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"PHOSPHINE, PHOSPHITE AND ISONITRILE COMPLEXES
OF GROUP (VIII) METAL CARBONYLS"

BY

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A thesis submitted to the University of Keele
in partial fulfillment of the requirements for
The Degree of Doctor of Philosophy.

Department of Chemistry
University of Keele.

August 1981.

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ACKNOWLEDGEMENTS

I would like to take this opportunity to thank all those who have helped me in the production of this work. Extra special thanks are extended to;

The Science Research Council for supporting me with a Studentship.

The Department of Chemistry (University of Keele) for providing the excellent laboratory facilities in which this work was performed.

My supervisor Dr.J.A.S. Howell for his guidance and support throughout the duration of the work.

The laboratory technicians within the Department of Chemistry for their assistance during the practical work.

Terry for his valuable time in the production of the spectra photographs illustrated herein.

Maureen and Sheila for their time and endless patience in the typing of this work.

My wife, Claire for her support in times of adversity.

My Parents for their moral support in the project.

ABSTRACT

The work in this thesis is concerned with the reactions of various ligands with group (VIII) metal carbonyls and is presented in five chapters.

Chapter one introduces the reader to the field of polynuclear metal cluster chemistry. First the structure and modes of bonding of various two electron donors (eg; CO, CS, PR_3) to metal clusters are described. This is followed by a brief description of the various methods for the preparations of polynuclear metal clusters, and in particular the metal-isonitrile clusters. Finally the application of n.m.r. spectroscopy to polynuclear metal complexes is examined.

Chapter two is concerned with the preparation and fluxional behaviour of the isonitrile complexes $[\text{Cp}_2\text{M}_2(\text{CO})_3(\text{CNR})]$ ($\text{M} = \text{Fe}$, $\text{R} = \text{Me}$, Et , Pr^i , Bu^t , Ph ; $\text{M} = \text{Ru}$, $\text{R} = \text{Me}$, Et , Pr^i , Bu^t) together with the preparations of the complexes $[\text{Cp}_2\text{M}_2(\text{CO})_3(\text{CNRH})][\text{PF}_6]$ ($\text{M} = \text{Fe}$, $\text{R} = \text{Me}$, Et , Pr^i , Bu^t , Ph ; $\text{M} = \text{Ru}$, $\text{R} = \text{Et}$) and $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNR}'\text{R}')][\text{PF}_6]$ ($\text{R} = \text{Me}$ or Pr^i , $\text{R}' = \text{Et}$) formed from electrophilic attack by H^+ or C_2H_5^+ on the neutral isocyanide derivative.

Chapter three is concerned with the preparation and fluxional behaviour of the isonitrile complexes $[\text{Cp}_2\text{M}_2(\text{CO})_2(\text{CNR})_2]$ ($\text{M} = \text{Fe}$, $\text{R} = \text{Me}$, Et , Pr^i ; $\text{M} = \text{Ru}$, $\text{R} = \text{Pr}^i$) and $[\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNR})_3]$ ($\text{R} = \text{Me}$, Et , Pr^i). The nitrogen inversion processes of these complexes are discussed.

Chapter four covers the reactions of the bidentate isonitriles $\text{CN}(\text{CH}_2)_n\text{-NC}$ ($n = 2, 3, 4, 6$) with $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ which yield only $[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2\text{-CN}(\text{CH}_2)_n\text{NC}$ derivatives. These complexes exhibit fluxional behaviour, and may be protonated to yield $\{[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2\text{CN}(\text{H})(\text{CH}_2)_n(\text{H})\text{NC}\}(\text{PF}_6)_2$ salts and can be cleaved with iodine to give $\text{CpFe}(\text{CO})_2\text{I}$ and $[\text{CpFe}(\text{CO})\text{I}]_2\text{CN}(\text{CH}_2)_n\text{NC}$. The reaction of $\text{CN}(\text{CH}_2)_n\text{NC}$ ($n = 2, 6$) with $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$ yields exclusively $[\text{Fe}(\text{CO})_4]_2\text{CN}(\text{CH}_2)_n\text{NC}$ ($n = 2, 6$) derivatives.

Chapter five details the reactions of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ with (a). $\text{P}(\text{OR})_3$

ligands ($R = \text{Me, Et, Bu}^n$) which yields $\text{CpRu}(\text{CO})_2\text{R}$, $\text{CpRu}(\text{CO})[\text{P}(\text{OR})_3]\text{P}(\text{O})(\text{OR})_2$, and $\text{CpRu}[\text{P}(\text{OR})_3]_2\text{P}(\text{O})(\text{OR})_2$ derivatives resulting from C-O bond cleavage.

(b). PPr_3 and PPhMe_2 which yield a mixture of the monosubstituted dimer $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PR}_3$ and the hydrides $\text{CpRu}(\text{CO})_x(\text{PR}_3)_{2-x}\text{H}$ ($x = 0, 1$) depending on reaction conditions. The reaction between $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OR})_3$ ($R = \text{Me, Et}$) and $\text{P}(\text{OR})_3$ ($R = \text{Me, Et}$) yields $\text{CpFe}(\text{CO})[\text{P}(\text{OR})_3]\text{COR}$, and $\text{CpFe}(\text{CO})[\text{P}(\text{OR})_3]\text{P}(\text{O})(\text{OR})_2$ derivatives. Reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPr}_3$ with PPr_3 yields the hydride $\text{CpFe}(\text{CO})(\text{PPr}_3)\text{H}$ and ferrocene. The mechanisms of these reactions and the fluxionality of the substituted dimers are discussed.

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CHAPTER 1

INTRODUCTION

Organo-transition metal chemistry has been a developing field over the past 25 years and continues to be of increasing interest. The field of synthetic organometallic chemistry has been extensively explored, but knowledge of structure and bonding was relatively limited until quite recently. Advances in this field have proceeded with the development of new methods in probing the properties of organometallic species. From the older known spectroscopic methods such as infrared and nuclear magnetic resonance spectroscopy information pertaining to structure and types of bonds in solution is obtained. X-ray diffraction coupled with neutron diffraction are useful in yielding electron density distributions within metal cluster compounds, as well as the solid state structure, and this data is useful for testing proposed bonding models. Newer techniques such as photo-electron spectroscopy are used to probe the electronic structure of metal clusters, and the ligands that bind to them. Rationalisation of the data obtained from these spectroscopic experiments into forming bonding models for various metal carbonyl complexes is a developing field. Although some progress has been made there are many observed effects that remain inexplicable. Why do some clusters contain bridging ligands whilst others do not? An attempt to pool together the experimental data and theoretical data to gain some insight into metal cluster bonding is presented below.

First a brief summary of metal cluster properties will be given, as the bonding models must fit in with the known properties of metal clusters. The thermal and photochemical reactions of metal carbonyl cluster complexes are brought about at temperatures of less than 200°C. The reactions are stoichiometric or catalytic in nature, and experimental data concerning mechanisms is obtained by normal methods. At present the work has been centred on the stoichiometric processes of mono-metallic species. Although mono-metallic species have been found to catalyse isomerisation, hydrogenation,

cyclisation, polymerisation, carbonylation, hydroformylation of olefins and acetylenes, and the interesting olefin metathesis process, more interest is now being focussed upon polynuclear complexes for a number of reasons. They are being found to be more versatile than mono-metallic species, and besides being able to catalyse the above processes they have been found to stereospecifically catalyse the hydrogenation of triply bonded species such as nitriles and isonitriles¹ and to catalyse the Fischer-Tropsch synthesis of carbon monoxide to alkanes.² An analogy between the chemiadsorbed metal surface and polynuclear metal complexes has been presented by Muetterties et al³, but the analogy was found to be most applicable to the larger clusters containing over fourteen metal atoms in the metal cluster core. The reactions are performed in a homogeneous phase and catalysis occurs at lower temperatures than are usually required for heterogeneous catalytic processes. The versatility of polynuclear metal complexes over mono-metallic species may be ascribed to their unique properties which can be listed as the following.

- a) Unsaturated organic molecules may bind to the metal cluster not only by ligand substitution, but also by reversible cleavage of metal-metal bonds.⁴
- b) Oxidative addition of substrates to clusters appears to be favoured by the proximity of two metal atoms.⁵
- c) The cluster framework can act as a reservoir for excess or missing electrons.⁶
- d) Substrates bound to the cluster framework exhibit fluxional behaviour. In particular carbon monoxide, hydrogen and isonitriles are able to migrate rapidly between sites on the cluster framework. The important feature of this process is that potentially reactive species are able to approach one another over the metal cluster surface for reaction.

Fluxional molecules are a subset that belong to the larger group of

molecules that exhibit stereochemical non-rigidity. Many mechanisms have been proposed from the experimental data accumulated concerning these molecules.⁷ Little work, however, has been done in correlating these mechanisms to the electronic perturbations that these processes may incur in polynuclear metal complexes. Thus before the mechanisms can be accepted energetic considerations concerning electronic perturbations must be accounted for in these fluxional processes.

