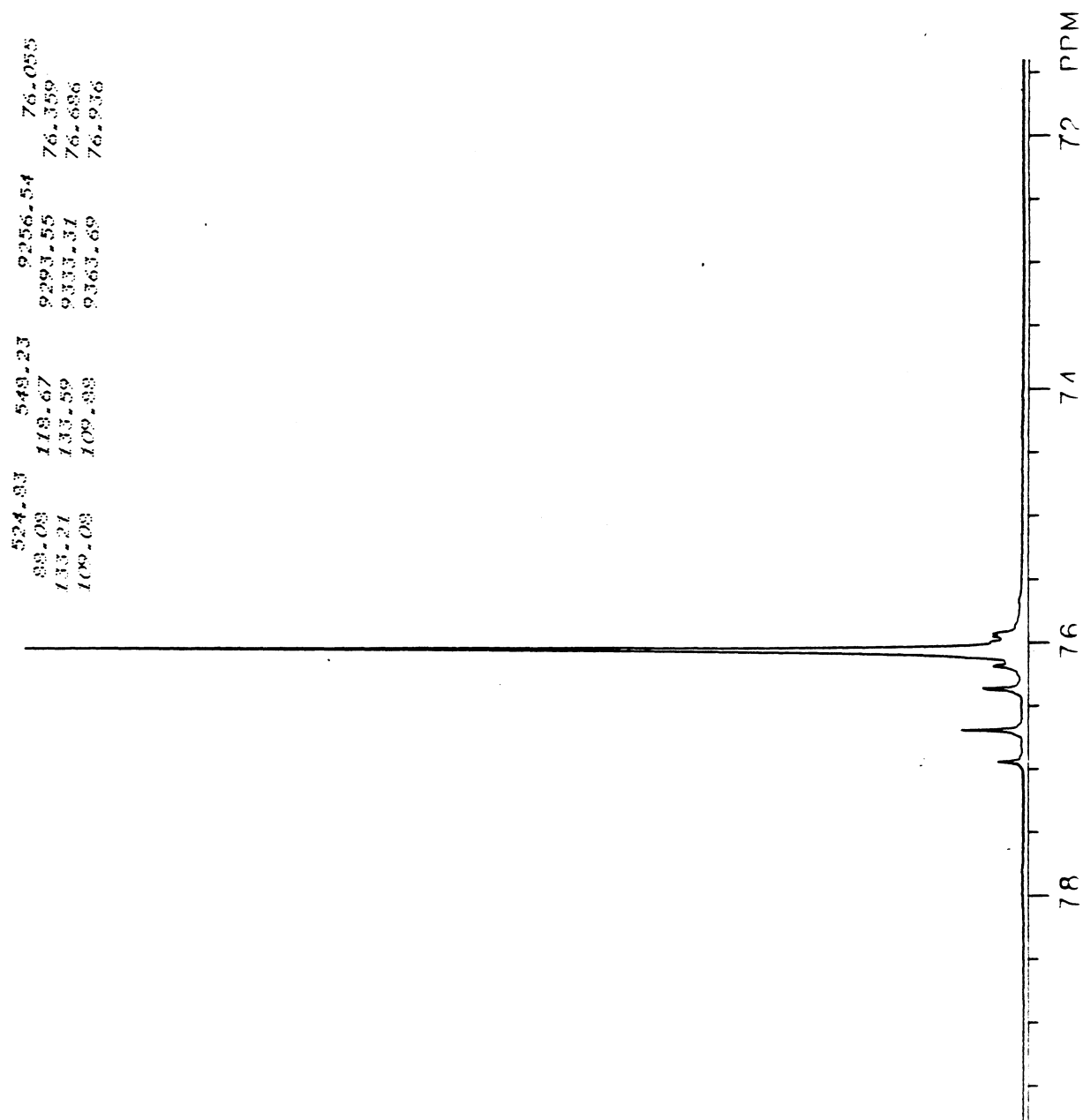


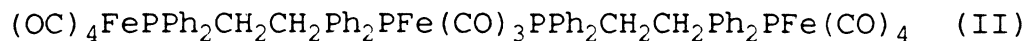
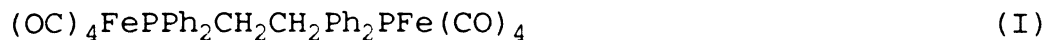
Figure 14. P-31 NMR spectrum of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$



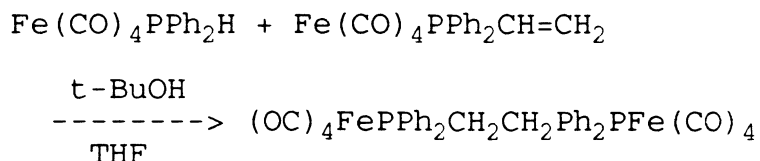
of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$ are shown in Figure 11 and 12, respectively. The separation of two peaks of 366 Hz in the coupled spectrum gives the coupling constant between the ^{31}P nucleus and the ^1H nucleus. The ^1H NMR spectrum of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$ (Figure 13) supports the presence of a P-H bond in the desired product. As found in $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$, one component of the expected doublet is hidden in the phenyl region. The other component is found at 6.5 ppm. The signal at 5.3 ppm is the result of CH_2Cl_2 .

In addition to the principal signal, observed at 76 ppm, one observes several low intensity signals in the proton decoupled P-31 NMR spectrum of trans- $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$ shown in Figure 14. The three downfield signals of low intensity are part of an AB quartet and arise from $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)(\text{PPh}_2\text{CH}_2\text{CH}_3)$. We can conclude that the reaction for the preparation of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$ leads to some reduction of the vinyl group to give trans- $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)(\text{PPh}_2\text{CH}_2\text{CH}_3)$.

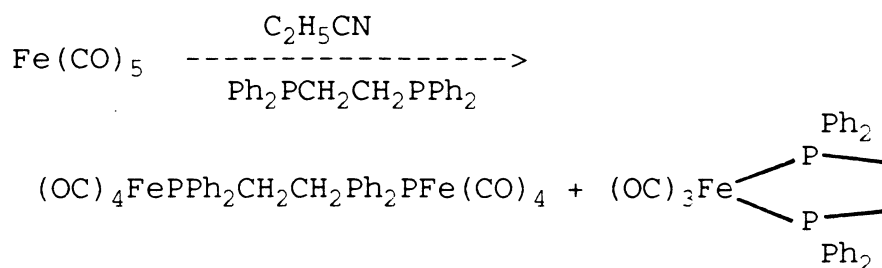
Before attempting to synthesize iron polymers, we tried to synthesize a series of oligomers in which the iron atom centers were linked by the bridges of the $\text{PCH}_2\text{CH}_2\text{P}$ units. The following two compounds have been constructed:



The bimetallic complex was prepared by using a base-catalyzed addition reaction.



The bimetallic complex has been reported by Reckziegel²² who used a substitution reaction for its preparation.



The bridging complex and the chelated complex can be separated by sublimation at reduced pressure.

Reckziegel provided the infrared data of the bridging complex, but the yield, melting point and NMR spectrum were not provided. It is obvious that it appeared as only a minor component.

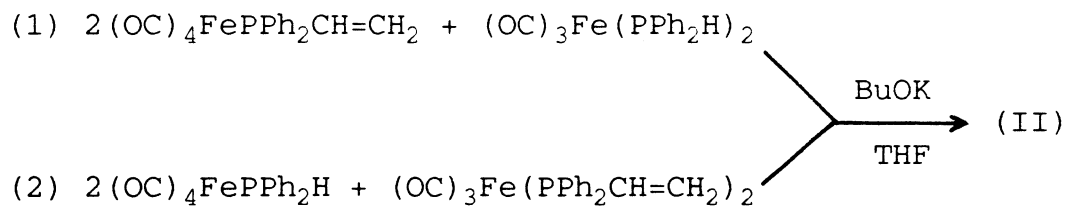
A good yield (69%) of bimetallic complex has been obtained from the base-catalyzed addition reaction and the product was free of contamination by bidentate complexes. This result demonstrated that the base-catalyzed addition between the monometallic complexes

is selective, unlike more traditional reactions.

Since the two $-\text{Fe}(\text{CO})_4$ moieties of the bimetallic complex have the same symmetry and electronic environment, the infrared spectrum (Figure 15) shows that expected of a complex with typical C_{2v} symmetry. The ^1H NMR spectrum is shown in Figure 16. The peak at 1.3 ppm, we believe, arises from vacuum grease. The same signal appears in many of our proton spectra. The peak at 2.7 ppm arises from the hydrogen atoms of the ethane bridge. These hydrogen atoms are chemically equivalent and magnetically nonequivalent. Unlike the hydrogen atoms in the starting materials, all phenyl protons give one strong signal at 7.5 ppm.

The proton decoupled P-31 NMR spectrum is shown in Figure 17. The phosphorus atoms in the bimetallic complex are magnetically equivalent and give rise to one peak at 69.5 ppm.

To our knowledge, the trimetallic complex of iron, $(\text{OC})_4\text{FePPh}_2\text{CH}_2\text{CH}_2\text{Ph}_2\text{PFe}(\text{CO})_3\text{PPh}_2\text{CH}_2\text{CH}_2\text{Ph}_2\text{PFe}(\text{CO})_4$ (II), has never been reported. Schemes for two synthetic routes are shown below:



We have examined each of the two reactions as routes

Figure 15. Infrared spectrum of $(OC)_4FePPh_2CH_2CH_2Ph_2PFe(CO)_4$ (in chloroform)

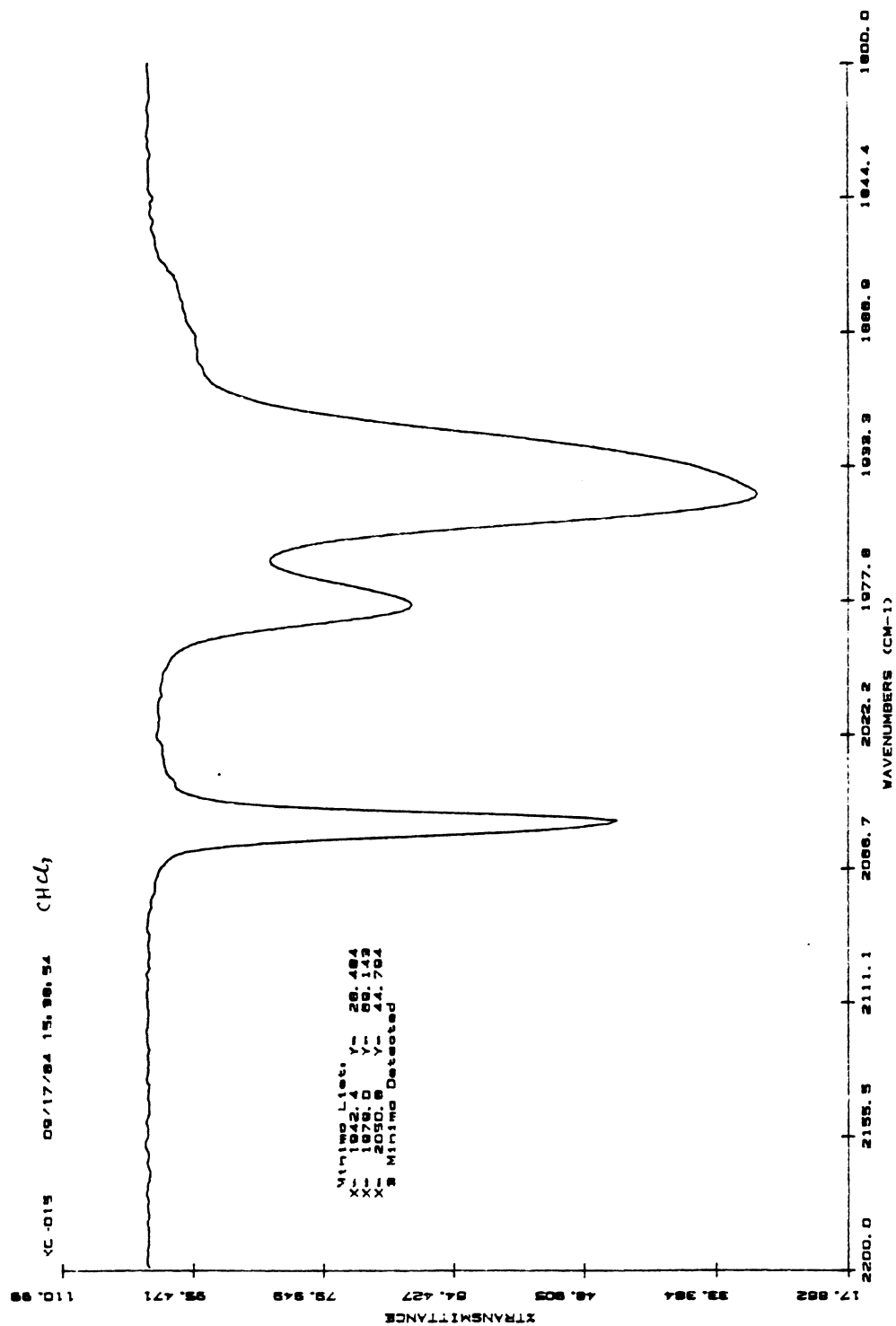


Figure 16. Proton NMR spectrum of $(OC)_4FePPh_2CH_2CH_2Ph_2PFe(CO)_4$

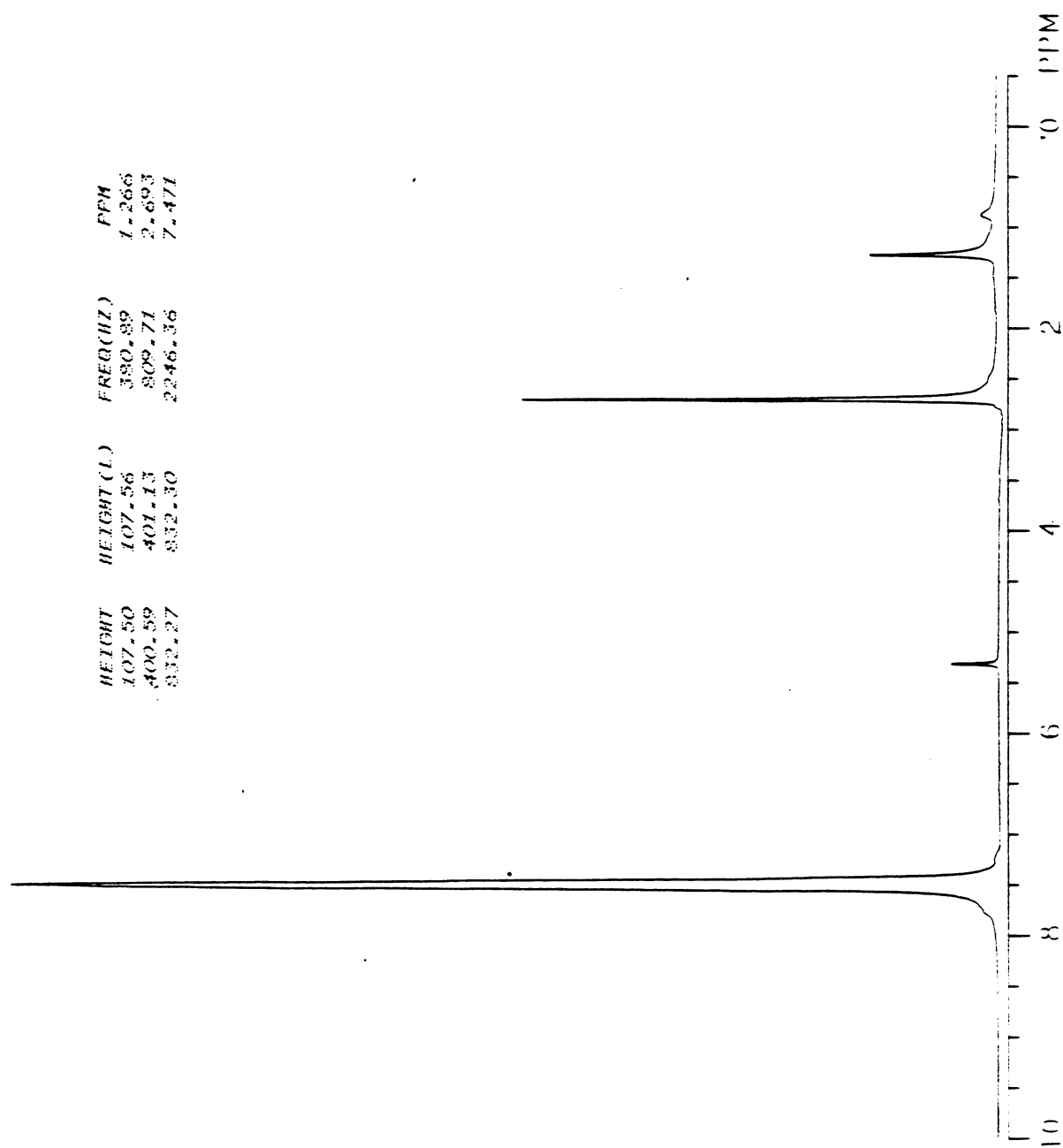
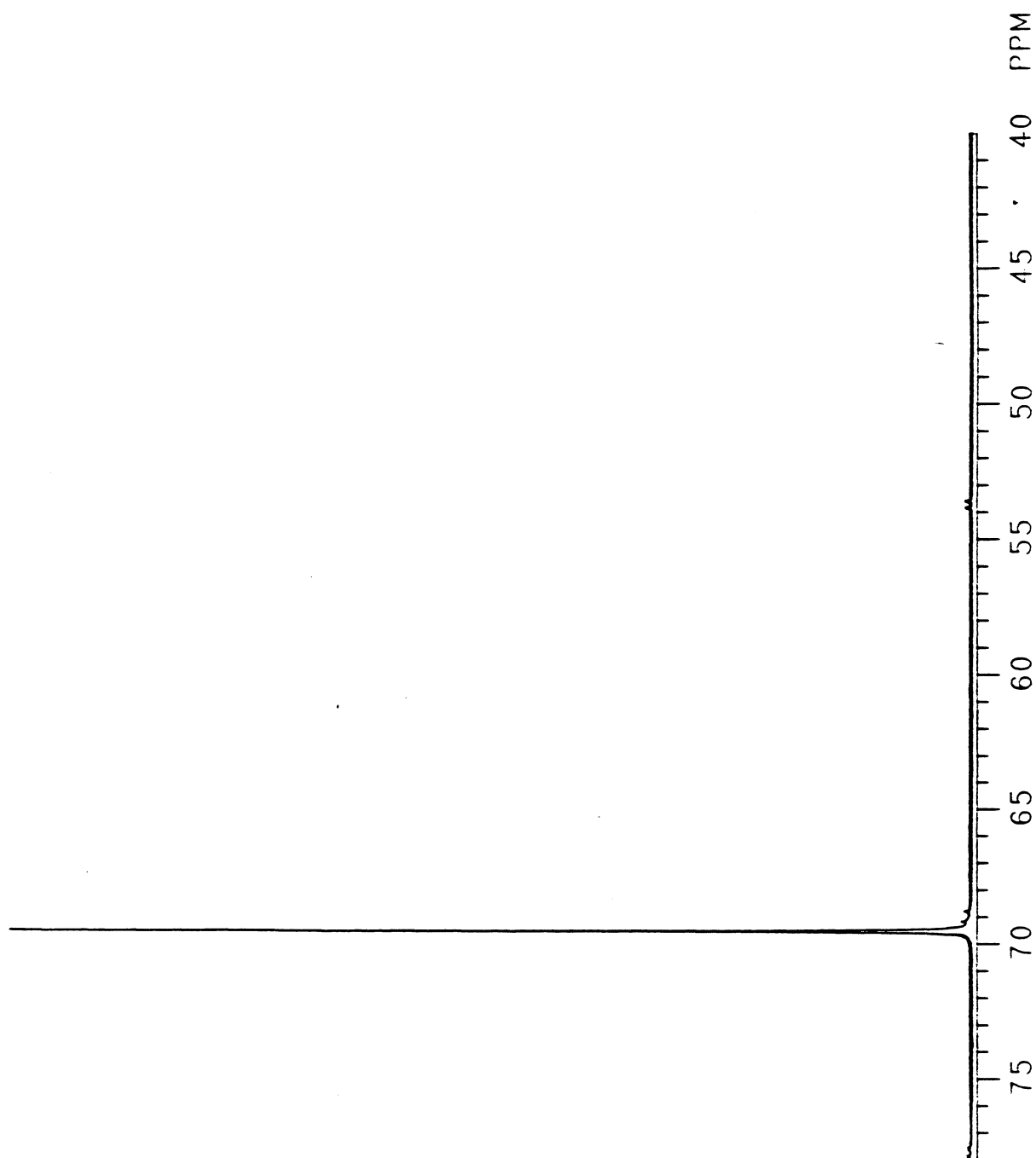