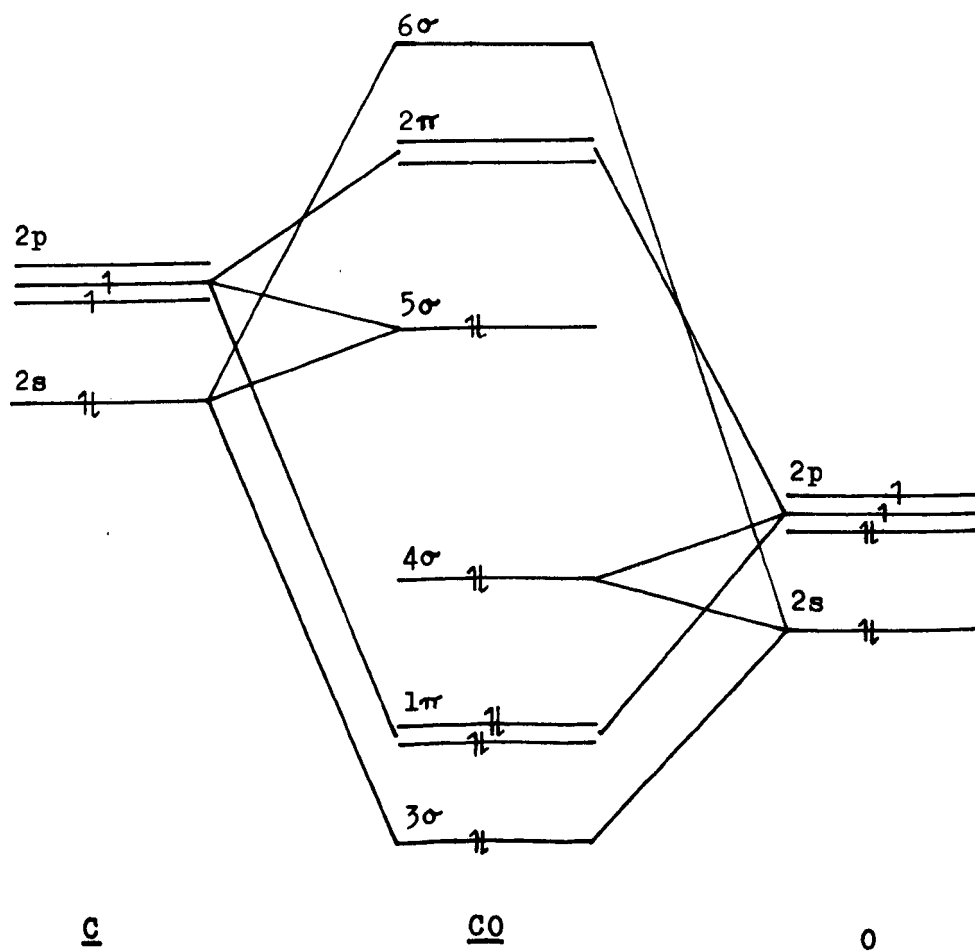
The simplest types of polynuclear metal complexes are the dimetal species. Recently much interest has been focussed upon the bonding of ligands in these complexes, and they feature most types of metal carbonyl bonds found in the higher order polynuclear metal clusters. It is reasonable therefore for the dimetal species to be taken as a representative of the polynuclear complexes for analysis.

There are a wide variety of two-electron donors available for metal-ligand interactions in dimetal species, and these ligands fall into three main groups. The first is formed of those ligands that are experimentally observed to occupy a terminal position in a dimetal cluster, and members include PR_3 , P(OR)_3 , AsR_3 and SbR_3 . The second group is formed from those ligands that are experimentally observed to occupy a bridging position between two metal atoms in a dimetal species, and members include CS and CR_2 . The third group of ligands are those that are experimentally observed to occupy both bridging or terminal positions in dimetal species, and members include CO and CNR . The metal-ligand bonding of all these species can be viewed as the sum of a σ bond, involving the donation of a lone pair of electrons from the ligand to unoccupied metal orbitals, and a π bond in which filled metal orbitals donate electrons to empty π or π^* orbitals on the ligand. All of the ligands of groups 1, 2 and 3 are potentially able to bond either in a bridging or terminal position in a dimetal species, and yet experimental evidence indicates that ligands will belong to one of the three groups.

This can be rationalised if the electronic structures of the ligands and the metal ligand bonds are examined at the molecular level.

The synergic model of bonding is well established for the terminal bonding of carbon monoxide to a metal centre⁸, but a description is given here as a basis for further discussion. Figure 1 shows the molecular

Figure 1. Molecular Orbital for Carbon Monoxide.

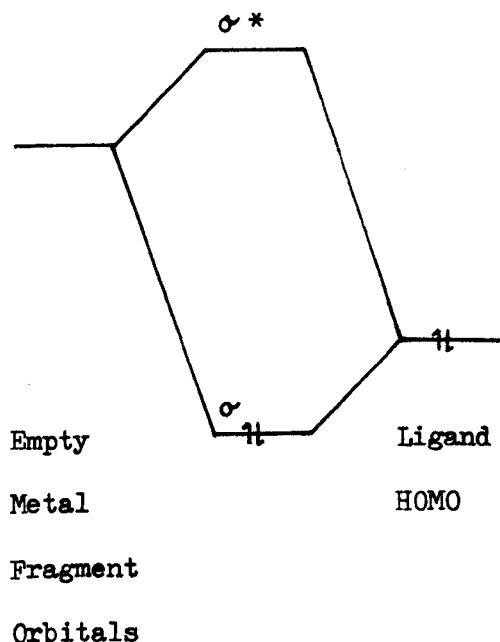


orbital diagram for carbon monoxide. It can be seen that the highest occupied molecular orbital (HOMO) is the 5σ level, which is localised over the carbon atom. The lowest unoccupied molecular orbitals (LUMO) are the 2π levels. These orbitals are of suitable symmetry for overlap with appropriate filled metal orbitals. These two orbitals are the ligands σ donor and π* acceptor functions, mentioned above, respectively. The 4σ level is localised over the oxygen atom, and contributes little to the bonding in the ligand.

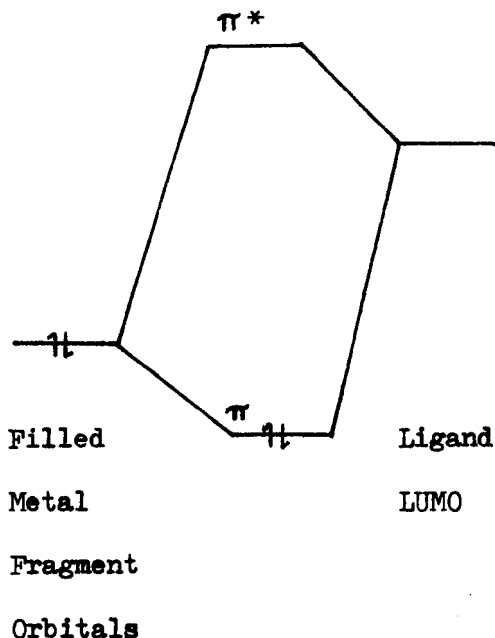
This leaves the 3σ and 1π levels, which are fully occupied, as the bonding orbitals; thus carbon monoxide has a bond order of three.

Figure 2. Metal-Ligand Frontier Orbital Interactions.

(a). σ - bond.

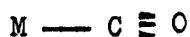


(b). π - bond.

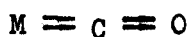


The metal-carbonyl bond can be viewed as an interaction between their respective frontier orbitals. Figure 2 (a) shows the interaction between the ligands occupied σ level, 5σ for carbon monoxide. The relative energies of the metal and ligand levels are dependent upon the ligand and metal employed, but one can see that either a lowering of the metal acceptor orbital or a raising of the ligand donor orbital in energy results in a stronger σ bond. The resulting σ bond has the effect of depopulating the ligands σ level, and is enhanced by the positive charge on the metal brought about by the back donation of electrons from filled metal orbitals into unoccupied π or π^* levels on the ligand seen in figure 2 (b). The relative energies of these levels in again dependent upon the metal and ligand employed. The lowering in energy of the ligands π acceptor function

or a raising in energy of the metal donor function results in better π overlap and a stronger π bond. This effect is most pronounced in methylene in which the ligand acceptor function is lower in energy than the metal donor function.⁹ The effect of a synergic bond is twofold. Firstly the 5σ level of carbon monoxide is slightly antibonding with respect to carbon and oxygen⁸ so that depopulation of this level strengthens the carbon-oxygen bond. Secondly the populating of the 2π level by back-bonding weakens the carbon-oxygen bond. Experimental data shows that a weakening of the carbon-oxygen bond is observed upon carbon monoxide co-ordinating to a dimetal cluster. The valence bonding of carbon monoxide to a metal can be pictured as a combination of the two canonical forms shown below. As back bonding



(I)



(II)

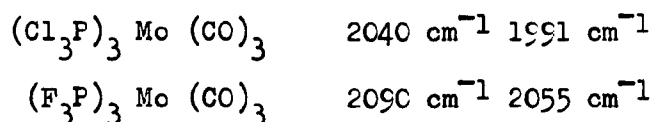
from the metal increases the canonical form (II) becomes more structurally important. The ability of carbon monoxide to accept excess electron density from the metal is a property of the particular bond, and carbon monoxide is described as an electron sink. The metal-carbonyl bond is sensitive to the oxidation state of the metal, to the d configuration of neutral metals, and to other ligands bound to the metal. As a metal becomes more negatively charged back-bonding increases, and the carbon-oxygen bond weakens. In terms of figure 2 (b) the metal orbitals are raised in energy with respect to the ligand orbitals with increasing negative charge accumulation at the metal centre, and this forms a more energetically favourable overlap with the ligand acceptor orbitals. Thus for the isoelectronic series $V(CO)_6^-$, $Cr(CO)_6$ and $Mn(CO)_6^+$ an increase in CO bond strength is predicted along the series V, Cr, Mn and this is observed experimentally using infrared stretching frequencies of CO as a probe.¹⁰

$$V(CO)_6^- = 1860 \text{ cm}^{-1}$$

$$Cr(CO)_6 = 2000 \text{ cm}^{-1}$$

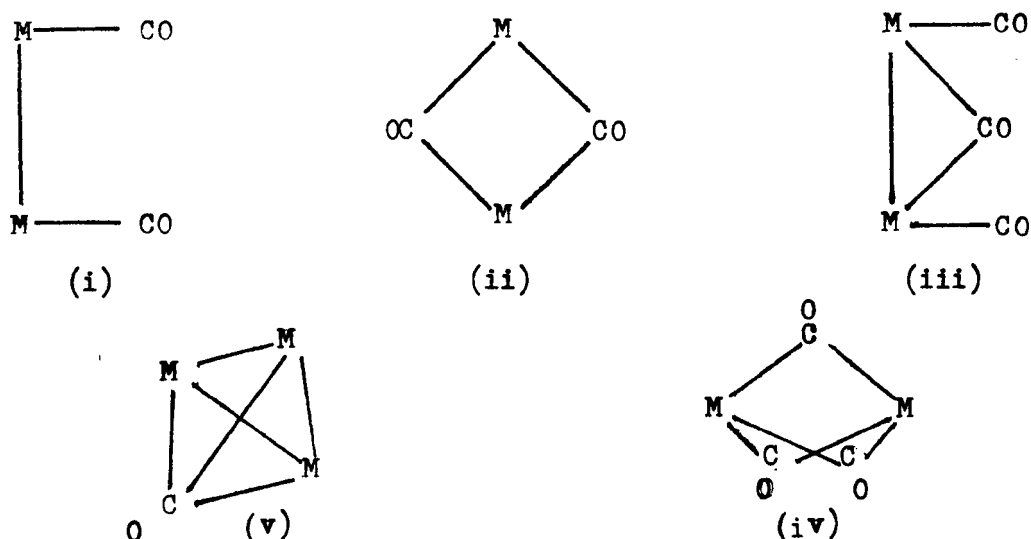
$$Mn(CO)_6^+ = 2090 \text{ cm}^{-1}$$

For the series $L_3Mo(CO)_3$ an increase in CO bond order is predicted as L becomes more electron withdrawing making the metal centre more positive. In terms of figure 2b the metal levels become lower in energy with respect to the ligand levels resulting in poorer overlap between the metal and CO orbitals. For $L = PCl_3$ and PF_3 the CO bond order should increase along the series PCl_3 , PF_3 and this is observed experimentally, again using CO infrared stretching frequencies as a probe.¹¹ If the metal orbitals available for



bonding, usually d, s, and p orbitals for transition metals, are nearly filled or empty a metal carbonyl bond is not possible, and equally well if the metal is in a high oxidation state. Thus most of the neutral binary metal carbonyls are found in the centre of the transition metal block.

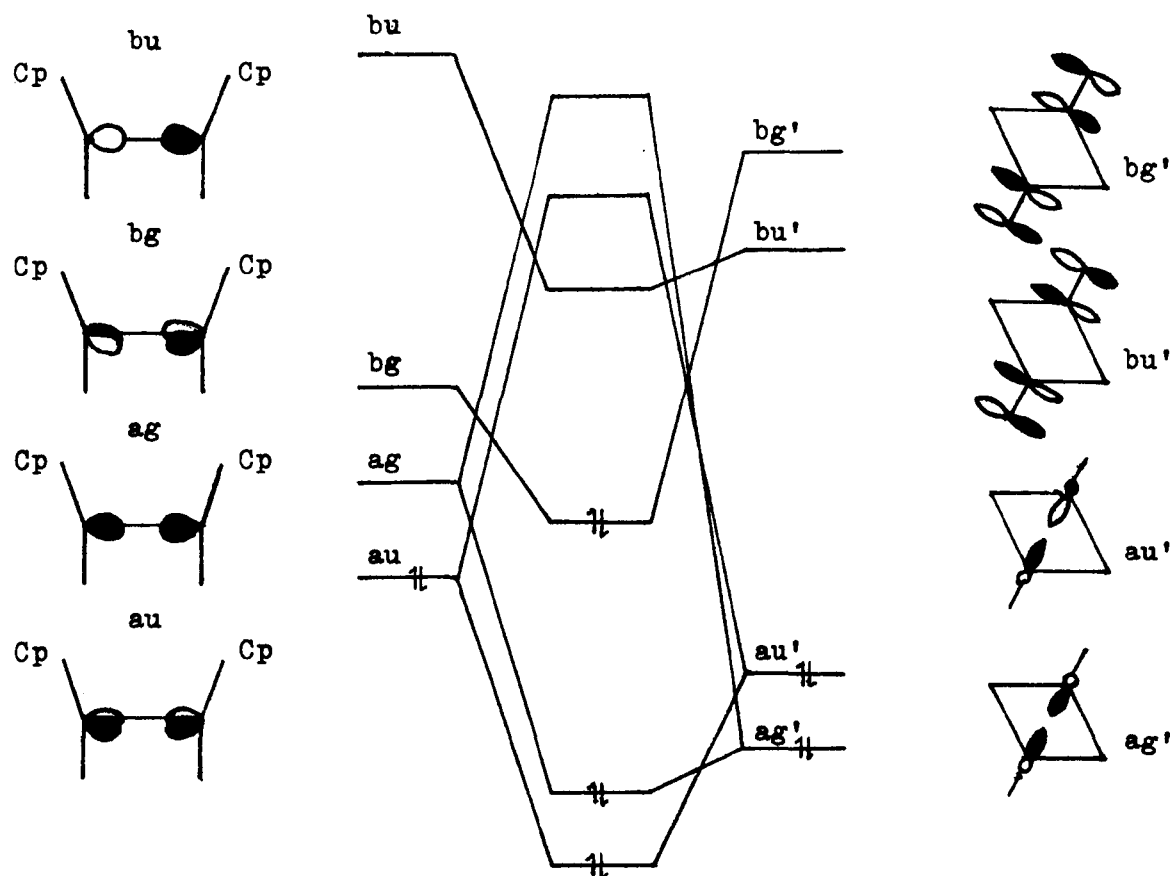
Figure 3. Metal Carbonyl Bonding Modes.



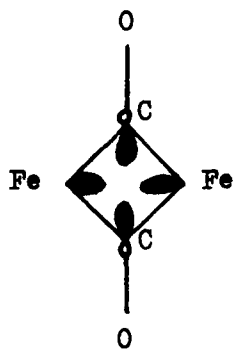
In figure 3 the metal cluster bonding alternatives for carbon monoxide are shown. Structure (i) shows the terminal carbonyl mode of bonding, which has been described above; (ii) (iii) and (iv) show carbonyl groups bridging two metal atoms. These bridging carbonyl systems, originally thought to be ketonic in nature,¹² have been studied theoretically and have been found to contain complex multicentred bonds.¹³ To simplify the description, $Cp_2Fe_2(CO)_4$

will be taken as a specific example,^{13b, c.} and this compound is known to contain the bridged structure (ii). This metal cluster contains two terminally bound carbonyl ligands, two bridging carbonyls, and two cyclopentadienyl groups. The formal electron count for this molecule shows that each iron atom has a $17e^-$ count, and so with a metal-metal bond in the complex both metals achieve an $18e^-$ configuration consistent with the diamagnetic nature of the compound. Figure 4 shows the relevant orbitals for interaction between a $Cp_2Fe_2(CO)_2$ fragment and the bridging carbonyl ligands. The $Cp_2Fe_2(CO)_2$ fragment is formed from the combination of two $CpFe(CO)$ fragments brought together along the metal axis with the (CO) groups either cis or trans to one another. The result is the formation of the four orbitals on the LHS of figure 4. The lowest in energy a_u is a metal-metal π interaction. The a_g orbital is second lowest in energy and is a metal-metal σ interaction. The b_g orbital is the third lowest in energy and is a metal-metal π^* interaction, and finally the highest in energy is the b_u orbital which is a metal-metal σ^* interaction. The ligands 5σ and 2π levels can be combined to form the symmetric a_g and b_g orbitals and antisymmetric a_u and b_u combinations shown on the RHS of figure 4. These ligand combinations interact with the metal cluster orbitals of the same symmetry. The a_u and a_g interactions form to low lying orbitals which are localised mainly along the metal carbon axes having little metal-metal bonding character, and the b_u and b_g interactions form the LUMO and HOMO for the system respectively. To maximise overlap the ligands 2π orbitals can rotate about the CO bond axis out of the $Fe_2(\mu CO)_2$ plane. For the cis isomer the CO ligands, to maximise overlap, would move out of the $Fe_2(\mu CO)_2$ plane, puckering the ring. This is observed for the cis isomer of $Cp_2Fe_2(CO)_4$ ¹⁴ and lends support to the above bonding model. For the trans isomer a planar $Fe_2(CO)_2$ ring is predicted by the model and this is substantiated by crystallographic evidence.¹⁵ The HOMO for the system is definitely antibonding with respect to a metal-metal bond and more than

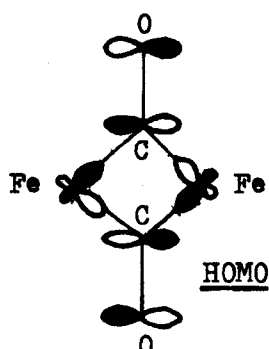
Figure 4. Molecular Orbital Diagram for Dicyclopentadienyldiirontetracarbonyl



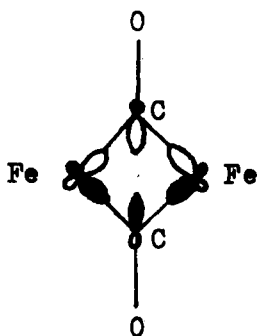
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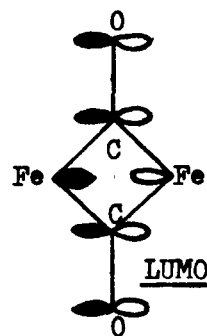
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au



bu



Ligand σ - donor bonding orbitals
with metal acceptor orbitals.