Figure 17. P-31 NMR spectrum of $(OC)_4FePPh_2CH_2CH_2Ph_2PFe(CO)_4$



to the trimetallic complex. We have been successful with reaction (1) but not successful with reaction (2).

In this compound, the center iron carbonyl has D_{3h} symmetry and both terminal iron carbonyls have C_{3v} symmetry. Accordingly, the infrared spectrum (Figure 18) shows signals for both $-Fe(CO)_3$ and $-Fe(CO)_4$ moieties. A splitting of the E mode ($1876, 1888\text{ cm}^{-1}$) is observed for $-Fe(CO)_3$. As in similar system described earlier the splitting is caused by symmetry that is somewhat lower than D_{3h} .

The hydrogen atoms in the ethane bridges have slightly different electronic environments and one might expect to see two signals in the 1H NMR spectrum. However, since instrumental resolution is not adequate, only one peak is shown in the spectrum (Figure 19).

The proton decoupled P-31 NMR spectrum (Figure 20) give rise to a XAA'X' spectrum that results from an XAA'X' spin system, where A and X represent center and terminal phosphorus nuclei, respectively. All four phosphorus atoms are magnetically nonequivalent. The phosphorus-phosphorus coupling constants can be obtained by analyzing the spectrum. One needs to analyze only the A part of the XAA'X' spectrum since the X part of the spectrum is identical to the A part.

Figure 18. Infrared spectrum of

$(OC)_4FePPh_2CH_2CH_2Ph_2PFe(CO)_3PPh_2CH_2CH_2Ph_2PFe(CO)_4$ (in chloroform)

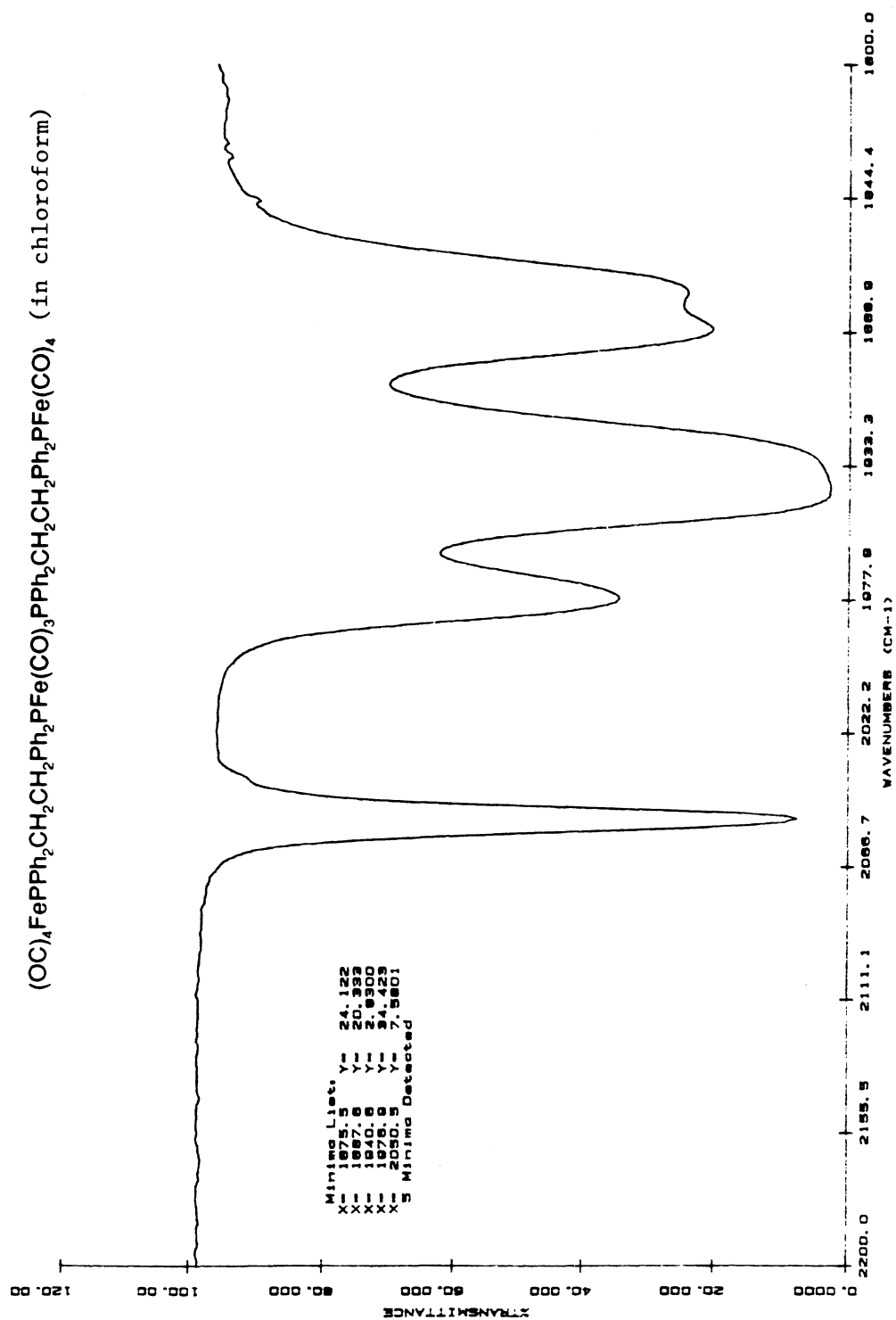


Figure 19. Proton NMR spectrum of

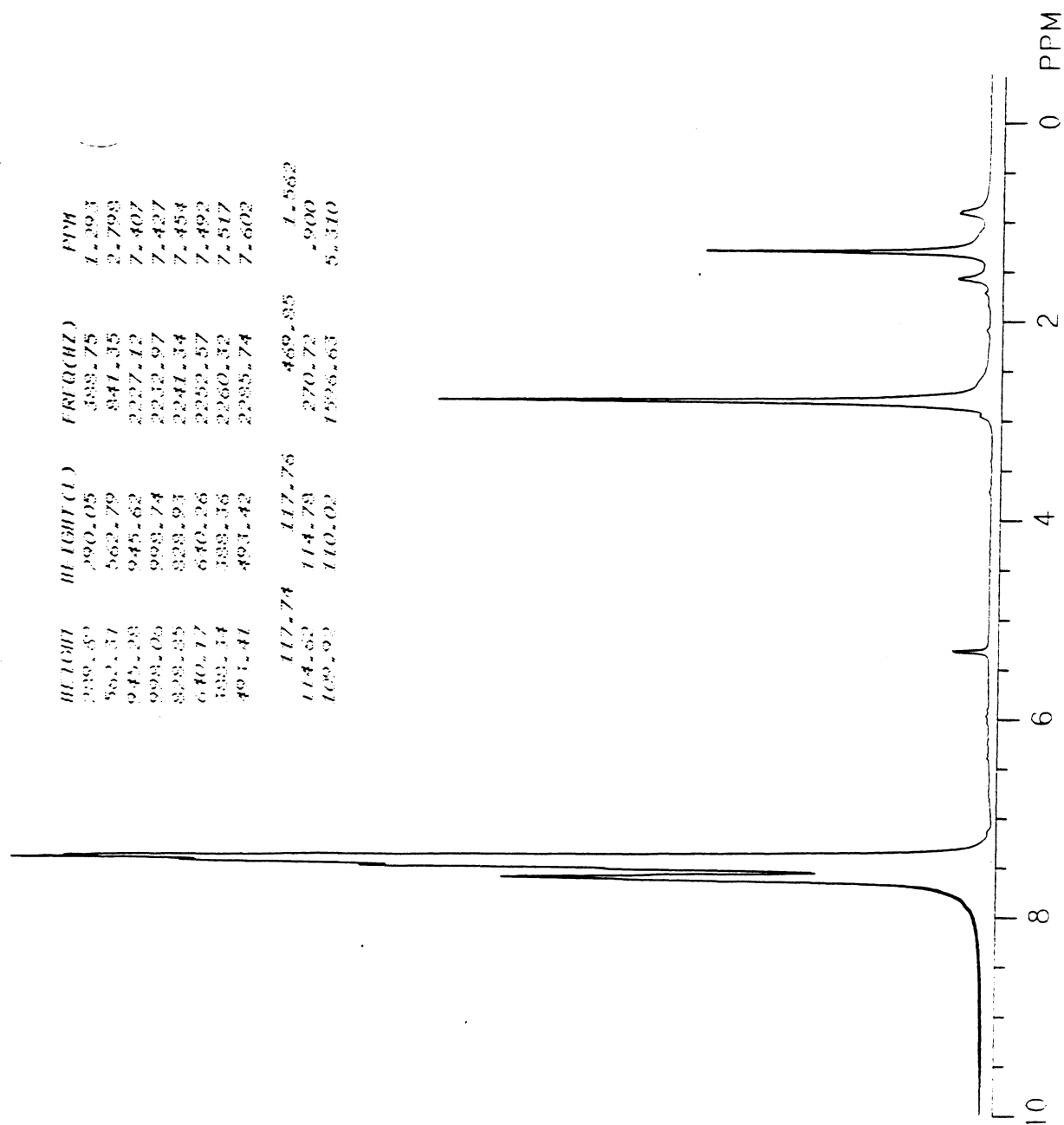
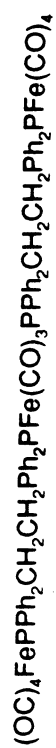
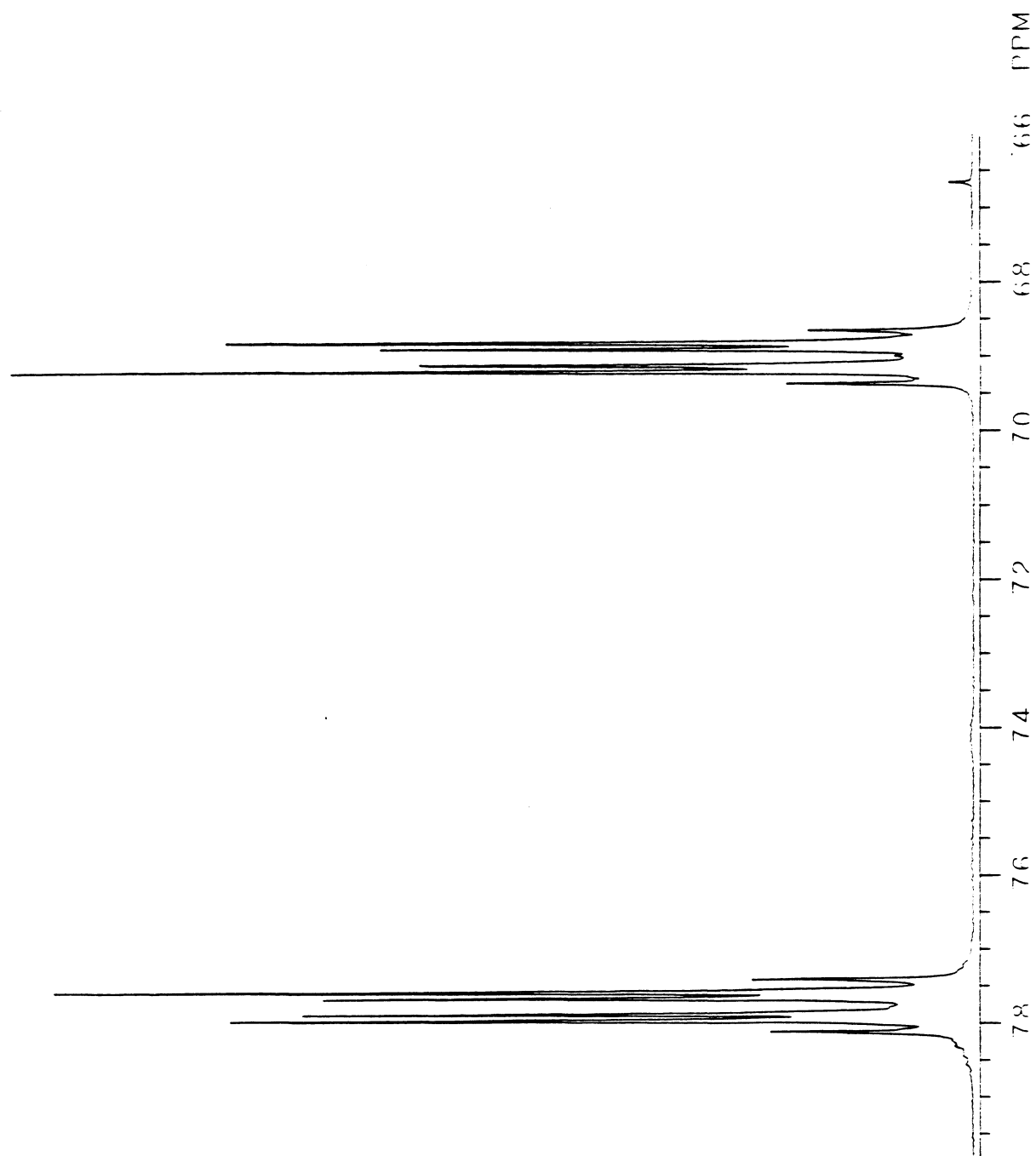
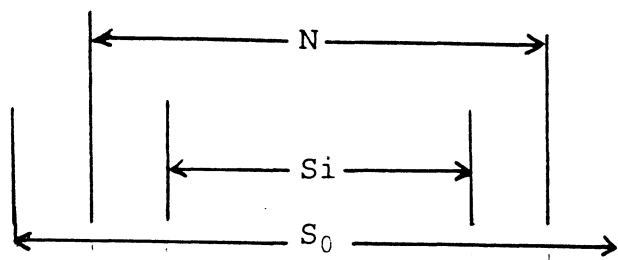


Figure 20. P-31 NMR spectrum of





The inner lines have a separation S_i given by

$$S_i = [(L^2 + J_{AA'}^2)^{1/2} - J_{AA'}]$$

whereas the outer lines have a separation S_0 given by

$$S_0 = [(L^2 + J_{AA'}^2)^{1/2} + J_{AA'}]$$

where $L = |J_{AX} - J_{AX'}|$, $N = |J_{AX} + J_{AX'}|$ and

assuming $J_{XX'} = 0$

According to the data in the A part spectrum (Figure 21),

$$N = 47.02 \text{ Hz}$$

$$S_i = 26.14 \text{ Hz}$$

$$S_0 = 86.63 \text{ Hz}$$

we can solve the both equations and obtain

$$J_{AX} = 47.30 \text{ Hz and } J_{AA'} = 30.25 \text{ Hz.}$$

By using these data, we have simulated the P-31 NMR spectrum of $XAA'X'$ spin system with a 300 MHz Fourier Transform NMR spectrometer. The simulated spectrum (Figure 22) matches the experimental spectrum (Figure 20).