Ligand π^* - acceptor orbitals with
metal donor orbitals.

compensates for the metal-metal bonding character of the lower lying states. The $\text{Fe}_2(\mu\text{CO})_2$ fragment can be thought of as being a delocalised multicentred bond, and this model predicts no metal-metal bonding character for structure (ii) of figure 3. This bonding model is further supported by electron density maps obtained from X-ray and neutron diffraction studies, which show very little electron density along the metal-metal axis, and that most of the electron density is delocalised over the M-CO-M linkages.

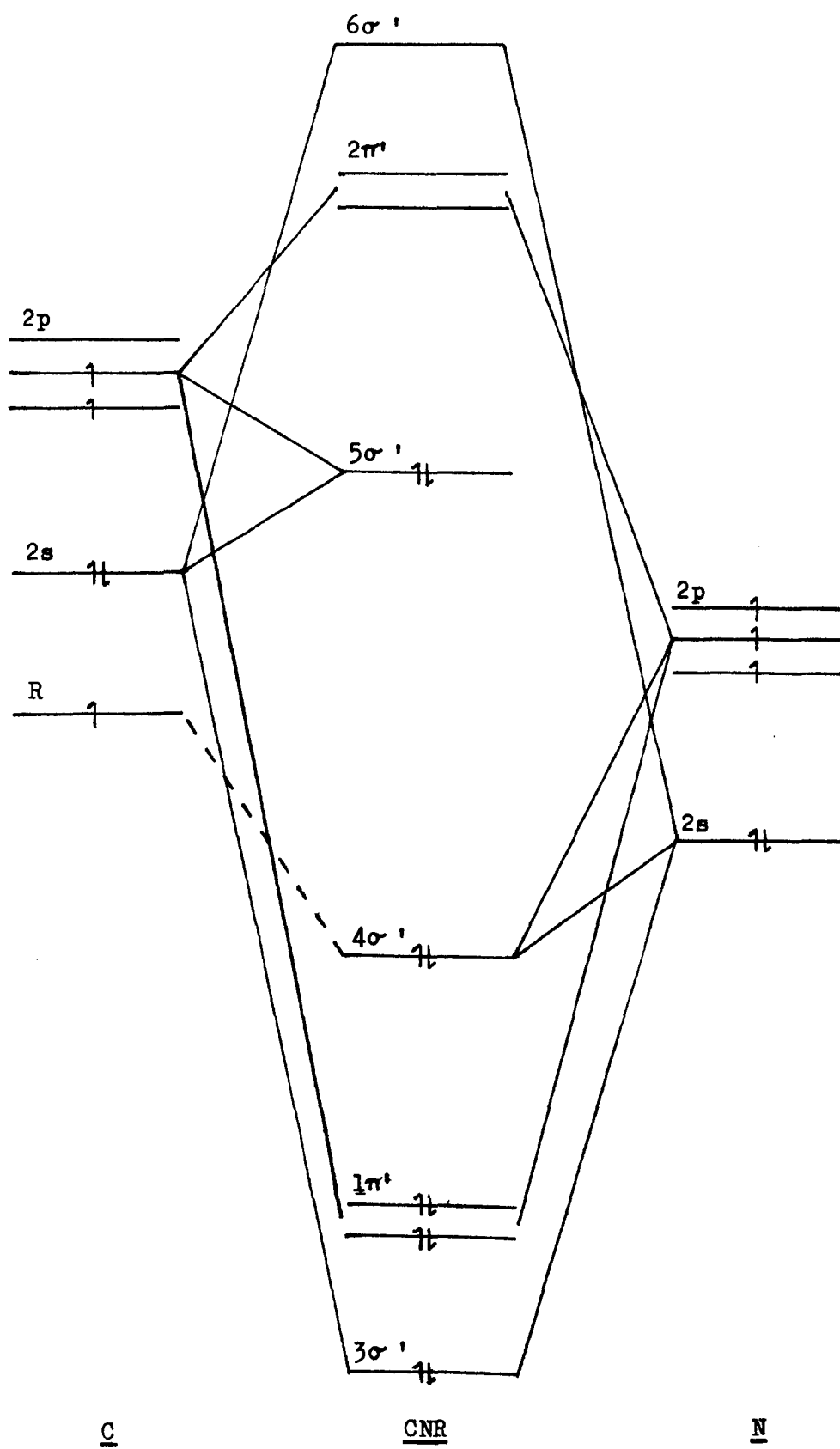
The bonding of carbonyls in $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ can now be extended to the complexes in which CO ligands are substituted by one or more other two electron ligands. First the isonitrile ligand will be considered.⁸ Isonitriles are isoelectronic to carbon monoxide and a molecular orbital diagram for the CNR ligand is shown in figure 5. The $5'\sigma$ and $2'\pi$ levels are the HOMO and LUMO as with carbon monoxide. The 4σ level becomes, in the isonitrile case, the bond between nitrogen and the R bonded group. The R group effects the relative energies of the nitrogen orbitals compared to the carbon orbitals and this effect will be discussed later. Using the same orbitals as carbon monoxide a synergic bond is formed upon co-ordination of the isonitrile to a metal. The bonding properties are dependant upon the energies of the HOMO and LUMO in the ligand. From figure 2 (a) it can be seen that a raising in energy of the $5'\sigma$ level results in a stronger σ bond through better orbital overlap; and that a lowering in energy of the $2'\pi$ level will result in better orbital overlap increasing metal-ligand back bonding. For carbon monoxide the 5σ and 2π levels are at a fixed energy, but for isonitriles the $5'\sigma$ and $2'\pi$ levels are dependant upon the nature of the R group.¹⁷ Table 1 shows the energies of the $5'\sigma$ and $2'\pi$ levels of some isonitriles in comparison with those of other ligands. It can be seen that changing the methyl group for a group with π -conjugation alters the 2π level drastically, whilst leaving the $5'\sigma$ level relatively unchanged. Thus while methyl isonitrile is a poorer acceptor than carbon monoxide,

TABLE 1

<u>LIGAND</u>	<u>σ HOMO</u>	<u>π LUMO</u>
	energy (au)	energy (au)
CO	-0.547	0.158
CNMe	-0.459	0.212
CNC(O)H	-0.480	0.082
CNC(O)OH	-0.493	0.086
CNC(O)Ph	-0.502	0.022
CS	-0.460	0.077
CH ₂	-0.477	-0.403
PH ₃	-0.391	0.201

benzoyl isonitrile is a better acceptor. A logical extension of this idea would be to calculate the HOMO and LUMO for systems in which the R group is electron withdrawing (eg. CF₃NC) and those in which the R group is electron donating. For a qualitative argument we may use figure 5, and take R = Me as the reference group. For an electron withdrawing group such as CF₃ the nitrogen levels would decrease in energy with respect to the carbon energy levels. This would result in a weaker 1π overlap causing this orbital to increase in energy with respect to the 1π orbital in CH₃NC. This would also have the effect of lowering the $2'\pi$ orbital in energy to compensate. The effect would be a lowering of the LUMO energy which is the criterion required for better metal ligand back bonding. The electron withdrawing group will decrease the negative charge on the carbon atom relative to MeNC causing the 5σ level, hence HOMO, to become relatively lower in energy. This would have the effect of reducing σ donation to metal complexes, because of poorer σ overlap. Conversely better electron donating species than CH₃ would have the effect of raising the $5'\sigma$ level and improving σ donor property; with the raising of the $2'\pi$ level and reducing metal ligand back bonding. The importance of these electronic effects is demonstrated in the structures of metal complexes containing

Figure 5. Molecular Orbital Diagram for Isonitrile Ligands.

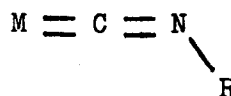


isonitrile ligands. Isonitriles can bond as 2 electron donors to metal clusters analogously to the metal carbonyl structures (i) - (v). For the metal cluster $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNR})$ the isonitrile may occupy a bridging or terminal position.¹⁸ In solution the methyl isonitrile complex exists as isomers with the isonitrile occupying bridging and terminal positions for different isomers, while the phenyl isonitrile complex exists solely as a bridged isonitrile isomer.¹⁹ There are two main reasons for this isomer shift for the two isonitriles mentioned. In the bridged position the increased back donation can be conjugated with the phenyl ring for phenyl isonitrile. The phenyl ring is also more electron withdrawing than the methyl group causing electron drift towards the nitrogen, and improving the acceptor abilities of the ligand. The electron withdrawing feature can be demonstrated further by looking at the series $\text{CNCH}_2\text{C}_6\text{H}_4\text{X-p}$ ($\text{X} = \text{H}, \text{Me}, \text{OMe}, \text{Cl}$) where the concentration of the bridged species increases in the order $\text{X}=\text{OMe}, \text{Me}, \text{H}, \text{Cl}$. This correlates with the total electron-withdrawing ability of X .¹⁸

The terminally bound isonitrile as with CO can be pictured as a combination of the two canonical forms shown below. It would be expected that the



(III)



(IV)

$\hat{\text{CNR}}$ bond angle would contract from 180° as the ligand accepts more back bonding from the metal, and the contribution from IV increases. A large deviation from 180° is reported for the electron rich species $\text{trans-}[\text{Mo}(\text{CNMe})_2(\text{dpe})_2]$ for which the $\hat{\text{CNR}}$ bond angle is 156° .²⁰ It has been suggested that this is an electronic rather than a steric effect. Back bonding reduces the CN bond order, and necessarily reduces the $\hat{\text{CNR}}$ bond angle. Supportive evidence comes from the species $[\text{Ru}(\text{CNBu}^t)_4\text{PPh}_3]$ and $[\text{Fe}(\text{CNBu}^t)_5]$ ¹⁸ which have $\hat{\text{CNR}}$ bond angles of 130° and 134° respectively. The complexes exhibit isonitrile stretching frequencies at approximately 1830 cm^{-1} representing a shift of 300 cm^{-1} from the resonance of the free

ligand.

The bonding within an $\text{Fe}_2(\mu\text{-CNR})_2$ fragment is qualitatively analogous to the $\text{Fe}_2(\mu\text{-CO})_2$ fragment discussed earlier for $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ in figure 4. Since there is no data available concerning the energies of the isonitrile ligand combinations $a'u$, $a'g$, $b'u$, $b'g$ for an $\text{Fe}_2(\mu\text{CNR})_2$ fragment, conclusions can be drawn from the wealth of experimental data concerning the species $\text{Cp}_2\text{Fe}_2(\text{CO})_{4-x}(\text{CNR})_x$ ($x=0,1,2,3$). In Table 2 there are shown some infrared stretching frequencies, and they form the basis for this qualitative argument. It would be reasonable to assume that increased back bonding to either the isonitrile or carbonyl ligands would reduce bond order and hence reduce the infrared stretching frequency. Replacing a terminal carbonyl for an isonitrile

TABLE 2

<u>Compound</u>	<u>νCO_b</u>	<u>νCO_t</u>	<u>νCN_b</u>
(A) $\text{Cp}_2\text{Fe}_2(\text{CO})_4$	1797 ^a	2007	
		1964	
(B) $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\mu\text{CNMe})$	1802	1998	1737
		1953	
(C) $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNMe})(\mu\text{CNMe})$	1784		1720
(D) $\text{Cp}_2\text{Fe}_2(\text{CO})_3(t\text{CNMe})$	1774		

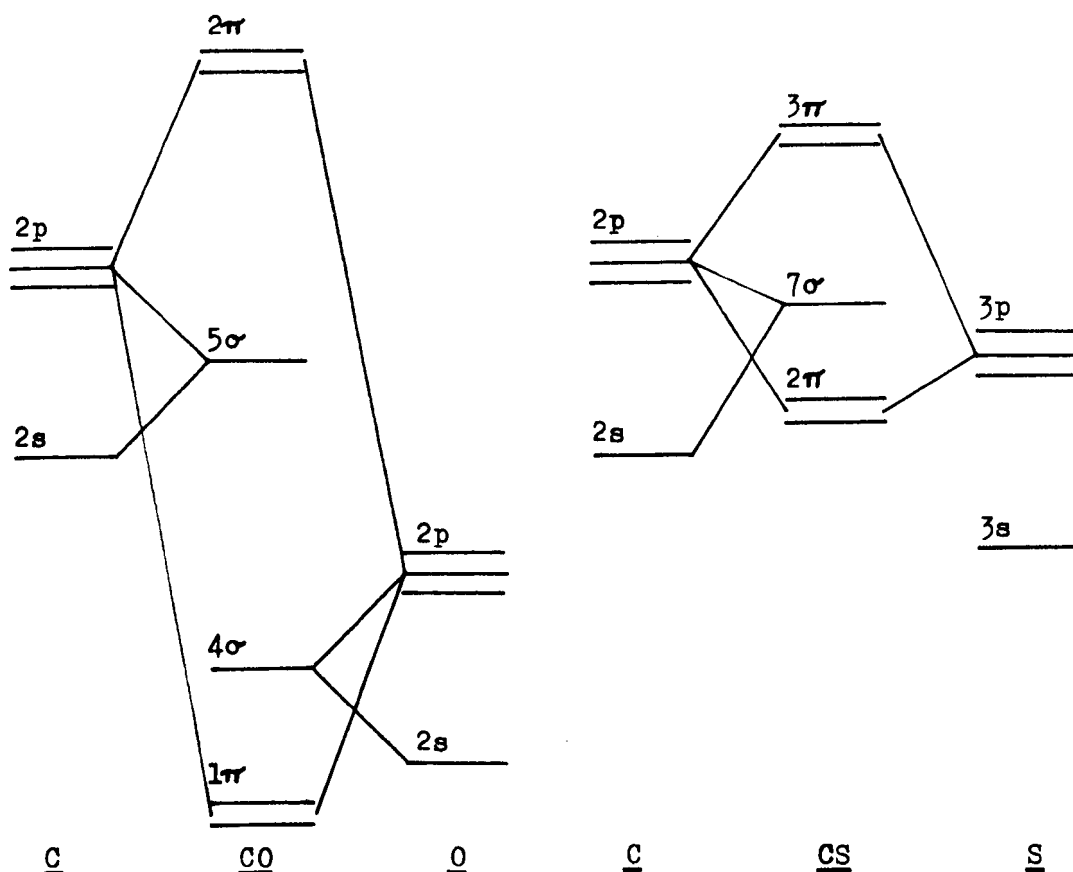
a. stretching frequencies measured in cm^{-1}

in (A) gives (D). This results in a drop in the infrared stretching frequency of the bridging carbonyl from 1797 cm^{-1} to 1774 cm^{-1} , and this illustrates the better donor, poorer acceptor facility of the methyl isonitrile ligand. The excess electron density is fed into the bridging carbonyl acceptor functions. This in terms of figure 4 would be brought about by a raising in energy of the metal orbitals relative to the ligand combinations. Replacing a bridging carbonyl for an isonitrile in (A) gives (B). This results in raising the infrared stretching frequency of the bridged carbonyl from 1797 cm^{-1} to 1802 cm^{-1} whilst lowering the terminal carbonyl infrared stretching frequencies by 9 cm^{-1} .

Replacing a terminal carbonyl for an isonitrile in (B) gives (C). Again a drop in the infrared stretching frequencies of the bridging ligands is observed as in the change from (A) to (D), and in terms of figure 4 the relative changes in energy of the orbitals similarly applies. From the above examples it can be seen that the replacement of carbonyl ligands by isonitrile ligands in metal clusters affects the bonding and electronic structure of the metal cluster. Although the trend for the replacement of terminal carbonyls by isonitrile is clear, the properties of the bridging isonitrile are more puzzling. It seems that backbonding to the terminal carbonyls increases, as would be expected for a ligand which is a poorer π acceptor, whilst the back bonding to the remaining bridged carbonyl is reduced which suggests that the situation is quite complex. This problem could probably be solved if the energies of the orbitals for (B) were calculated. From the information gained on the bonding of isonitriles and carbon monoxide to metal clusters the structure and modes of bonding of the other two electron donors will be discussed.

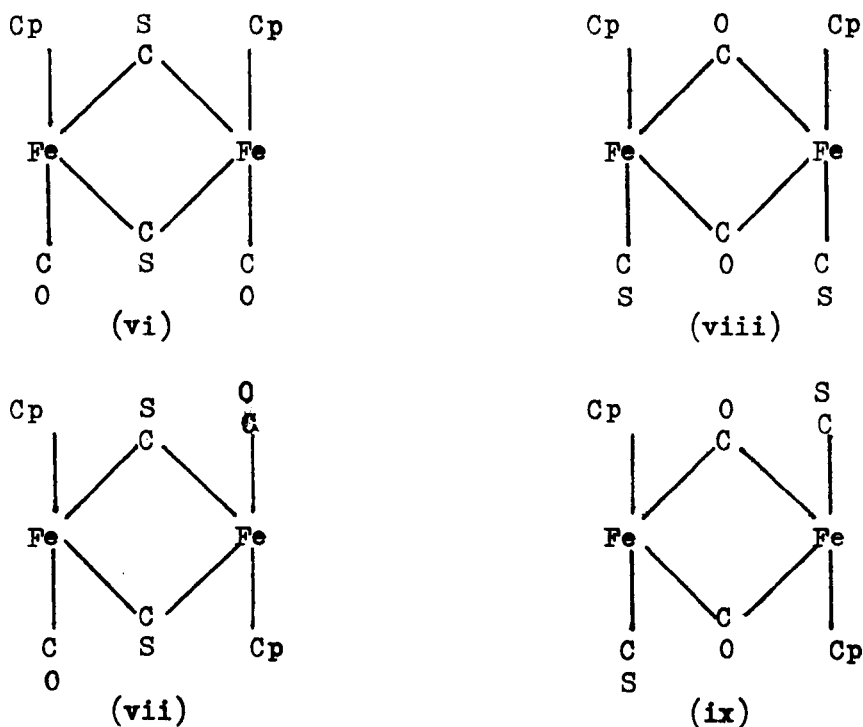
The other ligands that are observed to bridge in metal clusters include CS and CR_2 . A description of the CS ligand will be discussed first. The electronic structure of the CS ligand has been reported²², and the important features of the MO are shown in figure 6 in comparison to CO. The differences in electronic structure between CO and CS are caused primarily by the differences between the sulphur and oxygen atomic functions. Sulphur is less electronegative than oxygen, and the sulphur atomic functions are at a higher energy compared to those of oxygen. The poorer electron withdrawing of sulphur has the effect of increasing the negative charge at the carbon in CS compared to CO, which raises the energy of the 7σ carbon donor orbital, compared to the 5σ donor orbital of CO. The π bonding system in CS is weaker than in CO, and this is caused by the weaker carbon 2p - sulphur 3p interaction. The σ bond will also be weaker, and the bond energy of CS is 166 K cal/mol as compared to the bond energy of 256 K cal/mol for CO²³.

Figure 6. Molecular Orbital Diagram for Carbon Monosulphide.