Figure 23 shows the proton decoupled P-31 NMR spectrum of the isolated product from reaction (2) for the trimetallic complex. From the spectrum it can be

Figure 21. Expanded P-31 NMR spectrum of

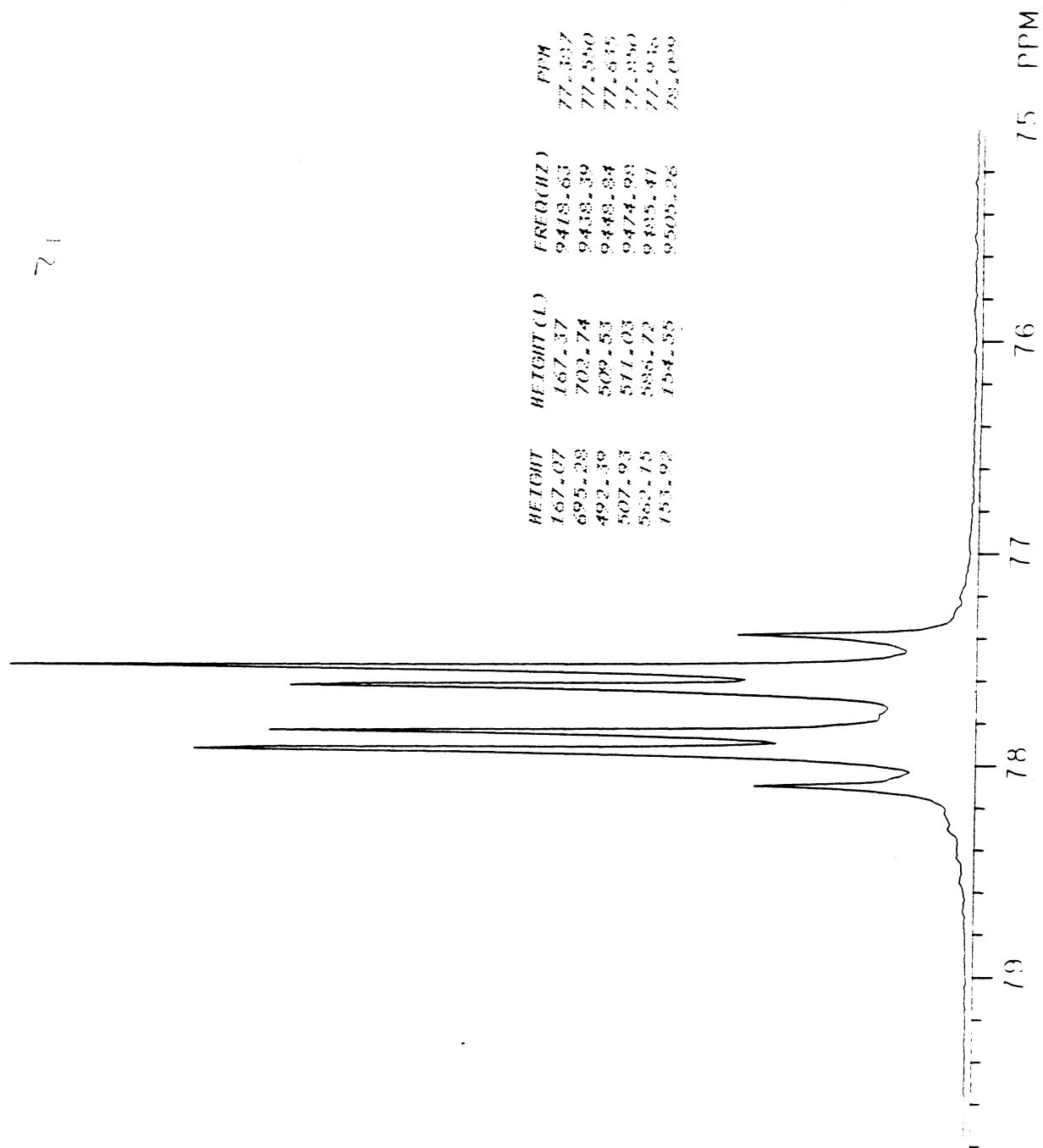


Figure 22. Simulated P-31 NMR spectrum of

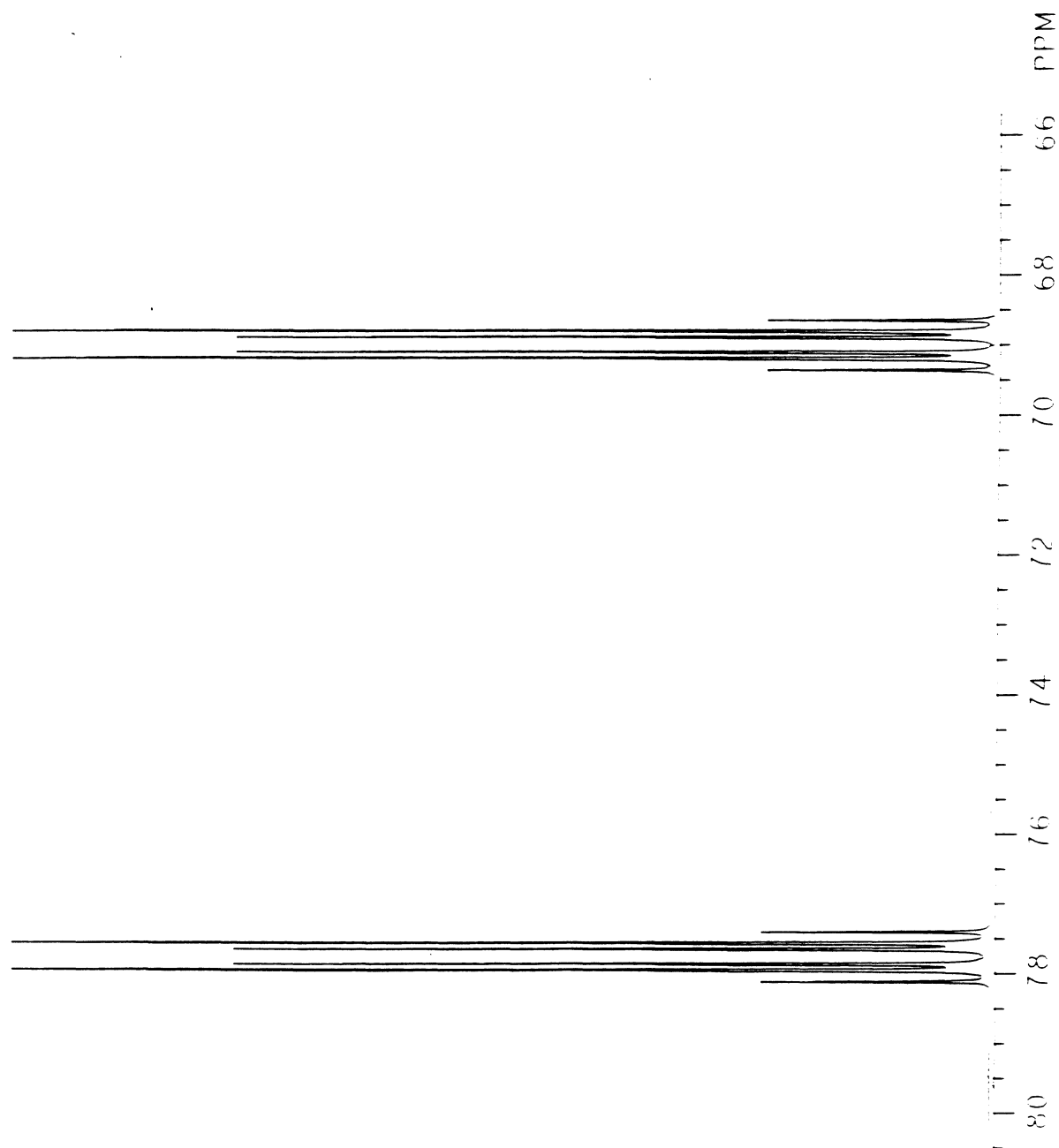


Figure 23. P-31 NMR spectrum of



(method 2)

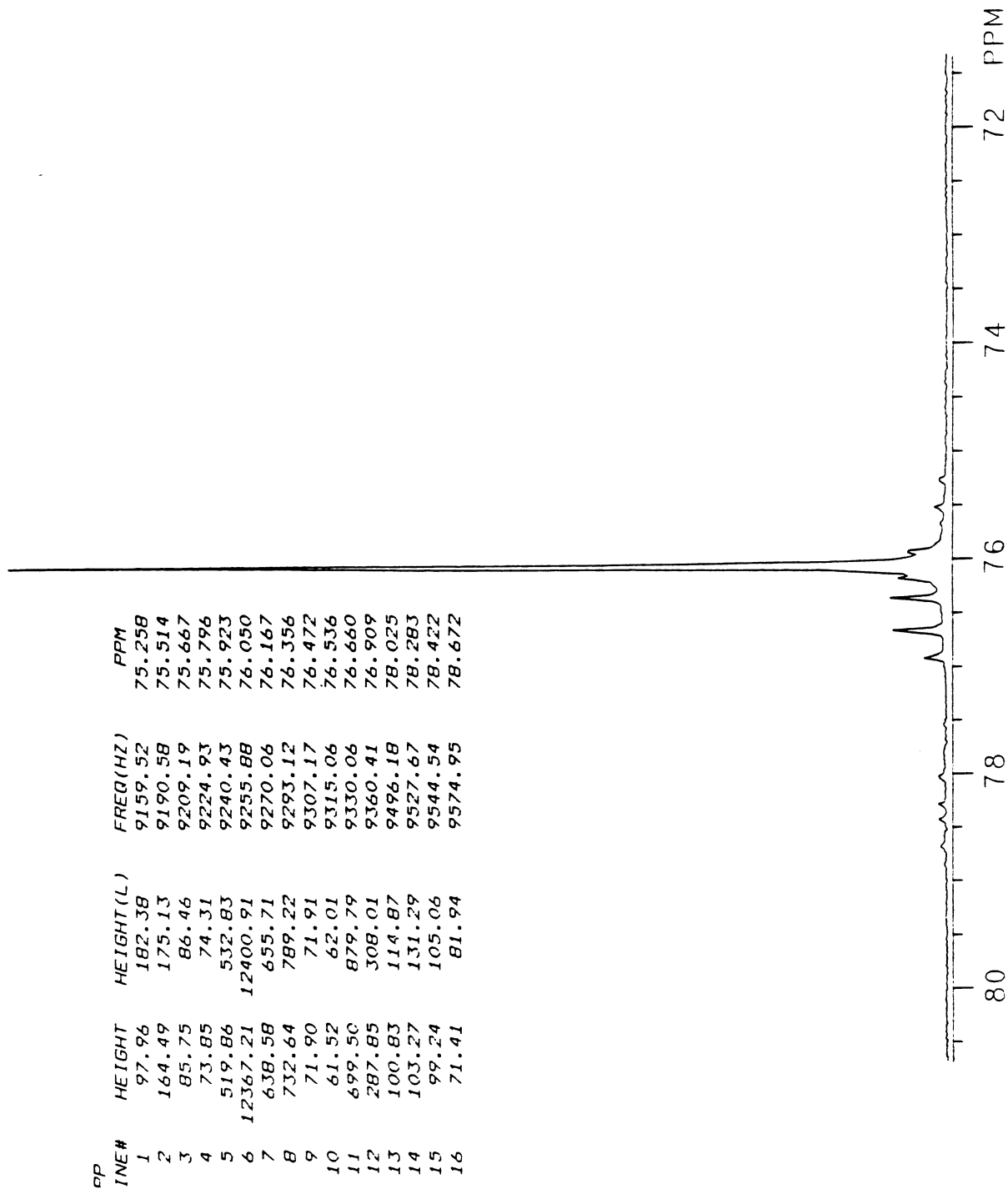
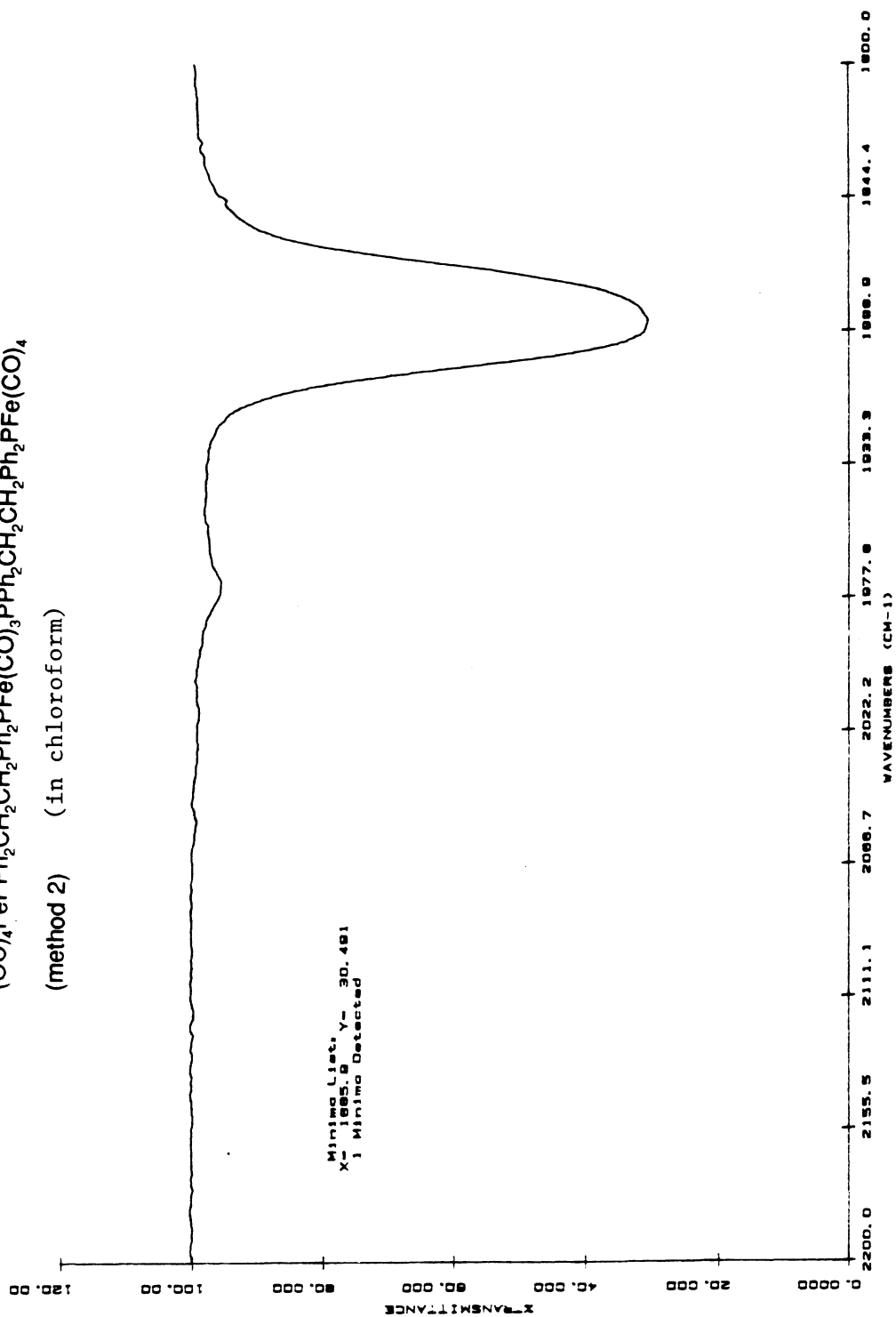


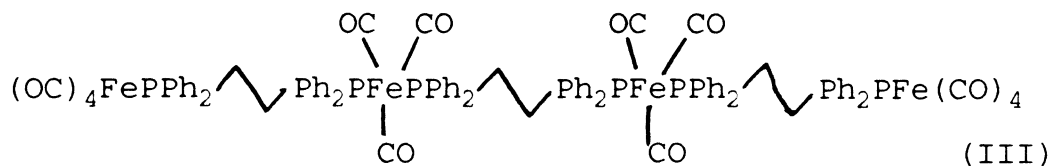
Figure 24. Infrared spectrum of
 $(OC)_4FePPh_2CH_2CH_2Ph_2PFe(CO)_3PPh_2CH_2CH_2Ph_2PFe(CO)_4$
 (method 2) (in chloroform)



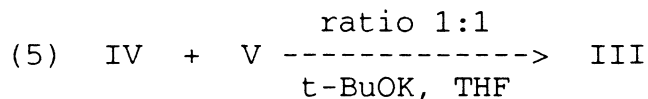
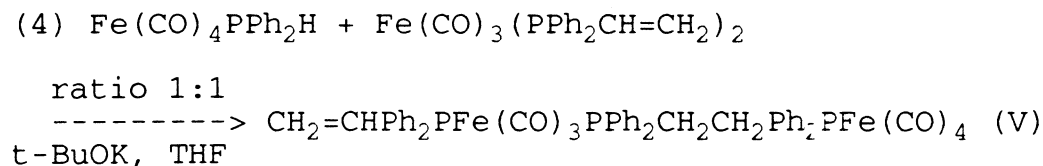
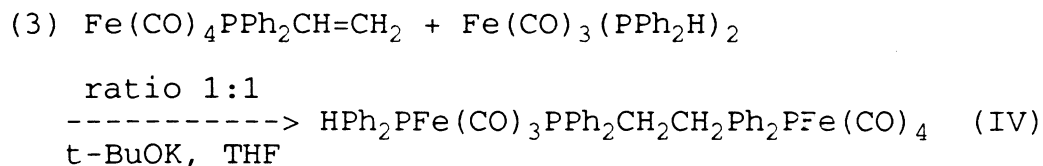
seen that unreacted $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$ is present by comparison with Figure 14. This is confirmed by the infrared spectrum (Figure 24) of this product which shows the single absorption characteristic of the unreacted starting material (see Figure 10). The fate of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$ was not established but its absence as shown by NMR and IR spectra indicated that it undergoes an alternate reaction and is destroyed.