The higher energy 2π bonding orbital in CS has a correspondingly lower energy 3π antibonding orbital. It can be inferred from figure 2 that the CS ligand should be a better σ donor and π acceptor than CO. Table 1 shows the calculated energies of the HOMO and LUMO for CS, and they show that CS is a better donor and acceptor than CO. These properties and the weakness of the CS π bond encourage stronger metal-ligand interactions. Using this information the structure of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$ may be discussed qualitatively in respect to $\text{Cp}_2\text{Fe}_2(\text{CO})_4$. The CS ligand could in principle occupy either the bridging position as in structures (vi) and (vii) of figure 7, or terminal positions as in structures (viii) and (ix). Using figure 4 the following deductions can be made concerning the bonding of CS in dimetal species. For (vi) and (vii) the better σ donating ability of CS should raise the energies of the ligand a'_g and a'_u combinations, relative to the metal levels, resulting in better σ overlap with the metal orbitals. The increased π acceptor ability of CS causes a lowering in energy of the

Figure 7. Isomers of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$

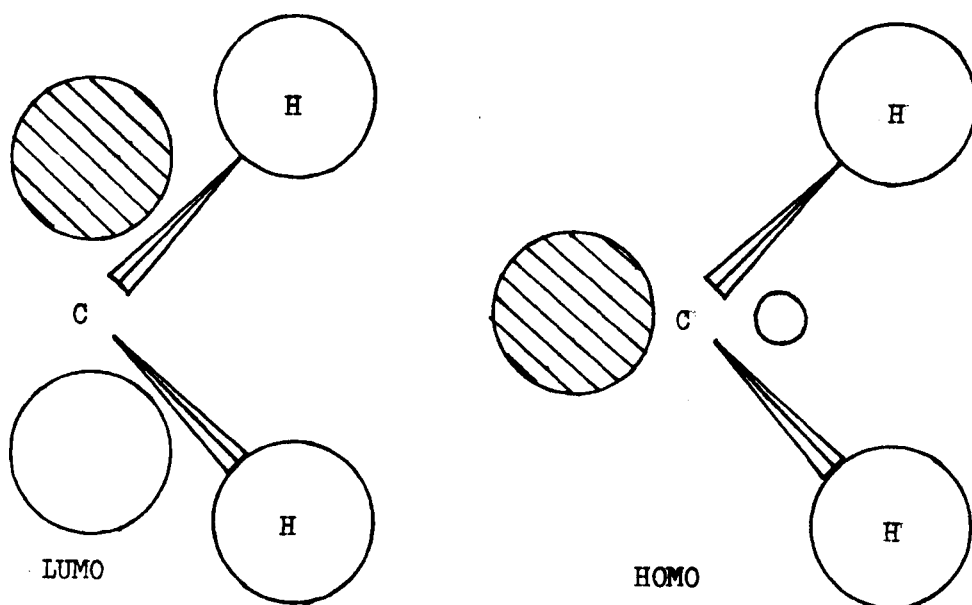


ligand b'_g and b_u combinations, relative to the metal levels, effecting a better π overlap. These two interactions are allied with a third important point. In a bridged position the ligands bond order is reduced to compensate for increased back donation from the metal orbitals into the ligand acceptor orbitals as compared to the back donation experienced in a terminal position. For CS this loss of ligand π bonding energy would be less than for the corresponding CO ligand, because of the weaker π bonding in CS. It can be postulated therefore that the CS bridged structure would be more energetically favourable than the CS terminal structure, because the increased metal-ligand interaction is gained at the loss of little CS π bonding energy in the CS ligand migrating from a terminal to a bridged position.²³ The crystalline structure of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$ is that depicted by (vi) in figure 7, which is the cis doubly thiocarbonyl bridged isomer.²⁴ The $\text{Fe}_2(\mu\text{CS})_2$ moiety is puckered with the metal-metal bond axis forming the fold, and this provides further support to the delocalised multicentred bonding model proposed

earlier for the $\text{cis Fe}_2(\mu\text{CO})_2$ system.

The carbene ligand CR_2 is another ligand that is observed to have bridged site preference, but differs in electronic structure to the ligands discussed so far. The ligand CH_2 will be taken as an example of the class of carbenes. The CH_2 σ orbital is, as with the other ligands, mainly an orbital localised over the carbon atom, the π acceptor orbital is different. The methylene π acceptor orbital is formed from a non-bonding p-orbital on the carbon atom, and the HOMO and LUMO for the system are depicted in figure 8.²⁵

Figure 8. HOMO and LUMO orbitals for Methylene.

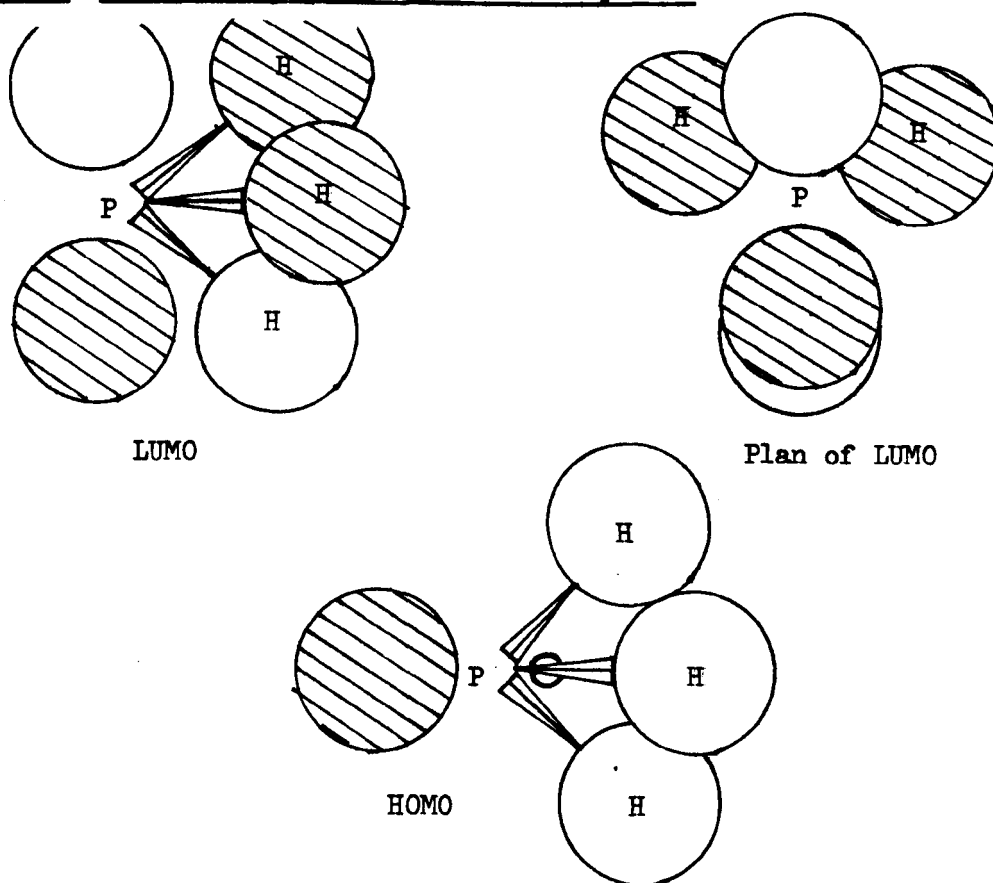


The energies of the HOMO and LUMO for methylene are tabulated in Table 1.²⁶ It can be seen that the ligand is a powerful π acceptor in comparison to carbon monoxide, and a slightly better σ donor. The LUMO of methylene is lower in energy than the metal donor orbitals, and this will aid back donation to the ligand π orbitals. In general it can be seen that increasing the π acceptor ability of a ligand increases the probability of the ligand occupying a bridged position in a dimetal species. For carbenes, therefore, it would be expected that they would occupy bridging positions. The dimetal species $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{CO})(\mu\text{CH(R)})$ have only recently been prepared, and the carbene is observed to occupy a bridged position.²⁷ Again the increased

back donation in a bridged position is probably responsible. Although there is no theoretical data concerning the species $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{CO})(\mu\text{CR}_2)$, there is data available for the species $\text{Cp}_2\text{Rh}_2(\text{CO})_2(\mu\text{CH}_2)$, and this will be discussed later.

The group V donor ligands PR_3 , $\text{P}(\text{OR})_3$, AsR_3 and SbR_3 have been found to bond to metal clusters exclusively in the terminal mode. The reasons for this can be described as being electronic in nature. The HOMO and LUMO of the ligand PH_3 are depicted in figure 9.²⁸ It can be seen that the HOMO

Figure 9. HOMO and LUMO orbitals for Phosphine.