Although all of the reaction conditions were the same as those used in reaction (1), the desired product was not obtained. The reason for the failure of this reaction might be that $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$ is less susceptible than $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ to attack by a nucleophilic reagent. Thus $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$ may react with itself faster than it reacts with the target substrate. Previous work has established that $[\text{W}(\text{CO})_5\text{PPh}_2]^-$ reacts with $\text{W}(\text{CO})_5\text{PPh}_2\text{H}$ to produce anionic species such as $[(\text{OC})_5\text{WPPh}_2\text{W}(\text{CO})_5]^-$, $[(\text{OC})_5\text{WPPh}_2\text{W}(\text{CO})_4\text{PPh}_2\text{H}]^-$ and $[(\text{OC})_4\text{W}(\text{PPh}_2)_2\text{W}(\text{CO})_4]^{2-}$.²³ It is possible that iron complexes analogous to these are present but we have not identified them.

The next oligomer we attempted to synthesize was a four-iron center complex:



The synthetic strategy is shown in the following scheme:



Reactions (3) and (4) were based on reaction (1) and (2), respectively. The stoichiometry was adjusted to optimize their formation. It was our hope to connect complexes IV and V by an addition reaction and thus obtain III. However, we could not obtain III because reaction (4) failed. It should be noted that this reaction is similar to reaction (2) which also failed. The P-31 NMR spectrum of the isolated product (Figure 25) revealed only starting material just as for reaction (2).

We successfully obtained compound IV which is a bimetallic complex. The P-31 NMR spectrum (Figure 26) shows three groups of peaks which correspond to three

Figure 25. P-31 NMR spectrum of

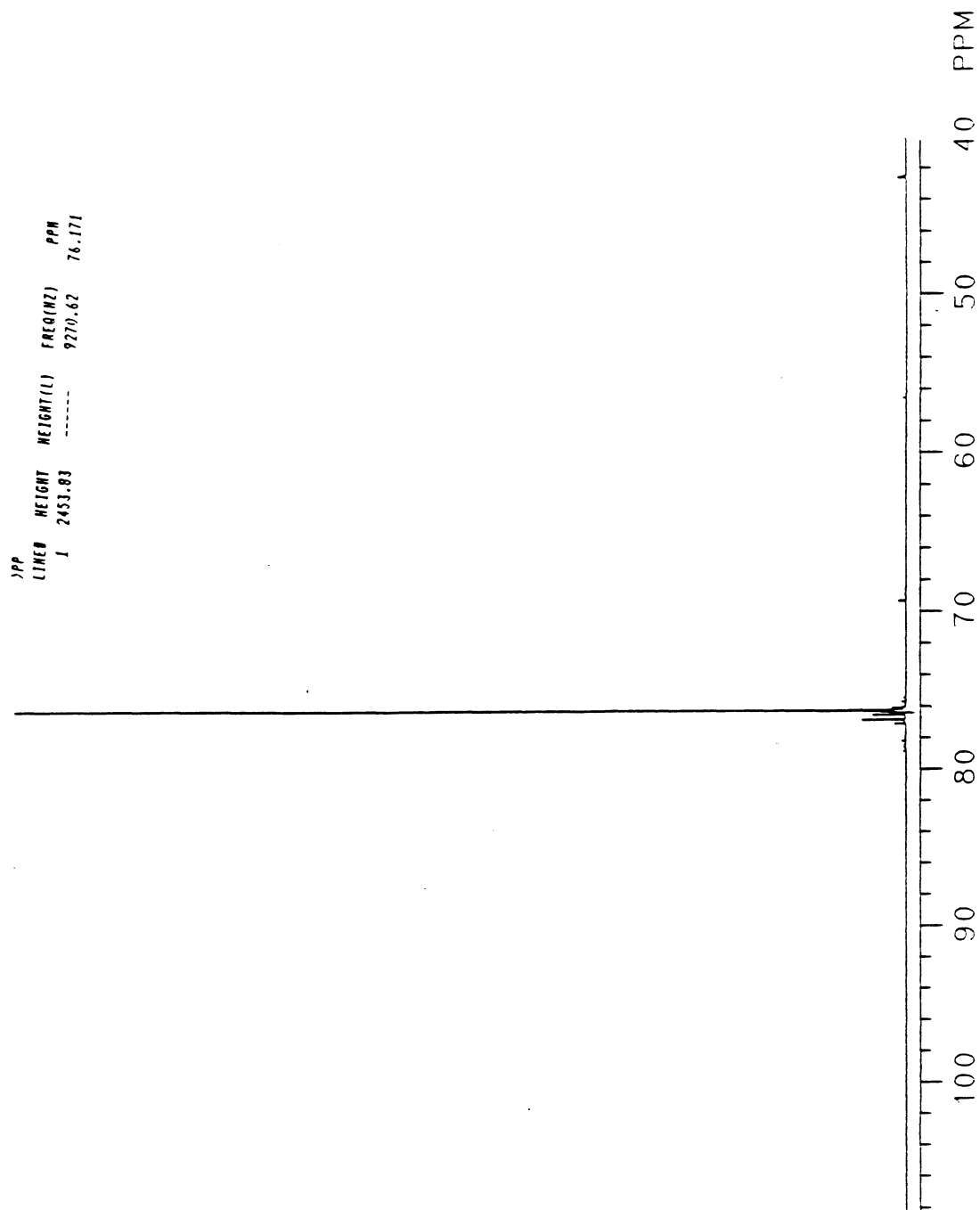
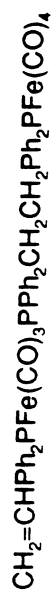


Figure 26. P-31 NMR spectrum of

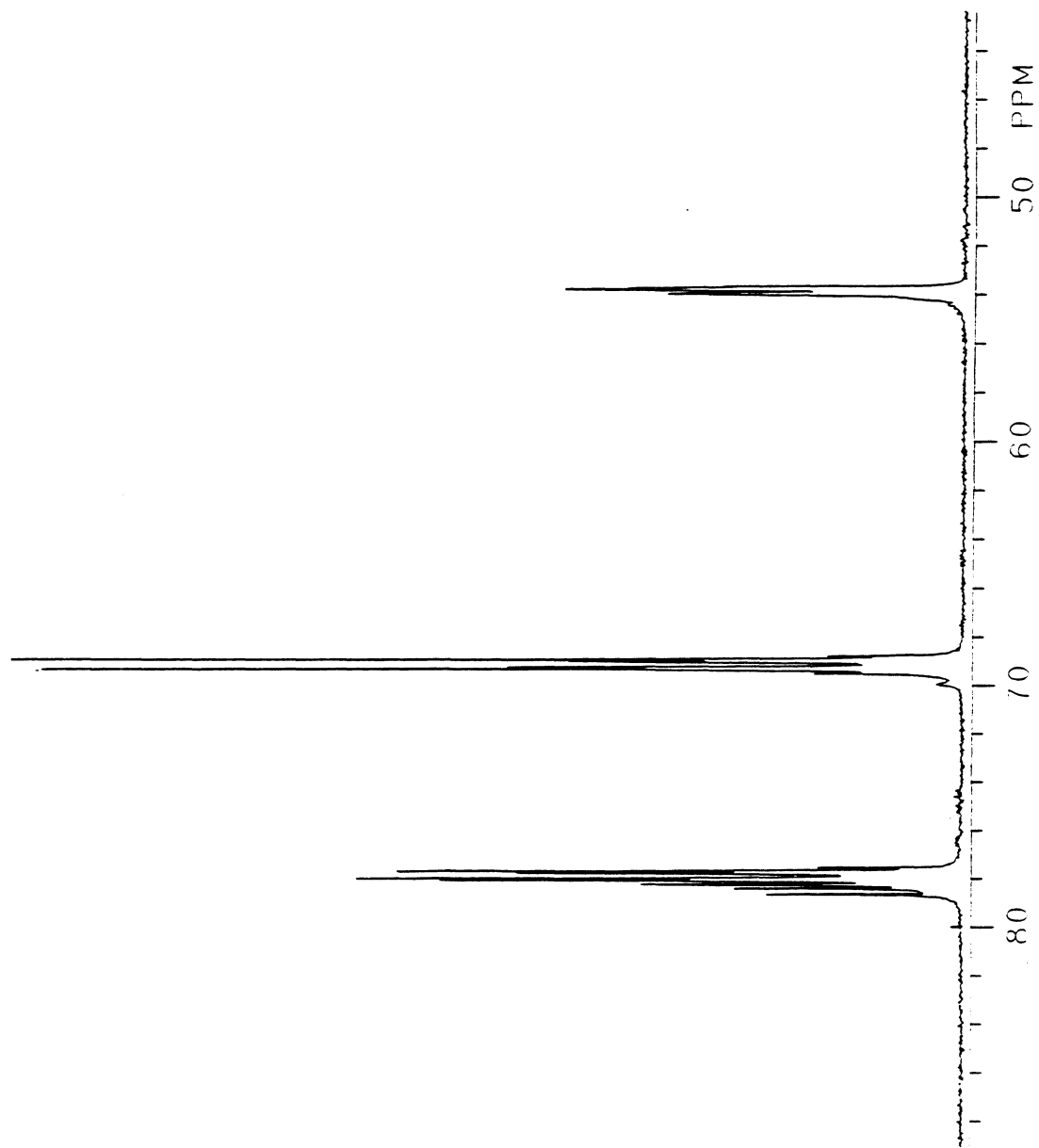
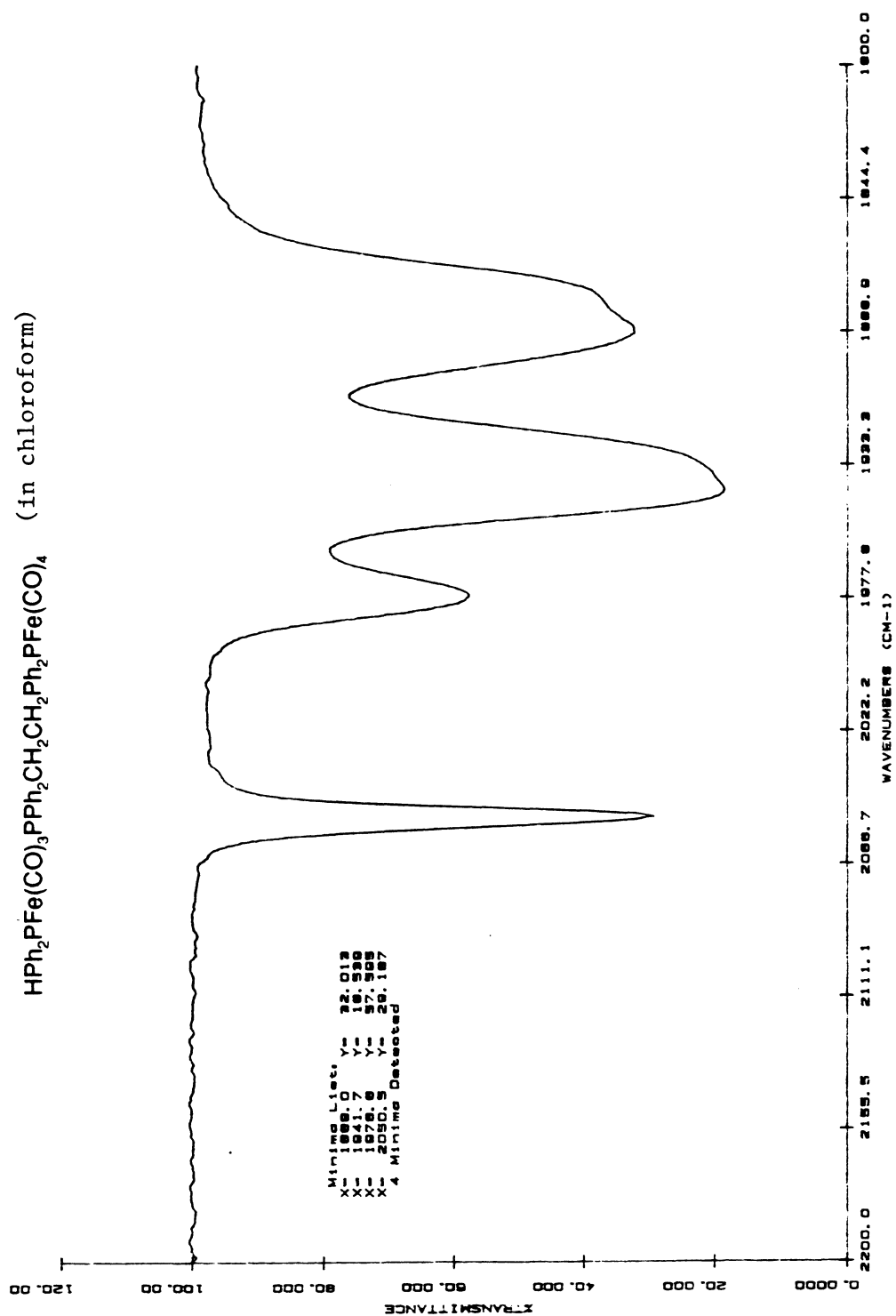


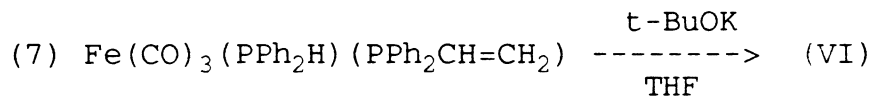
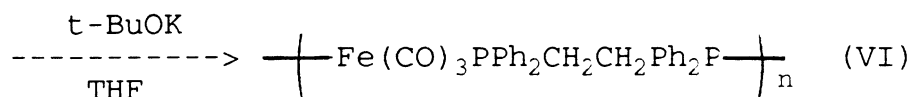
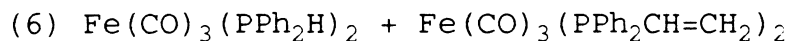
Figure 27. Infrared spectrum of
 $\text{HPh}_2\text{PFe(CO)}_3\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{PFe(CO)}_4$ (in chloroform)



phosphorus atoms in the complex. The signals centered at 54.0 ppm arise from the phosphorus bound to the $-\text{Fe}(\text{CO})_4$ fragment. The signals centered at 69.5 ppm correspond to the phosphorus of the $\text{PCH}_2\text{CH}_2\text{P}$ bridge and that is bound to the $-\text{Fe}(\text{CO})_3-$ fragment. The signals centered at 78.0 ppm belong to the other phosphorus atom bound to $-\text{Fe}(\text{CO})_3-$.

The infrared spectrum of complex IV (Figure 27) shows the expected absorption for both $-\text{Fe}(\text{CO})_4$ and $-\text{Fe}(\text{CO})_3$ fragments. The signals at 1942, 1977, and 2051 cm^{-1} arise from the former fragment and the signal at 1889 cm^{-1} belongs to the latter.

The iron polymer in which the iron centers are linked by $\text{PCH}_2\text{CH}_2\text{P}$ bridges was to be synthesized by the two different methods:



For reaction (6), we faced the same problem as found for reaction (2) and reaction (4). In other words addition across the double bond did not occur. The infrared (Figure 28) and P-31 NMR (Figure 29) spectra indicated that the solid recovered from the reaction was

Figure 28. Infrared spectrum of product mixture of
polymer reaction (in chloroform)

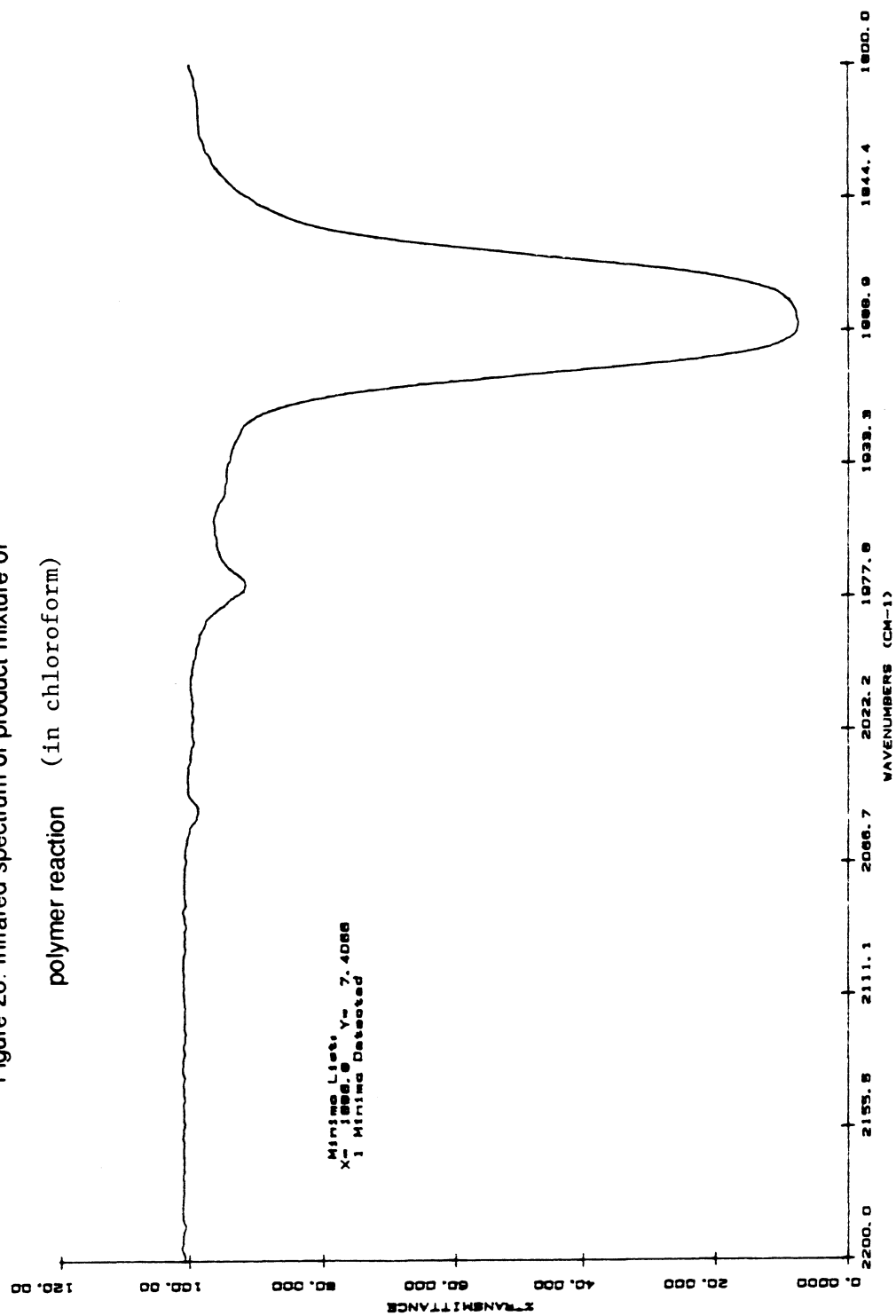
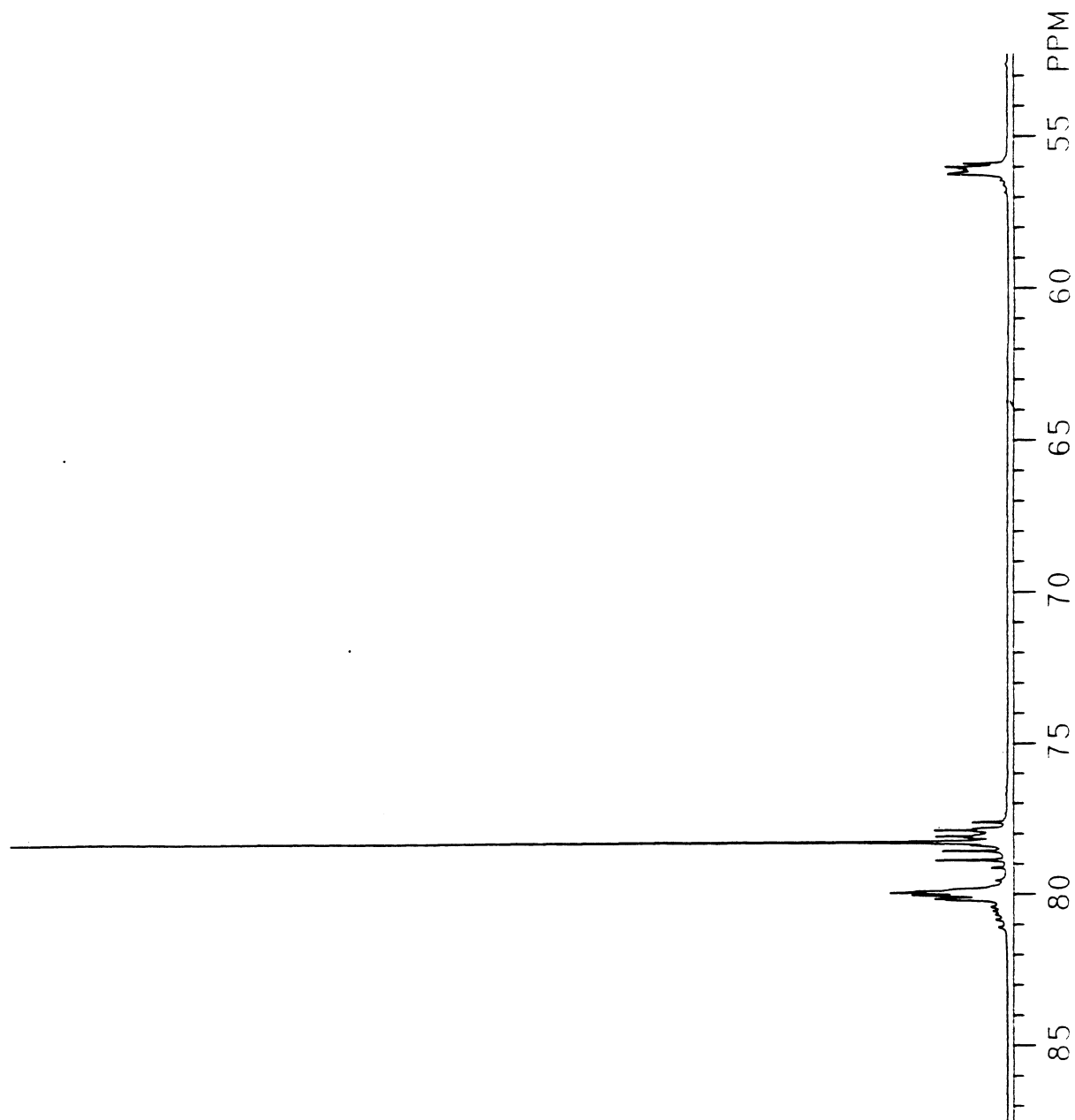


Figure 29. P-31 NMR spectrum of product mixture of

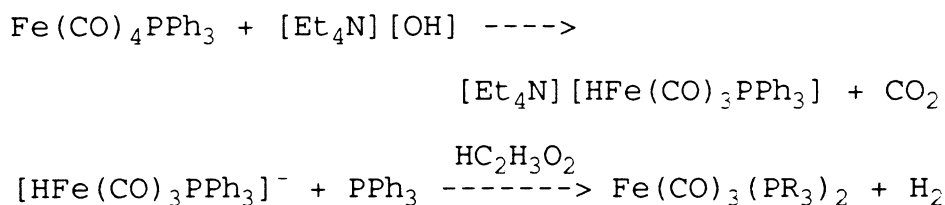
polymer reaction



the unreacted starting material, $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$. The complex sets of less intense signals in the P-31 NMR spectrum undoubtedly are decomposition products from side reactions of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$.

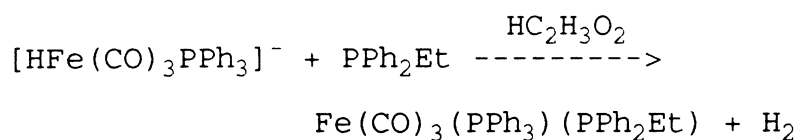
For reaction (7), a disubstituted iron complex with mixed phosphine ligands would be expected to undergo self-polymerization in the presence of base. However, obtaining a disubstituted complex with mixed ligands proved to be quite difficult. There are few literature reports for the synthesis of this kind of compound.

Our first approach was based on work reported by Ellis.²⁴ Although he did not prepare mixed ligand complexes, he did prepare $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$, utilizing a two-step reaction:



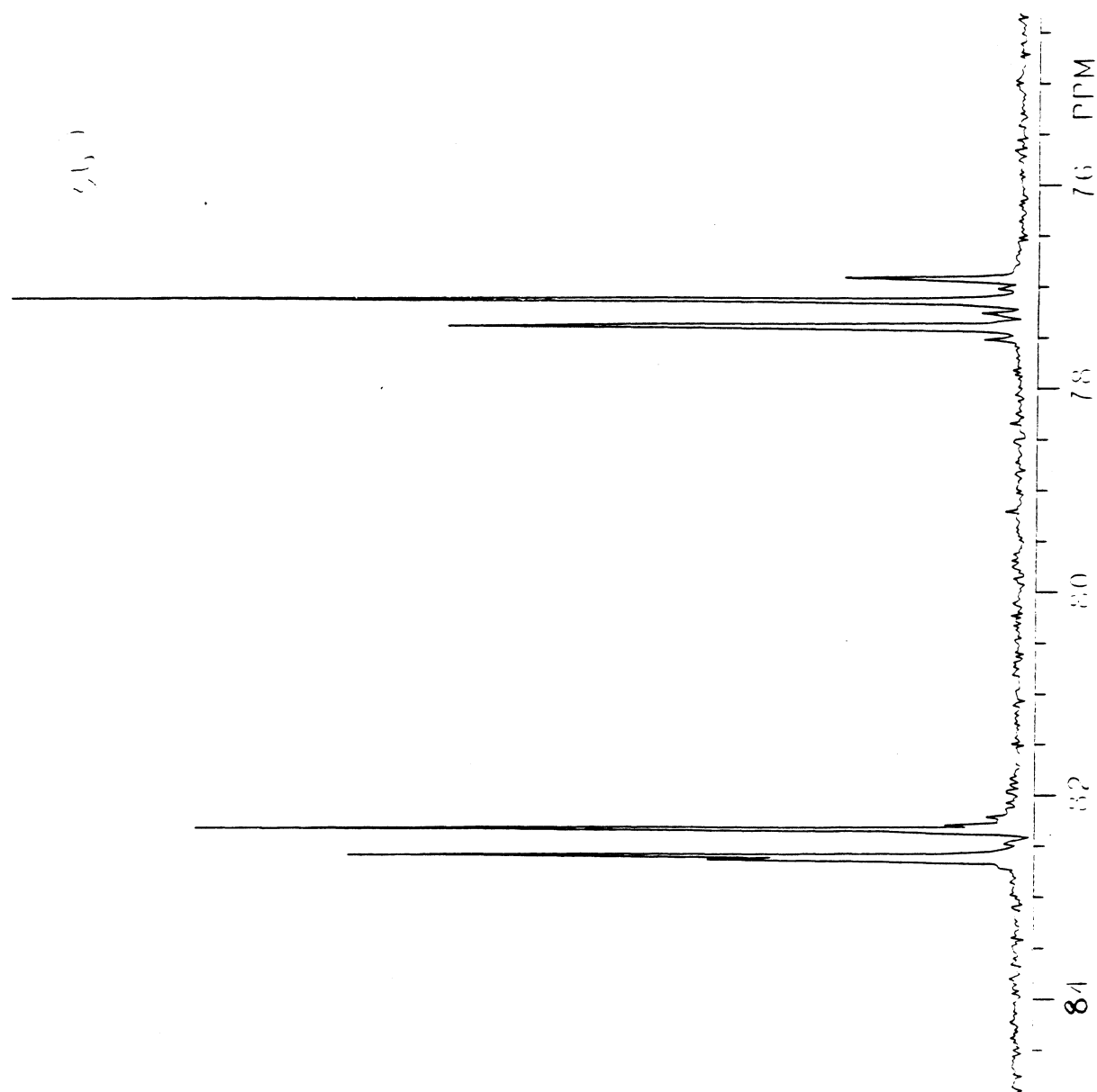
The mechanism of this two-step reaction has been also investigated by Brunet.²¹

To see if we could put two different ligands on iron with the Ellis method, we first synthesized $\text{Fe}(\text{CO})_3(\text{PPh}_3)(\text{PPh}_2\text{Et})$:



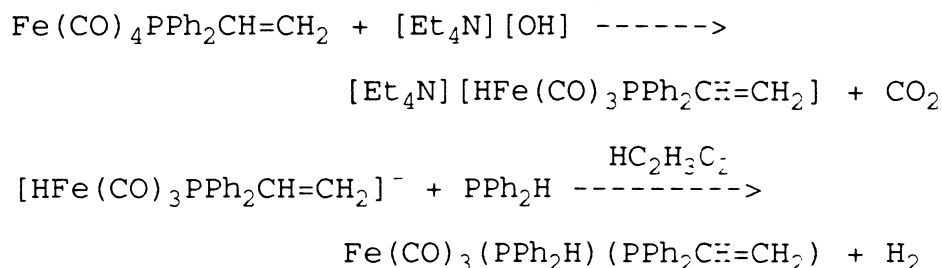
We were successful in this reaction as shown by the

Figure 30. P-31 NMR spectrum of $\text{Fe}(\text{CO})_3(\text{PPh}_3)(\text{PPh}_2\text{Et})$



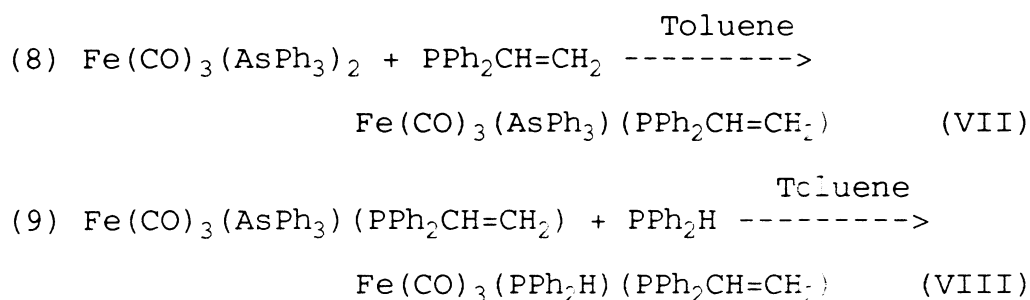
P-31 NMR spectrum of the product (Figure 30). The two doublets are as expected from an AX spin system. One can also see small amounts of both starting materials appearing as singlets outside the two doublets. This compound was prepared previously by C. A. Boecker in our research group.

Unfortunately we were not successful in the synthesis of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})(\text{PPh}_2\text{CH}=\text{CH}_2)$:



Perhaps, the reason was that such a strong reducing environment was too harsh for the diphenylphosphine ligand.

Another synthetic method for the preparation of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})(\text{PPh}_2\text{CH}=\text{CH}_2)$ involved a two-step substitution reaction based on displacement of AsPh_3 :



Recently, we found that the above reaction is effective for phosphine replacement of arsine ligands in a stepwise fashion.

Figure 31. P-31 NMR spectrum of $\text{Fe}(\text{CO})_3(\text{AsPh}_3)(\text{PPh}_2\text{CH}=\text{CH}_2)$

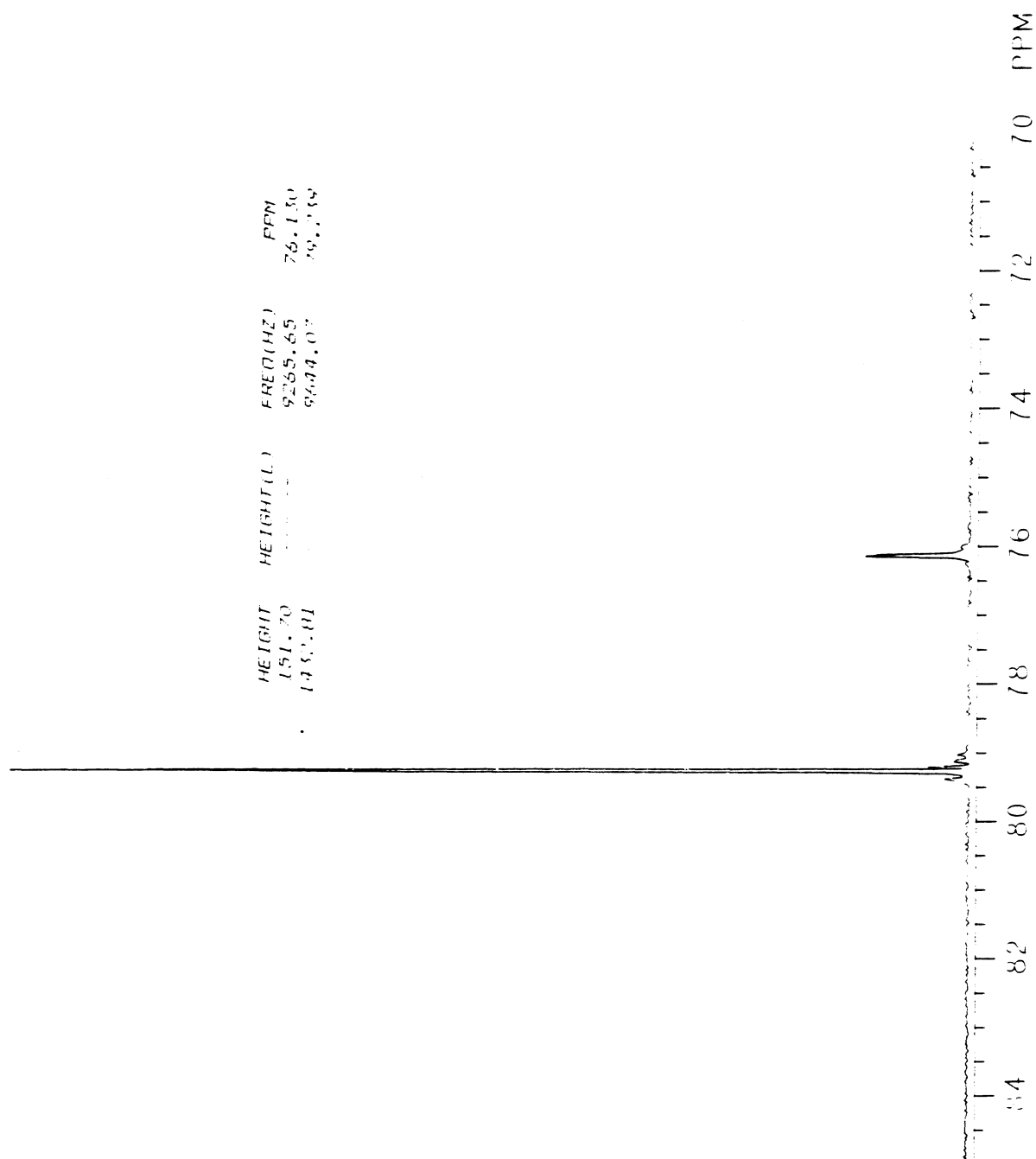


Figure 32. P-31 NMR spectrum of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})(\text{PPh}_2\text{CH}=\text{CH}_2)$

(crude product)