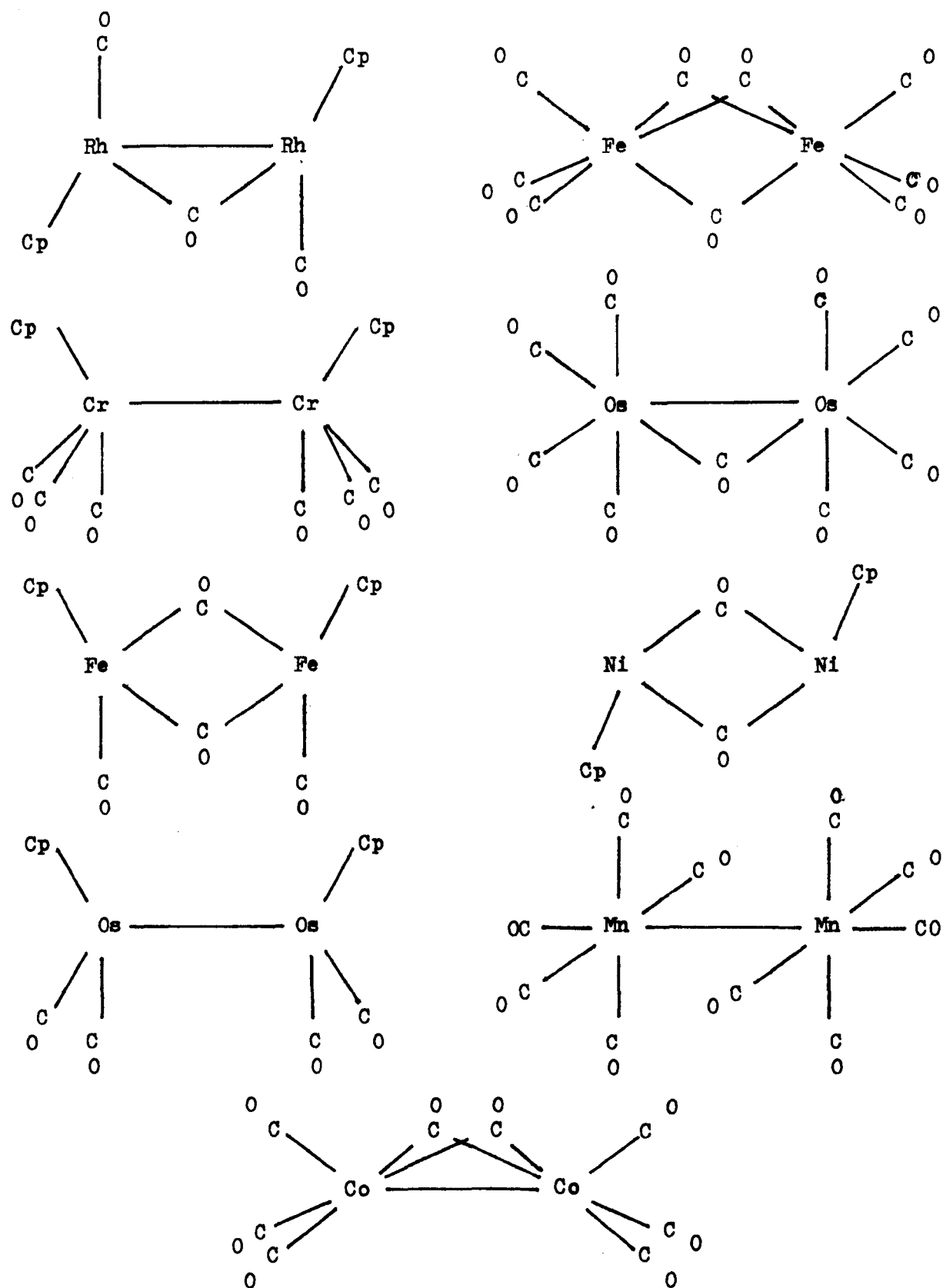


for the system is a p type donor orbital which σ bonds to the metal, and the LUMO is a d type orbital which can back bond with the metal orbitals of the same symmetry. The energies of the HOMO and LUMO are tabulated in Table 1.²⁹ It can be seen that PH_3 is a poorer π acceptor than CO, but is a strong σ donor. The LUMO energy of PH_3 is almost equivalent to that of methyl isonitrile, which is known to occupy bridging positions in dimetal species, and using this argument there appears to be no reason why PH_3 should

not be able to occupy a bridged position in a dimetal species. The fact that no group V $2e$ donor ligands are known to occupy bridged positions in dimetal species would suggest some other governing factors. For the alkylated phosphines and phosphites there will be increased steric hindrance in the bridged position as compared to a terminal position as the alkyl groups increase in size. This effect will be coupled with the fact that these species are poorer π acceptors and better σ donors than PH_3 , which would not enhance the probability of bridged occupation by these ligands. The $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{PR}_3)$ derivatives have been prepared, and the phosphine occupies a terminal position.²⁹ The strong σ donating property of the PR_3 ligand, and weaker π acceptor ability is shown in the infrared stretching frequency of the bridged carbonyls for the substituted species ($1740 - 1750 \text{ cm}^{-1}$) as compared to (1797 cm^{-1}) for the parent dimer (A). This is a good example of the electron sink property of carbon monoxide, and it could be postulated that when in competition a phosphine or phosphite will occupy a terminal position, because carbonyls are superior π acceptors and are better able to relieve a build up of negative charge on the metal atoms. If any group V donor ligand were to occupy a bridging position it would be PF_3 . The electron withdrawing effect of the fluorines would lower HOMO and LUMO energies compared to the PH_3 ligand, and in doing so increase the π acceptor ability and lower the σ donating ability. Dimetallic PF_3 metal complexes are known,³⁰ but none are known to contain bridging PF_3 ligands; with the continuing preparation of new PF_3 complexes it may only be a short time before one such cluster may be found.

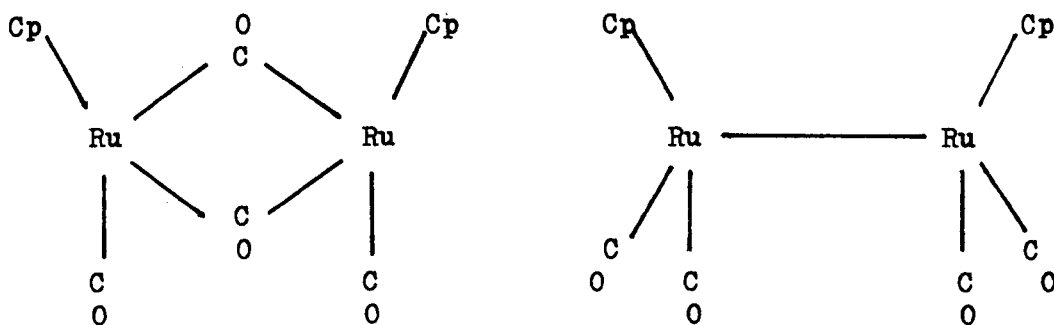
So far the discussion has been limited to dimetal clusters, but with the knowledge gained from these clusters it is an easy transformation to bonding in higher order polynuclear complexes. Before the bonding description of high order clusters is discussed, a brief description of two other bridged modes of bonding will be given. Structures (iii) and (iv) of figure 3 show

Figure 10. Some Dimetal Complexes.



two such possibilities. Like structure (i), (iii) contains a metal-metal bond, but it also contains a bridging carbonyl ligand. Structure (iv) like (ii) contains no metal-metal bond, but contains three bridging carbonyls rather than two. The structure (figure 10) and bonding of $\text{Cp}_2\text{Rh}_2(\text{CO})_3$, which contains structure (iii), has been studied theoretically.⁹ Other complexes, such as $\text{Os}_2(\text{CO})_5$, (figure 10) also adopt this type of bridged structure. The structure, shown in Figure 10, and bonding of $\text{Fe}_2(\text{CO})_5$ has been studied theoretically.^{13a} The structures (i) to (iv) are related by the opening or closing of a pair of carbonyl bridges shown in figure 11, but the structure and bonding within these species are quite different. The structures shown in figure 11 may be extended to those structures that contain other 2 electron donor ligands by simple substitution.

Figure 11. A Bridged and Non-bridged Isomer of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$



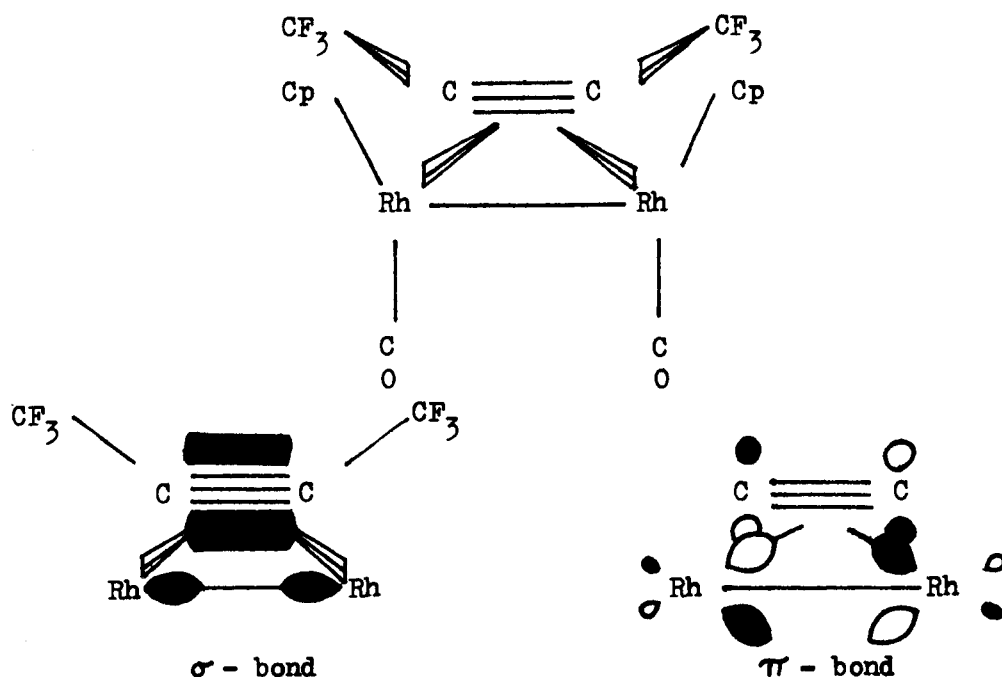
Given the choice of two structures why do some dimetal complexes opt for (i) rather than (ii) or (iii) rather than (iv)? The adopted structure is dependant upon the ligands bound to the cluster and upon the metal itself. There are many examples to choose from, and the trends observed are discussed below.