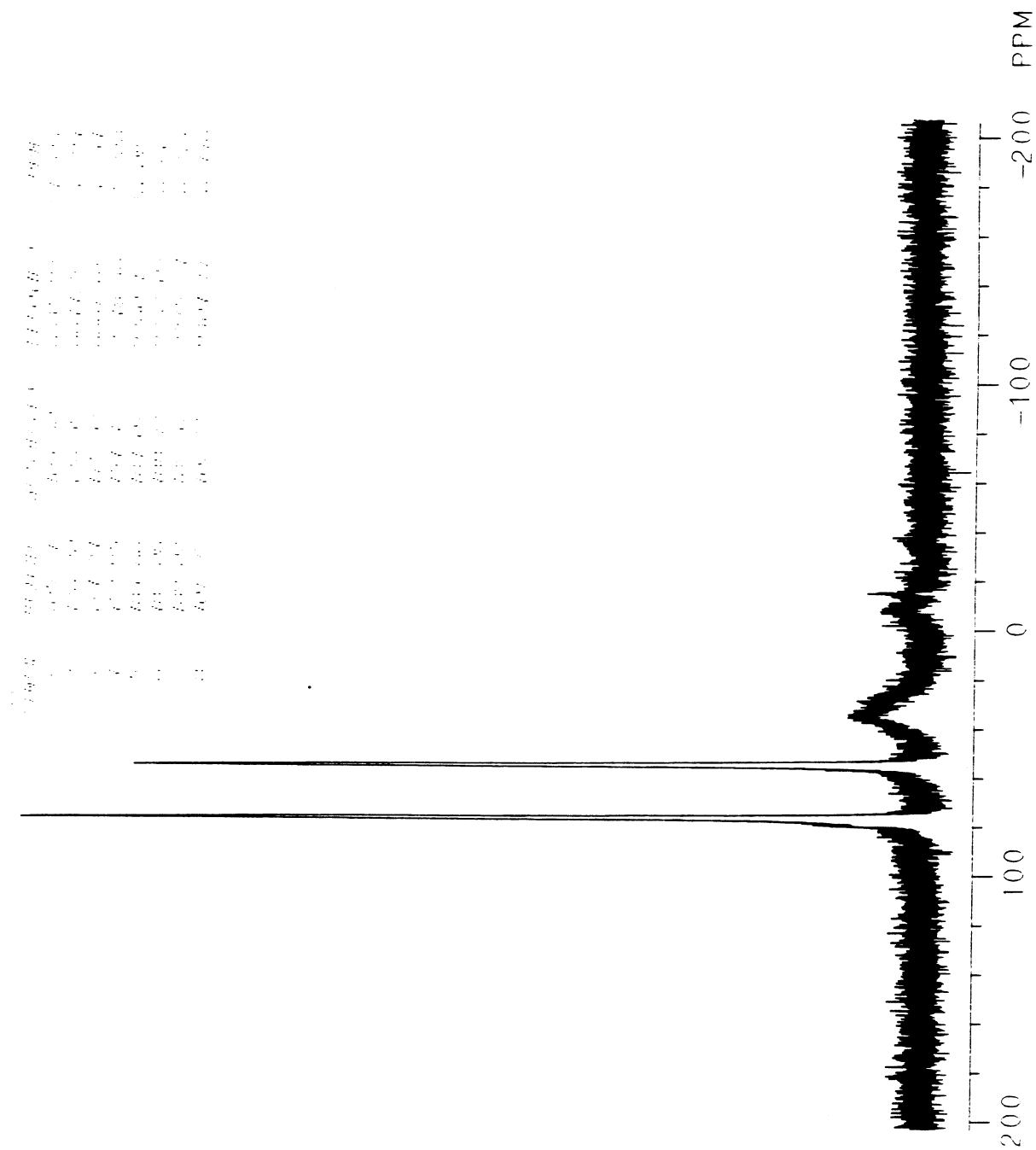


Figure 33. P-31 NMR spectrum of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})(\text{PPh}_2\text{CH}=\text{CH}_2)$

(purified)

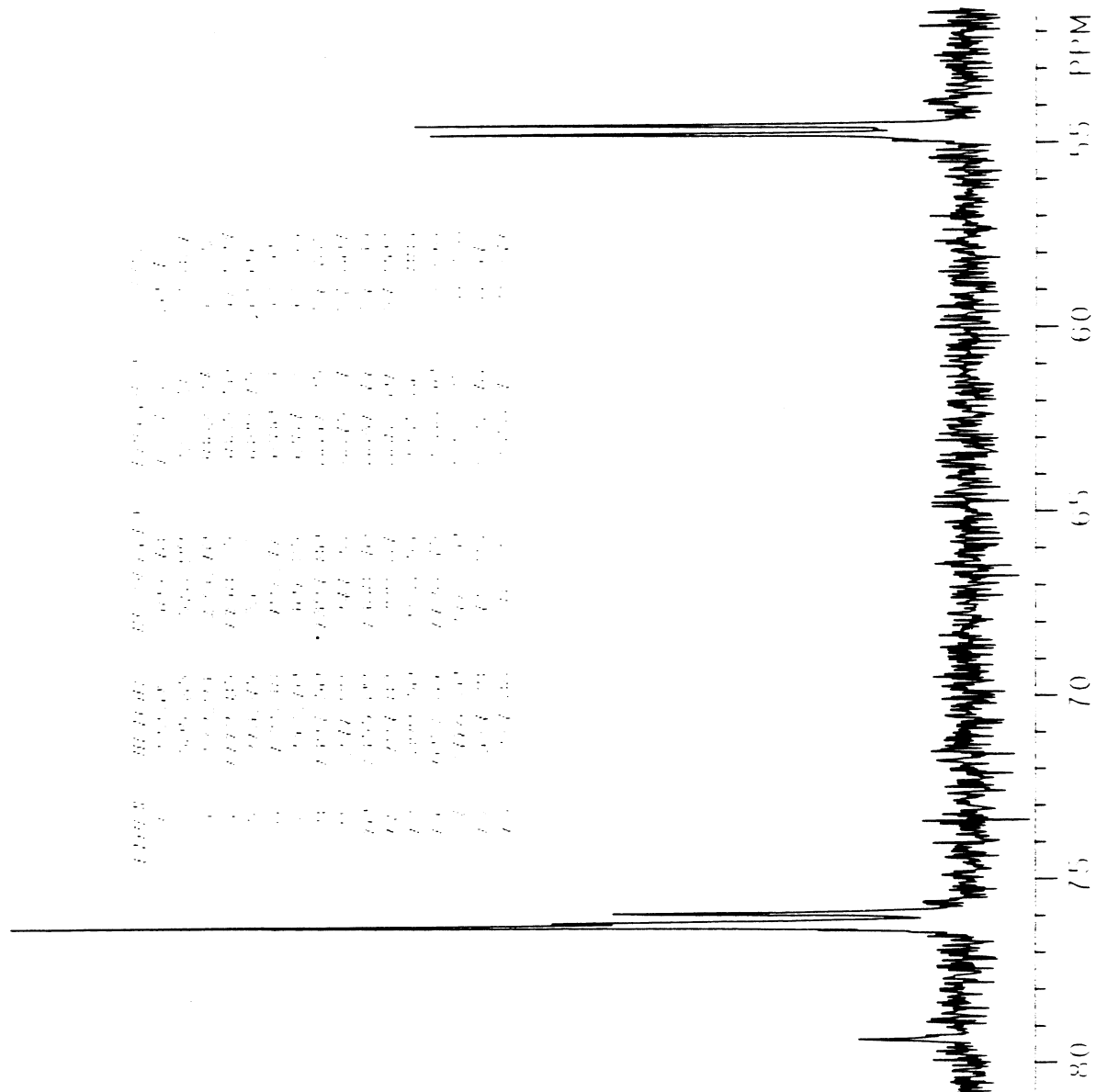
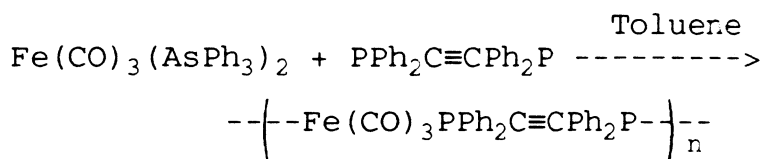


Figure 31 shows the proton decoupled P-31 NMR spectrum of the product of reaction (8). The peak at 76.1 ppm arises from the disubstituted complex, $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$, which was the minor product of reaction (8). The peak at 79.2 ppm arises from the major product, $\text{Fe}(\text{CO})_3(\text{AsPh}_3)(\text{PPh}_2\text{CH}=\text{CH}_2)$, which is 90.4% pure in the product mixture.

Figure 32 shows the P-31 NMR spectrum of the product of reaction (9). The two peaks correspond to two phosphorus atoms in $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})(\text{PPh}_2\text{CH}=\text{CH}_2)$. The downfield signal arises from the phosphorus in the diphenylvinylphosphine group while the upfield signal arises from the phosphorus in the diphenylphosphine group. The AX spin system of this compound should give a spectrum consisting of two doublets. However, this was not observed. The two signals are very broad and as a result coupling could not be resolved. The broadening of the signals probably results from para-magnetic impurities in the product mixture. Purification attempts of this mixture led to some decomposition but as seen in Figure 33 the expected two doublets are observed.

Since we did not obtain adequate amounts of pure $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})(\text{PPh}_2\text{CH}=\text{CH}_2)$, we did not run the self-polymerization (reaction 7).

We have also tested the substitution reaction between $\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ and $\text{PPh}_2\text{C}\equiv\text{CPh}_2\text{P}$, expected to form the polymer (3):



In order to elucidate the course of the reaction, experiments were run with two reactant ratios.

The reaction of $\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ with $\text{PPh}_2\text{C}\equiv\text{CPh}_2\text{P}$ in a 1:1 ratio might be expected to give the polymer. The infrared spectrum of the crude product is shown in Figure 34. There is only one broad signal consistent with a disubstituted product. The P-31 NMR spectrum (Figure 35 and 36) of the crude product shows a group of signals downfield from 60 ppm. All of these must belong to complexes in which all phosphorus atoms of $\text{PPh}_2\text{C}\equiv\text{CPh}_2\text{P}$ are coordinated. Free $\text{PPh}_2\text{C}\equiv\text{CPh}_2\text{P}$ has a chemical shift at -32.0 ppm (CH_3OH).²⁵ When one end of the molecule is quaternized, $[\text{Ph}_2\text{PC}\equiv\text{CPh}_2(\text{CH}_2\text{Ph})]^+$, the chemical shift of the uncoordinated end becomes -32.2 ppm (CH_3OH).²⁵ In the complex, $(\text{OC})_5\text{WPPh}_2\text{C}\equiv\text{CPh}_2$, the chemical shift becomes -32.2 ppm.²⁵ Thus it is apparent that the chemical shift of one end of the ligand is little changed when the other end becomes coordinated. One can determine, however, the difference between free $\text{PPh}_2\text{C}\equiv\text{CPh}_2\text{P}$ and $[\text{RPPh}_2\text{C}\equiv\text{CPh}_2]^+$ by looking for a

Figure 34. Infrared spectrum of product mixture of

$\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ reaction (ratio: 1:1) (in chloroform)

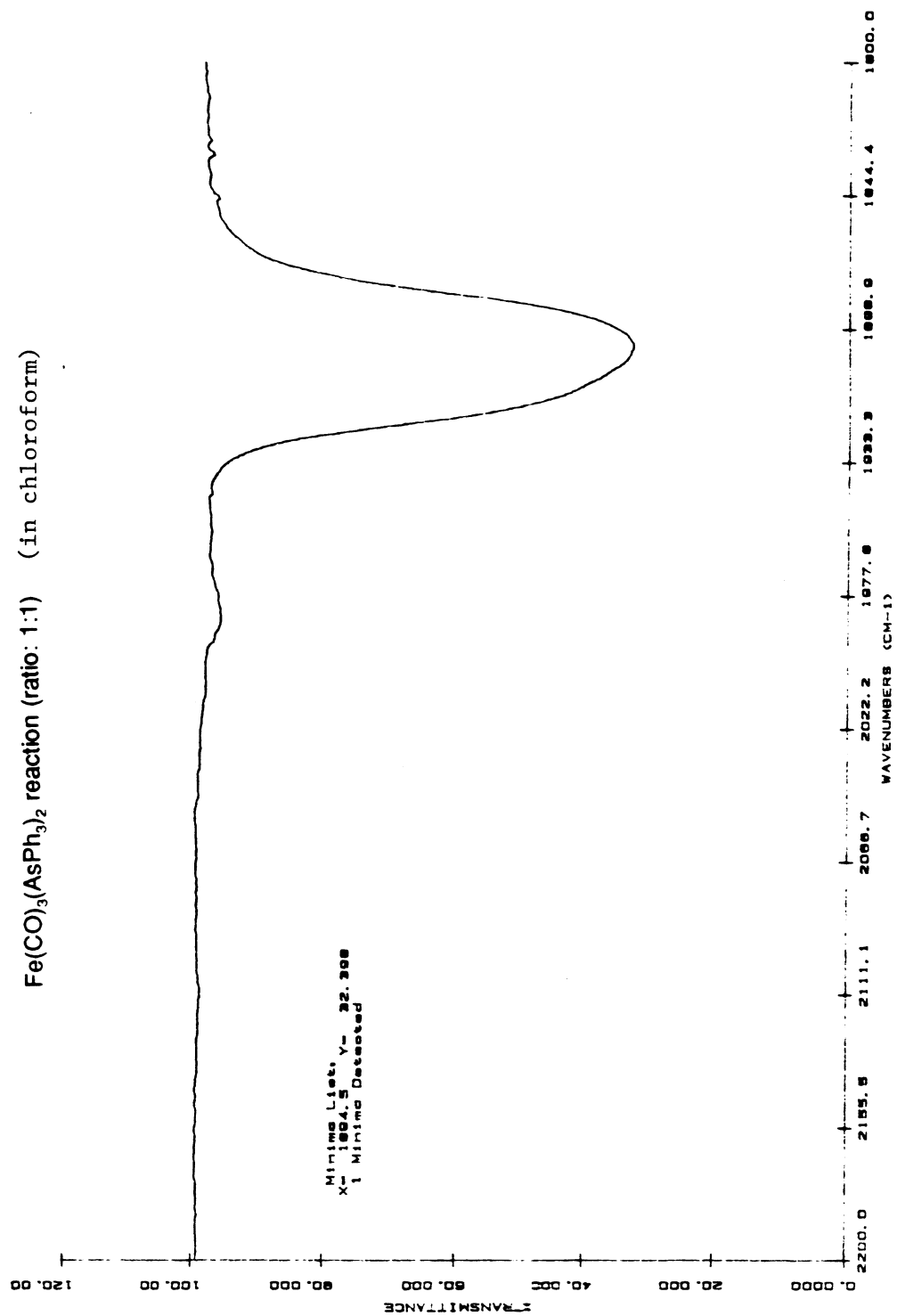


Figure 35. P-31 NMR spectrum of product mixture of

$\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ reaction (ratio: 1:1)

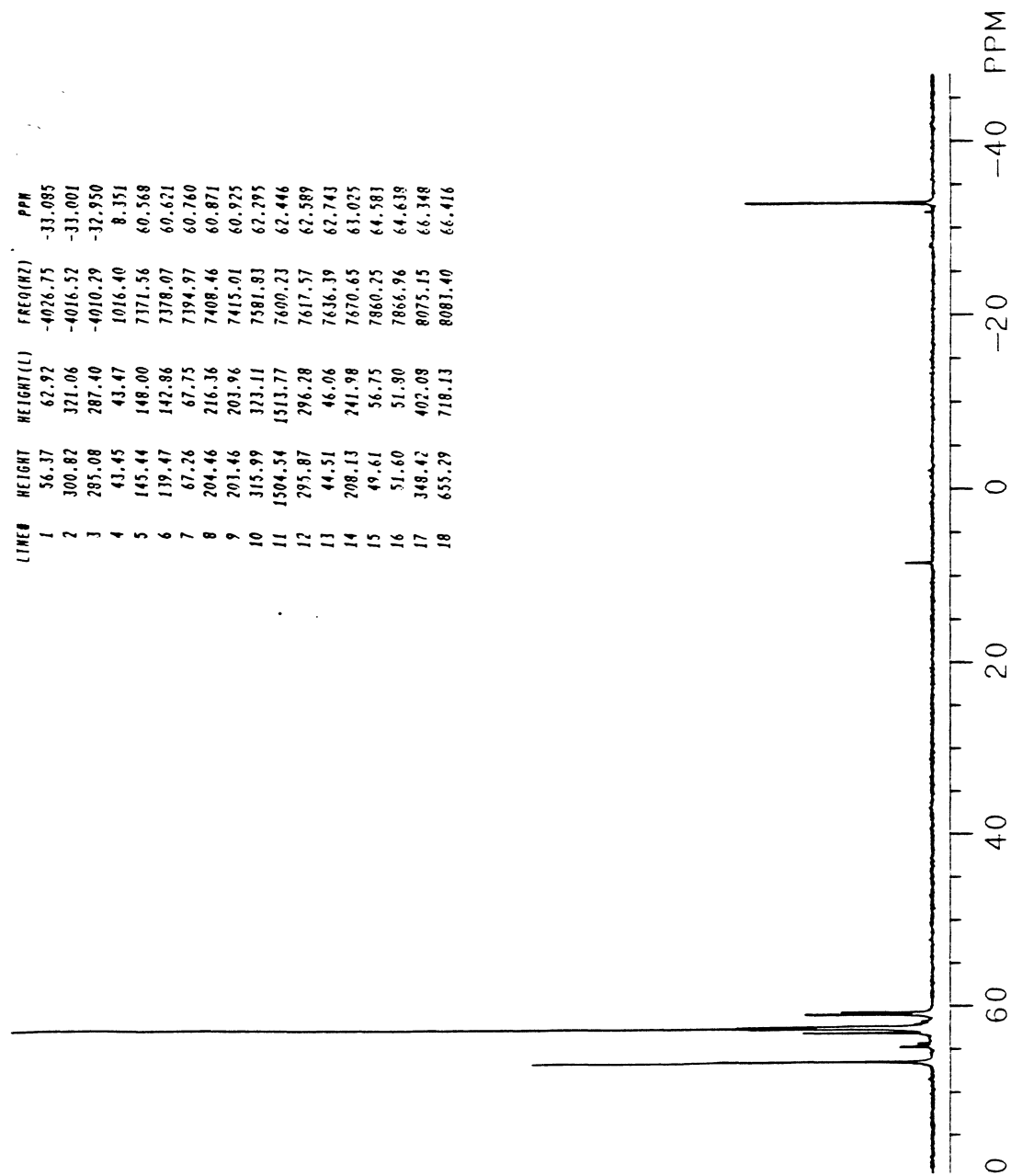
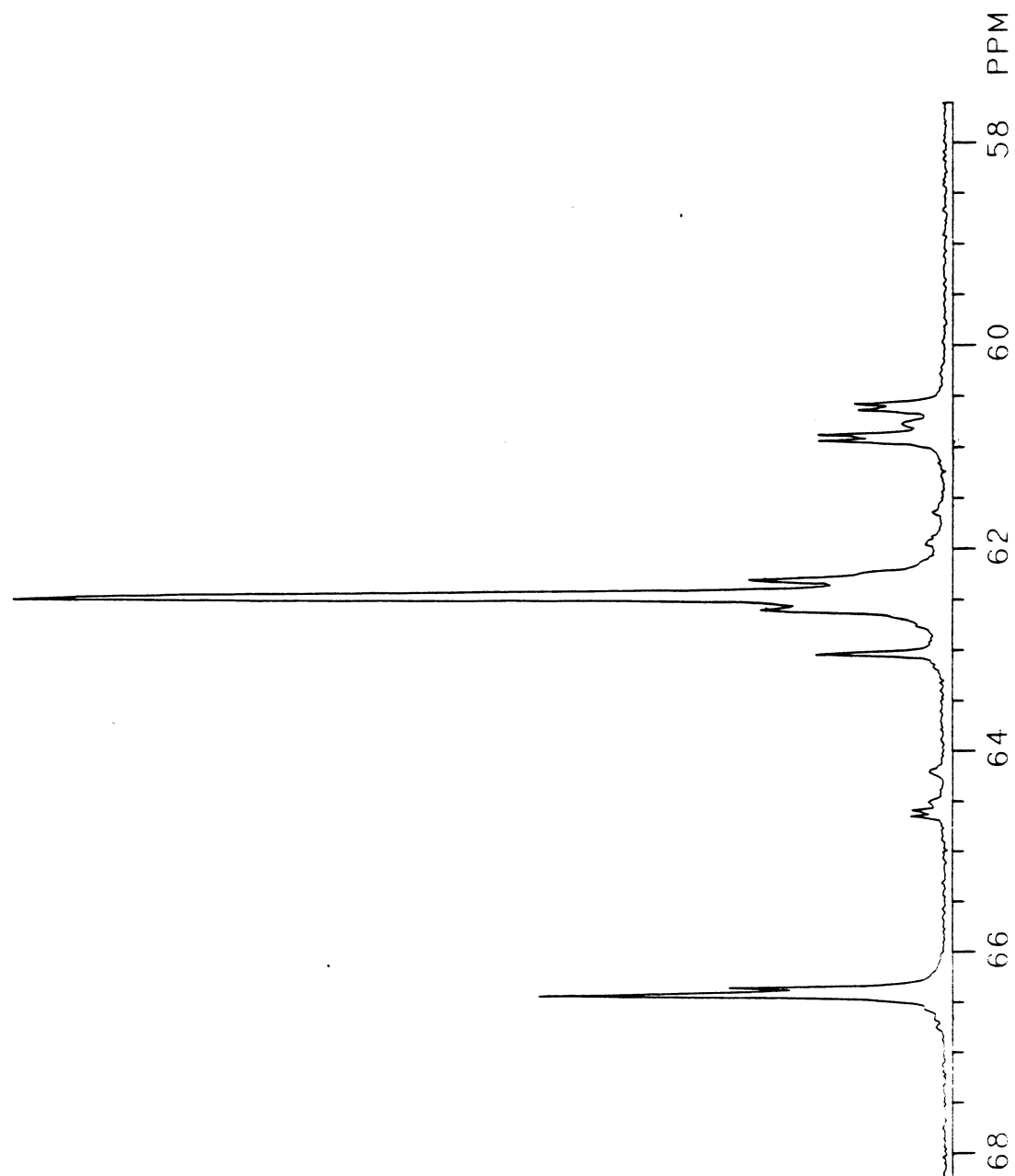
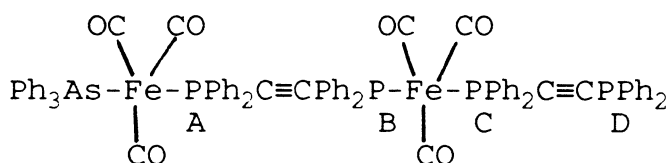


Figure 36. Expanded P-31 NMR spectrum of product mixture of

$\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ reaction (ratio: 1:1)



phosphorus-phosphorus coupling constant. These coupling constants are small. For example, J_{pp} in $[\text{PhCH}_2\text{PPh}_2\text{C}\equiv\text{CPh}_2]^+$ is 6.8 Hz and in $(\text{OC})_5\text{WPPh}_2\text{C}\equiv\text{CPh}_2\text{P}$ is 5.6 Hz. We might, therefore, expect to see a coupling constant of around 6 Hz if one end of $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ is bound to iron. This is the value observed in Figure 35. Two signals at -33.0 and -32.95 ppm represent a doublet with a coupling constant of 6.2 Hz. We tentatively assign these signals to phosphorus D in the complex



Phosphorus C should appear as a doublet of doublets in which one doublet is 6.2 Hz (coupled to phosphorus D) and the other coupled to phosphorus B should be approximately 32 Hz based on other mixed ligand iron system. A doublet of doublets centered at 60.82 ppm shows phosphorus-phosphorus coupling of 6.5 Hz and 36.9 Hz. We would also expect phosphorus B to appear as a doublet of doublets and phosphorus A to appear as a doublet. The coupling between phosphorus A and phosphorus B is expected to be quite small. For example, in the complex $(\text{OC})_5\text{WPPh}_2\text{C}\equiv\text{CP}^+\text{Ph}_2\text{CH}_3$ the phosphorus-phosphorus coupling is only 2.2 Hz. While one might be expected to resolve this coupling for

tungsten, it is unlikely for iron because of the presence of unavoidable amounts of trace paramagnetic impurities. Thus instead of seeing a doublet and a doublet of doublets for A and B, it is likely that a singlet and a doublet is more realistic. We assign the doublet centered at 62.4 ppm ($J_{pp} = 35.7$ Hz) to phosphorus B. The coupling constant of 35.7 Hz differs from 36.9 Hz but this difference is thought to arise because of distortion caused by the high intensity signal at 62.4 ppm. Based on intensities we assign the single broad absorption at 66.4 ppm to phosphorus A. A summary of the data is shown in the table below:

	P _A	P _B	P _C	P _D
Chemical Shift (ppm)	66.4	62.4	60.82	32.98
Coupling Constants	$J_{CD} = 6.2$ Hz, 6.5 Hz $J_{BC} = 36.9$ Hz, 35.7 Hz $J_{AB} =$ unresolved			

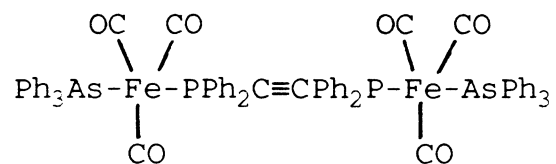
The J_{CD} and J_{BC} values of 6.2 Hz and 36.9 Hz, respectively, are probably the most accurate because they are in a region of less overlap with other signals.

The minor signal at 66.35 ppm may arise from $\text{Ph}_3\text{AsFe}(\text{CO})_3\text{PPh}_2\text{C}\equiv\text{CPh}_2\text{PFe}(\text{CO})_3\text{AsPh}_3$. This assignment is based on the above analysis in which one AsPh_3 and three CO ligands are attached to the same iron atom as the acetylene ligand.

The major signal at 62.45 ppm may well be a polymer of undetermined molecular weight. The chemical shift value is in the region expected for two phosphorus ligands bound to iron, as compared to one phosphorus and one arsenic ligand. It is so much more intense than the other signals present that it does not appear to be coupled to other phosphorus nuclei. It is very broad but this is what you would expect for a polymer with a range of molecular weights.

The second reaction was run with a 2:1 ratio of $\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ to $\text{PPh}_2\text{C}\equiv\text{CPh}_2\text{P}$. The crude product of this reaction was purified by filtration through a fritted funnel containing some neutral alumina. The P-31 NMR spectrum (Figure 37) shows only three signals. The chemical shifts of all of these are downfield from phosphoric acid and must belong to $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ that is coordinated on both ends.

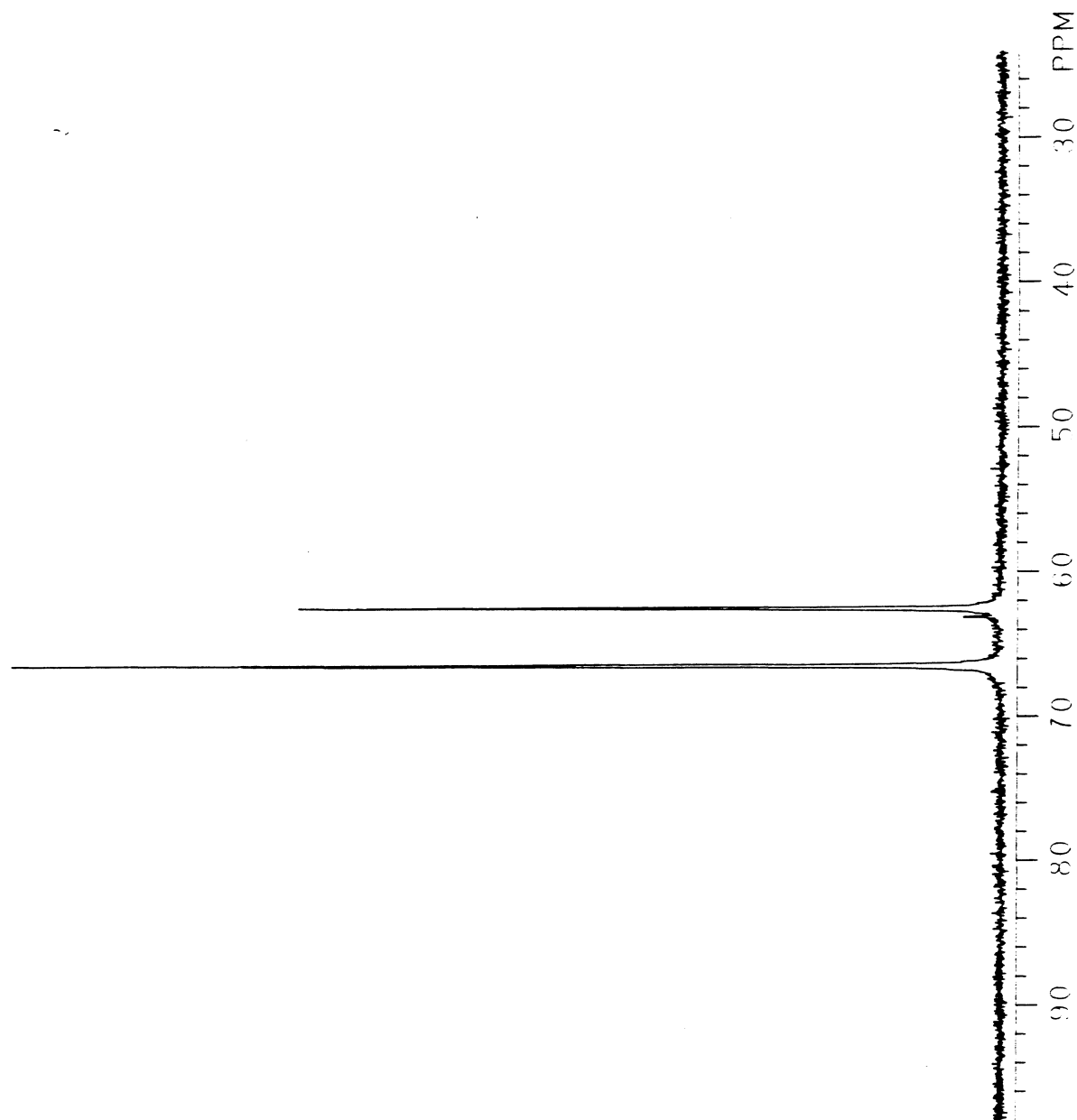
The 2:1 ratio of $\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ to $\text{PPh}_2\text{C}\equiv\text{CPh}_2\text{P}$ should optimize the stoichiometry for the formation of

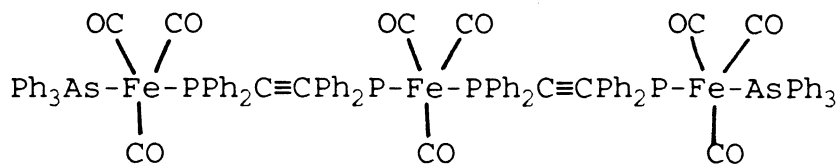


We believe the intense signal at 66.4 ppm corresponds to this compound. The singlets at 66.3 and 62.4 ppm may belong to

Figure 37. P-31 NMR spectrum of product mixture of

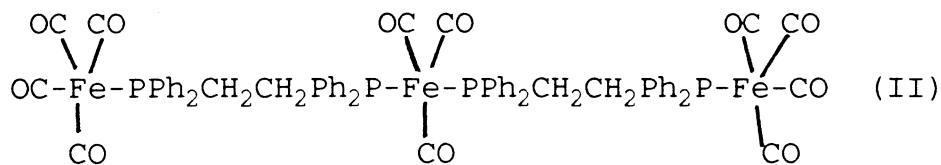
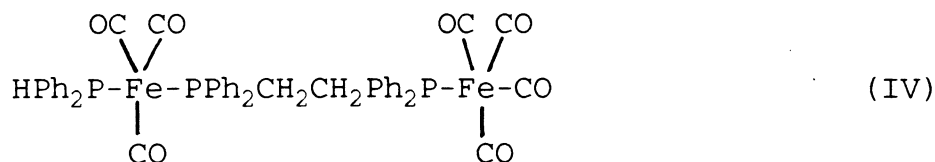
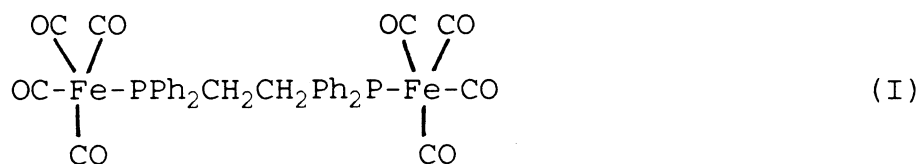
$\text{Fe(CO)}_3(\text{AsPh}_3)_2$ reaction (ratio: 2:1)





Phosphorus-phosphorus coupling is too small to be resolved.

In conclusion, we have successfully synthesized three iron complex oligomers (two bimetallic and one trimetallic) in which the iron centers are linked by the $-\text{PCH}_2\text{CH}_2\text{P}-$ bridges:



All of these iron complexes are soluble in dichloromethane, chloroform, benzene, toluene, and insoluble in methanol, heptane, and petroleum ether.

Attempts to synthesize larger oligomers, even polymers, failed because $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$ failed to

react with $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$ or $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$ in the base-catalyzed addition reaction.

The current direction of this research is to obtain pure $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})(\text{PPh}_2\text{CH}=\text{CH}_2)$ which is expected to undergo self-polymerization to form iron polymer.

For future work, it is suggested that the base-catalyzed addition reaction be carried out under different conditions. Bases other than KO^tBu should be tried and reaction times should be varied in order to obtain larger iron oligomers. In addition, the mechanism of the reaction of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$ should be investigated in detail.

The substitution reaction of $\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ with $\text{PPh}_2\text{C}\equiv\text{CPh}_2\text{P}$ need to be further investigated. The components of the crude product need to be identified and purified. It would appear from this work that arsine substitution reactions have greater promise than vinyl addition reactions for the preparation of iron polymers. Unlike vinyl addition reactions they allow for the introduction of olefinic and acetylic bridges into the polymer chain.

Experimental Section

I. General Considerations

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran was predried over calcium hydride and was freshly distilled from sodium and benzophenone as needed. All other solvents were used without further purification. However, all solvents were thoroughly purged with nitrogen before use. Iron pentacarbonyl, diiron nonacarbonyl, phosphines, reducing agents, and other chemicals were obtained from various commercial suppliers and were used without further purification.

Melting and decomposition points were obtained on an Arthur H. Thomas Unimelt apparatus, and are reported uncorrected. A Nicolet 20 DX-B Fourier Transform Infrared instrument was used to record infrared spectra in the carbonyl region, 2200 to 1800 cm^{-1} . P-31 NMR spectra were obtained by using a GE 300 MHz Fourier Transform NMR instrument and were recorded at 122 MHz. Phosphoric acid (85%) was used as external standard (downfield is positive), and CD_2Cl_2 was used as the solvent. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN and from the University of Illinois at Urbana.

II. Synthesis

1. Preparation of $\text{Fe}(\text{CO})_4\text{PPh}_3$

A modified procedure, originally described by Albers and Coville,¹⁶ was used. Cobalt(II) chloride dihydrate, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, was dried under vacuum at 85°C for 48 hours to afford anhydrous cobalt (II) chloride, CoCl_2 , which functions as a catalyst in this procedure.

Solid PPh_3 (5.2 g, 20 mmol) and CoCl_2 (0.082 g, 6.3 mmol) were placed in a 250 ml round-bottom flask which had a side arm and contained a magnetic stirring bar. Toluene (100 ml) which had been purged with nitrogen gas for 30 minutes, was introduced into the flask. To this stirred solution 5.3 ml of $\text{Fe}(\text{CO})_5$ (40 mmol) was slowly injected by syringe. The solution turned green immediately after adding iron pentacarbonyl, after which it was heated to reflux. The reaction mixture turned brown after approximately 20 minutes, and 6 hours later, it was cooled to room temperature and filtered through a $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ /neutral alumina/silica gel column (three layers: 8g/40g/40g). The solvent of the filtrate was removed by vacuum and a yellow crude product was obtained.

This crude product was crystallized by dissolving

it in a minimum amount of dichloromethane and adding an equal amount of methanol. The solution was kept in the refrigerator (-5°C) for 24 hours to produce 5.75 g (66.8% yield) of the light yellow crystals (m.p. $201-203^{\circ}\text{C}$). The identity and purity of the product were confirmed by IR and P-31 NMR spectroscopy. Infrared spectrum: lit.¹⁶ 2052, 1978, 1940 cm^{-1} ; obtained 2050, 1977, 1944 cm^{-1} . P-31 NMR: $\delta_{\text{p}}=72.6$ ppm.

2. Preparation of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$

2.1 Method 1

The procedure was described by Butts and Shriver.¹⁷ To a 100 ml round-bottom flask, equipped with a side arm and containing a magnetic stirring bar and 20 ml of a blue THF solution of sodium benzophenone ketyl (prepared by adding sodium metal to a solution of benzophenone in dry, oxygen-free THF) was added pentacarbonyliron (3.6 ml, 27 mmol) and $\text{PPh}_2\text{CH}=\text{CH}_2$ (2.5 ml, 12 mmol). The blue color of the THF solution was discharged instantly on contact with pentacarbonyliron and some brown precipitate formed. The reaction mixture was stirred and refluxed under nitrogen for 3 hours. The solution quickly turned deep red-brown. After refluxing and cooling to room

temperature, volatiles were removed by vacuum evaporation, and 100 ml of heptane was added to dissolve the crude solid. The solution was brought to reflux for 20 minutes in the air, leading to the formation of some brown insoluble solid. The hot solution was filtered and concentrated to 20 ml of solution. After 24 hours in a freezer (-5°C), some yellow crystals formed. The yield of the desired product was 1.07 g (18%), m.p. $54-55^{\circ}\text{C}$. The identity was confirmed by comparing IR and P-31 NMR spectra with the literature.

Infrared spectrum: lit.¹¹ (CCl_3H) 2054, 1979, 1946 cm^{-1} ; (C_6H_{12}) 2055, 1981, 1946 cm^{-1} . obtained (CCl_3H) 2051, 1977, 1945 cm^{-1} ; (heptane) 2053, 1981, 1946 cm^{-1} . P-31 NMR: lit.¹¹ $\delta_{\text{p}}=66.5\text{ ppm}$; obtained $\delta_{\text{p}}=66.7\text{ ppm}$.

2.2 Method 2¹⁹

A magnetic stirring bar and 100 ml of benzene were placed into a 250 ml side-armed round-bottom flask. The solution was purged with nitrogen gas for 20 minutes. In an air bag under a nitrogen atmosphere, diiron nonacarbonyl (9.0 g, 25 mmol) was transferred into the flask. The reaction solution was purged with nitrogen again for another 20 minutes, and then $\text{PPh}_2\text{CH}=\text{CH}_2$

(4.4 ml, 20 mmol) was syringe-injected.

Under nitrogen, the solution was stirred at room temperature for 48 hours at which time all solids were dissolved. The solvent and unreacted $\text{Fe}(\text{CO})_5$ were taken off under reduced pressure and the residue was chromatographed through a 100 cm alumina column (heptane eluant). Infrared spectroscopy was used to track $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ in the eluate. The first fraction was collected and concentrated to 20 ml and placed in a freezer for 24 hours. Light yellow crystals of the desired product formed (7.88 g, 69.0%). The purity of the product was confirmed by its melting point and by IR and P-31 NMR spectroscopy.

3. Preparation of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$

The same procedures and precautions were taken as described for preparation of $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ (method 2). Diiron nonacarbonyl (11 g, 30 mmol), diphenylphosphine (5.5 ml, 30 mmol) and 100 ml of benzene were used in this reaction.

After being stirred at room temperature for 48 hours, the reaction solution was dark brown. The solvent was removed and the residue was chromatographed through an alumina column. About 1 liter of eluant was collected and concentrated to 20 ml. The solution was

cooled to -5°C for 24 hours to afford 7.2 g (68.8% yield) of product crystals (m.p. $62-63^{\circ}\text{C}$). The IR spectrum and

P-31 NMR spectrum were compared with the literature values to further confirm the purity of the product.

Infrared spectrum: lit.¹⁸ (hexane) 2056, 1984, 1953, 1946 cm^{-1} ; obtained (heptane) 2056, 1985, 1953, 1947 cm^{-1} . P-31 NMR spectrum: $\delta_{\text{p}}=42.4\text{ ppm}$.

4. Preparation of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$ ²⁰

Into a 250 ml, 3-necked round-bottom flask which was equipped with a magnetic stirring bar, condenser and dropping funnel was placed 120 ml of n-butanol, diphenylvinylphosphine (13.6 ml, 64 mmol) and sodium borohydride (2.2 g, 60 mmol). This solution was purged with nitrogen for 30 minutes and iron pentacarbonyl (4.0 ml, 30 mmol) was slowly added into the strongly stirred solution by means of the dropping funnel. An immediate vigorous reaction resulted with the evolution of hydrogen gas. The oil bath of the reaction mixture was heated to 120°C and held constant for 2 hours. The color of the solution turned brown. The solution was allowed to cool to room temperature under nitrogen gas, and then was kept in a freezer (5°C) for 12 hours to precipitate the crude product (32 g). The solid was

purified by crystallization from 25 ml of dichloromethane and 25 ml of methanol. Yield was 12.5 g (73.8%), m.p. 168-170⁰C. The identity and purity of the desired product were further confirmed by comparison of the IR and ³¹P NMR spectra with literature data.

Infrared spectrum: lit.²⁰ (CCl₃H) 1880, 1886 cm⁻¹; obtained (CCl₃H) 1882, 1888 cm⁻¹. P-31 NMR spectrum: lit.²⁰ δ_p =76.5 ppm; obtained δ_p =76.1 ppm.

5. Preparation of Fe(CO)₃(PPh₂H)₂

The same procedure was used as described above. Diphenylphosphine (8.5 ml, 46 mmol), pentacarbonyliron (3.0 ml, 23 mmol), sodium borohydride (1.74 g, 46 mmol) and n-butanol (100 ml) were used for this preparation.

After being refluxed for 2 hours, the reaction solution was cooled to 5⁰C to afford the crude product (30 g). Purification was accomplished by crystallization from 20 ml of dichloromethane and 20 ml of methanol. The yield was 8.9 g (73.5%) and the product has a melting point of 173-175⁰C. The identity of the product was confirmed by comparison of its IR and P-31 NMR spectra with the literature values.

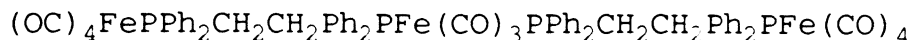
Infrared spectrum: lit.²⁰ 1880, 1886 cm⁻¹ (CHCl₃); obtained 1897 cm⁻¹ (CHCl₃). P-31 NMR spectrum: lit.²⁰ δ_p =53.9 ppm, obtained δ_p =53.7 ppm.

6. Preparation of $(\text{CO})_4\text{FePPh}_2(\text{CH}_2)_2\text{PPh}_2\text{Fe}(\text{CO})_4$

The reactants, $\text{Fe}(\text{CO})_4\text{PPh}_2\text{H}$ (0.53 g, 1.5 mmol) and $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ (0.57 g, 1.5 mmol) were added to dry tetrahydrofuran (50 ml) in a 100 ml round-bottom flask which had a side arm attached and contained a magnetic stirring bar. The solution was purged with nitrogen for 30 minutes. Potassium t-butoxide (0.04 g, 0.35 mmol) was introduced into the flask and the solution was heated to reflux for 1 hour. During the heating period, the color of the solution turned brown and the t-BuOK dissolved. The solution was allowed to cool to room temperature and the solvent was taken off under reduced pressure. The residue was a brown-colored solid. The solid was dissolved in 20 ml of dichloromethane and the solution was passed through a fritted funnel which contained 20 g of neutral alumina. Methanol (20 ml) was added to the filtrate which was cooled in a freezer (-5°C) for 24 hours to afford yellow crystals. A yield of 0.76 g (69%) was realized (m.p. $188-190^\circ\text{C}$).

Calc. for $\text{C}_{34}\text{H}_{24}\text{O}_8\text{P}_2\text{Fe}_2$: C 55.62, H 3.30, P 8.45, Fe 15.21. Found: C 56.21, H 3.53, P 8.11, Fe 14.76. IR: lit.²² 2050.9, 1978.8, 1944.5, 1937.6 cm^{-1} ; obtained 2050.8, 1979.0, 1942.4 cm^{-1} . P-31 NMR: $\delta_{\text{p}}=65.5$ ppm.

7. Preparation of



7.1 Method 1

Into a 100 ml side-armed flask containing a magnetic stirring bar was placed $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$ (1.02 g, 2 mmol), $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ (1.52 g, 4 mmol) and dry THF (50 ml). The solution was purged with nitrogen gas for 30 minutes. Potassium t-butoxide was added and the solution was brought to reflux for 1 hour. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The residue was a brown-colored solid. The solid was dissolved in dichloromethane (20 ml) and filtered through a fritted funnel which contained 20 g of neutral alumina. The filtrate was concentrated to about 5 ml and 10 ml of methanol was added. Some yellow precipitate formed immediately. This mixture was placed in the freezer for 24 hours. The desired product was collected by filtration. Yield: 1.30 g (51%).

Thin layer chromatography confirmed some trace impurities. Purification of this product is in progress.

Calc. for $\text{C}_{63}\text{H}_{48}\text{O}_{11}\text{P}_4\text{Fe}_3$: C 59.46, H 3.80, P 9.74, Fe 13.17. Found: C 60.19, H 4.13, P 9.31, Fe 12.86.

IR: (CCl₃H) 1875, 1887, 1941, 1977, 2050 cm⁻¹.

P-31 NMR: δ_{p1} =69.0 ppm, δ_{p2} =77.7 ppm, $^2J_{PP}$ =30.2 Hz,

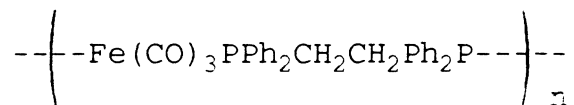
$^3J_{PP}$ =47.3 Hz.

8.2 Method 2

The same procedure as described above was used for this reaction. The reactants, Fe(CO)₄PPh₂H (1.42 g, 4 mmol), Fe(CO)₃(PPh₂CH=CH₂)₂ (1.13 g, 2 mmol), t-BuOK (0.04 g) and dry THF (50 ml) were used. After being refluxed for 1 hour, the solution turned dark-brown and was allowed to cool to room temperature. The solvent was removed by vacuum. The residue was a brown-colored oil which was treated by adding 20 ml of dichloromethane and an equal amount of methanol.

A P-31 NMR spectrum confirmed that the precipitate was starting materials, Fe(CO)₃(PPh₂CH=CH₂)₂ and a small amount of Fe(CO)₄PPh₂H.

8. Attempted preparation of iron complex polymer,



The same procedure was used as described above. The reaction mixture consisted of Fe(CO)₃(PPh₂H)₂ (1.02 g, 2 mmol), Fe(CO)₃(PPh₂CH=CH₂)₂ (1.13 g, 2 mmol), t-BuOK

(0.04 g) and dry THF (50 ml).

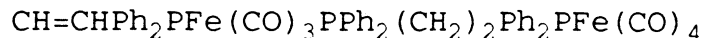
After refluxing for 1 hour, the solvent was removed by vacuum. The remaining dark-brown oil was treated by adding 20 ml of dichloromethane and an equal amount of methanol. some precipitate resulted. A P-31 NMR spectrum confirmed that this precipitate was the starting material, $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)_2$.

9. Preparation of $\text{HPh}_2\text{PFe}(\text{CO})_3\text{PPh}_2(\text{CH}_2)_2\text{Ph}_2\text{PFe}(\text{CO})_4$

The same procedure was used as described for reaction 6. A mixture of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{H})_2$ (1.03 g, 2 mmol), $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ (0.76 g, 2 mmol), t-BuOK (0.04 g) and dry THF (50 ml) was used.

After refluxing, the solvent was taken off under vacuum. The remaining brown-colored solid was dissolved in 20 ml of dichloromethane. This solution was filtered through a fritted funnel which contained 20 g of neutral alumina. The filtrate was concentrated to 5 ml and methanol (10 ml) was added. Some precipitates formed immediately. The mixture of precipitate and solution was placed in the freezer for 24 hours. The crude product was collected by filtration. The yield of impure material was 1.12 g (62%). A P-31 NMR spectrum indicated some impurities. Purification of this product is in progress.

10. Attempted preparation of



The same procedure was used as described for reaction 8. The reaction mixture consisted of $\text{Fe(CO)}_3(\text{PPh}_2\text{CH=CH}_2)_2$ (1.13 g, 2 mmol), $\text{Fe(CO)}_4\text{PPh}_2\text{H}$ (0.70 g, 2 mmol), *t*-BuOK (0.04 g) and dry THF (50 ml). The solution was heated for 2 hours and the solvent was taken off under vacuum. The remaining dark-brown oil was treated with 20 ml of dichloromethane and 20 ml of methanol to afford some precipitate. A P-31 NMR spectrum confirmed this precipitate was the starting material, $\text{Fe(CO)}_3(\text{PPh}_2\text{CH=CH}_2)_2$.

11. Reaction of $\text{Fe(CO)}_3(\text{AsPPh}_3)_2$ and $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ (1:1)

Into a 100 ml round-bottom flask, equipped with a side arm and containing a magnetic stirring bar, was added $\text{Fe(CO)}_3(\text{AsPh}_3)_2$ (1.15 g, 1.5 mmol), $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ (0.60 g, 1.5 mmol) and toluene (50 ml). After being purged with nitrogen gas for 30 minutes, the reaction solution was heated to 120°C for 24 hours. The color of the solution changed to black after refluxing for 20 minutes. Toluene was removed by vacuum. The remaining black-colored oil was treated with 10 ml of dichloromethane and 10 ml of methanol. Some precipitate

resulted. The crude solid was collected by filtration after 12 hours at -5°C . Yield: 0.77 g. The P-31 NMR spectrum showed the solid was a mixture of complexes.

12. Reaction of $\text{Fe}(\text{CO})_3(\text{AsPPh}_3)_2$ and $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ (2:1)

The same procedure was used as described above except the amount of $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ was reduced by one-half (0.30 g, 0.70 mmol). The yield of the crude product was 0.49 g. The P-31 NMR spectrum of this product showed it to be a mixture of complexes.

13. Preparation of $\text{Fe}(\text{CO})_3(\text{AsPh}_3)(\text{PPh}_2\text{CH}=\text{CH}_2)$

Into a 100 ml round-bottom flask, equipped with a side arm and containing a magnetic stirring bar, was added $\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ (1.77 g, 2.35 mmol), $\text{PPh}_2\text{CH}=\text{CH}_2$ (0.499 g, 2.35 mmol) and toluene (50 ml). After being purged with nitrogen gas for 20 minutes, the solution was heated to reflux for 24 hours. The solvent was removed by vacuum. The remaining brown-colored solid was dissolved in 10 ml of dichloromethane. This solution was filtered through a fritted funnel which contained 20 g of neutral alumina. The filtrate was concentrated to 5 ml and methanol (5 ml) was added. Some precipitate

formed. The product was collected by filtration after 24 hours at -5°C . The yield was 0.88 g (5%). The melting point was $198-201^{\circ}\text{C}$.

Infrared spectrum: (CH_2Cl_2) 1883cm^{-1} . P-31 NMR spectrum: $\delta_{\text{p}}=79.2$ ppm.

14. Preparation of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{CH}=\text{CH}_2)(\text{PPh}_2\text{H})$

14.1 Method 1

The same procedure was used as described above. The reaction mixture consisted of $\text{Fe}(\text{CO})_3(\text{AsPh}_3)(\text{PPh}_2\text{CH}=\text{CH}_2)$ (0.78 g, 1.18 mmol), PPh_2H (0.21 g, 1.18 mmol) and toluene (50 ml). After the solution was refluxed for 24 hours, the solvent was removed by vacuum. The remaining solid was treated with 10 ml of dichloromethane and 10 ml of methanol to afford some precipitate. The presence of the compound was confirmed with P-31 NMR spectroscopy.

$\delta_{\text{p}}(\text{PPh}_2\text{H})=54.7$ ppm, $\delta_{\text{p}}(\text{PPh}_2\text{CH}=\text{CH}_2)=76.0$ ppm, $J_{\text{pp}}=30.7$ Hz.

14.2 Method 2

A modified procedure, originally described by Ellis²³, was used for this preparation. Into a 250 ml

round-bottom flask, equipped with a side arm and containing a magnetic stirring bar, 55 ml of a 20% methanolic solution of $[\text{Et}_4\text{N}][\text{OH}]$ (74 mmol) was added to solid $\text{Fe}(\text{CO})_4\text{PPh}_2\text{CH}=\text{CH}_2$ (1.88 g, 5.0 mmol). After the solution was stirred for 20 minutes, methanol was slowly removed by vacuum, yielding a light yellow slurry. It was rinsed with ethanol (3 30 ml) and hexane (2 30 ml) under nitrogen.

Diphenylphosphine (0.93 g, 5.0 mmol) and toluene (80 ml) was added by syringe. Glacial acetic acid (4.5 g, 5.0 mmol) was added dropwise into the solution. A reaction occurred as evidenced by gas evolution and gradual disappearing of solid. The solvent was removed under reducing pressure. The infrared and P-31 NMR spectra showed that the remaining solid was a mixture of complexes. Separation of the product from this mixture was not successful.

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