It is observed along the series $\text{M}=\text{Fe}, \text{Ru}, \text{Os}$ a trend from bridged to

non-bridged structure for dimetal and polynuclear metal systems. Thus while $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ contains the doubly bridged structure (ii), $\text{Cp}_2\text{Os}_2(\text{CO})_4$ is totally non-bridged.³¹ The complex $\text{Fe}_2(\text{CO})_9$ contains the triply bridged structure (iv) while $\text{Os}_2(\text{CO})_9$ contains the singly bridged structure (iii).³² It is observed along the series $\text{M}=\text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ a trend from non-bridged to bridged structure. Thus $\text{Cp}_2\text{Cr}_2(\text{CO})_6$ (Figure 10) is totally non-bridged while $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ and $\text{Cp}_2\text{Ni}_2(\text{CO})_2$ contain the doubly bridged structure (ii); and while $\text{Mn}_2(\text{CO})_{10}$ (Figure 10) is totally non-bridged, $\text{Co}_2(\text{CO})_8$ contains the doubly bridged structure (ii).³² The effect of ligand upon structure can be seen noticeably for substituted $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ complexes. In solution the parent exists as an approximate 50/50 mixture of the bridged and non-bridged forms (Figure 11). Mono substitution by CS ,²³ PR_3 ³⁴ or CNR ¹⁹ of a carbonyl group results in complexes that contain only the bridged structure. This latter ligand effect may be a property of the energy difference between the bridged and non-bridged forms for the substituted species. For example it has already been shown that CS has bridged site preference. Phosphines and isonitriles are better σ donors than CO and this will have the effect of increasing the negative charge on the metal. The metal can release this charge by back bonding, and since back bonding is greater for bridged carbonyls than for terminal carbonyls the tendency for these mono-substituted species to bridge seems reasonable.

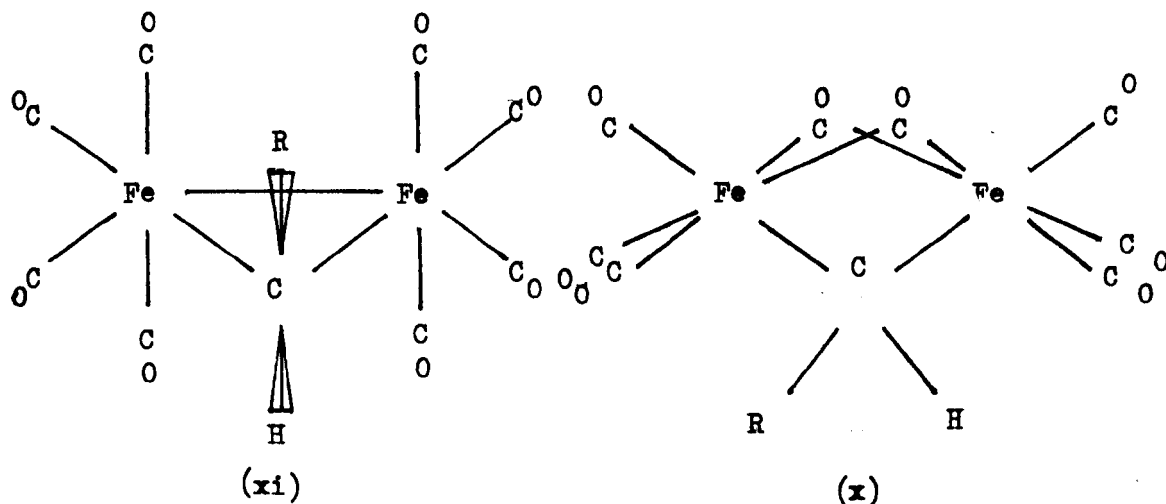
The carbene substituted species $\text{Cp}_2\text{Rh}_2(\text{CO})_2\text{CH}_2$ has been studied theoretically⁹ and while the $\text{Cp}_2\text{Rh}_2(\text{CO})_2$ fragment is more energetically stable in the dibridged form (ii), the composite molecule containing a bridged carbene with two terminal carbonyls was found to be more energetically stable than the molecule containing the bridged carbene with bridging carbonyls.^{13d} Experimentally the structure of $\text{Cp}_2\text{Rh}_2(\text{CO})_2\text{CH}_2$ supports the theory. The bonding model is further supported by the structure of $\text{Cp}_2\text{Rh}_2(\text{CO})_2\text{CF}_3\text{C}\equiv\text{CCF}_3$ in which the acetylenic bond lies normal to the metal-metal bond (Figure 12).³⁵

Figure 12. Structure and Bonding of $\text{Cp}_2\text{Rh}_2(\text{CO})_2\text{CF}_3\text{C}\equiv\text{CCF}_3$



In this position the acetylenic π system σ bonds to the metal system, and the metal system back bonds into the π^* molecular orbitals of the acetylene. The carbene substituted $\text{Fe}_2(\text{CO})_9$ species provide an interesting example of a triply bridged structure becoming a mono bridged structure upon substitution.

Figure 13. $\text{Fe}_2(\text{CO})_9(\text{CHR})$.

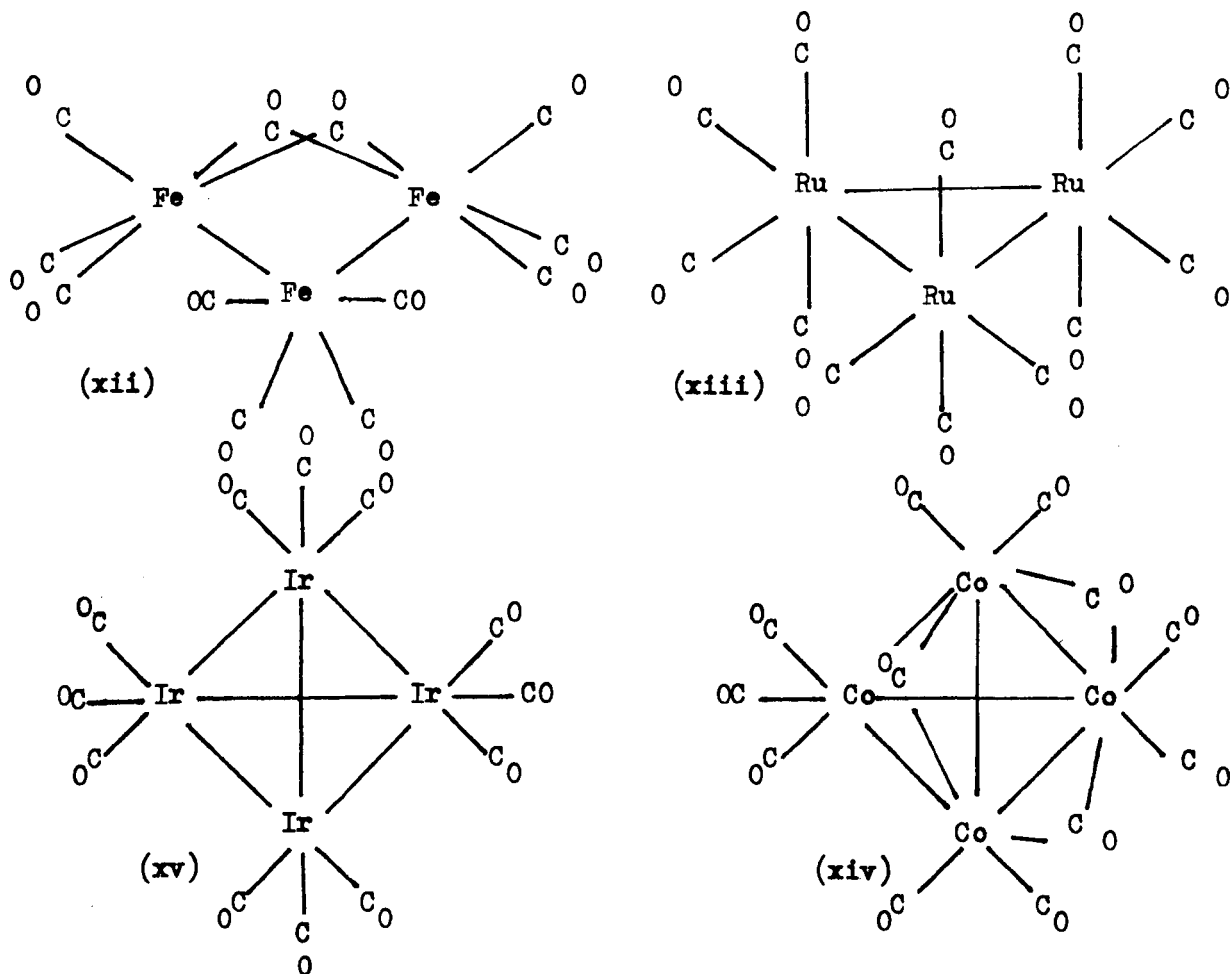


Structure (x) of figure 13 describes the solid state structure of $\text{Fe}_2(\text{CO})_8\text{CHR}$ ($\text{R}=\text{H}, \text{Ph}$), whilst in solution the structure (xi) has been detected.³⁶ This type of conversion may be explained by the increased acceptor ability of carbenes over that of carbon monoxide. For example back bonding to the bridging and terminal carbonyls as observed by infrared stretching frequencies, in $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CS})$ is reduced compared to those of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ reflecting the increased acceptor ability of CS over CO.³⁷ The reduced back bonding in $\text{Fe}_2(\text{CO})_8(\text{CHR})$ ($\text{R}=\text{H}, \text{Ph}$) to the carbonyls may be sufficient to convert the triply bridged structure (x) to the singly bridged carbene structure (xi).

It can be seen that the structure of these dimetal systems is dependent upon the donor-acceptor properties of the ligands bound to the metal. The change of structure brought about by the change of metal follows a trend, but as yet there appears to be no complete rationale as to why one structure should be adopted preferentially to another. What is observed is a tendency towards bridged structures the smaller the atomic radius of the metal.

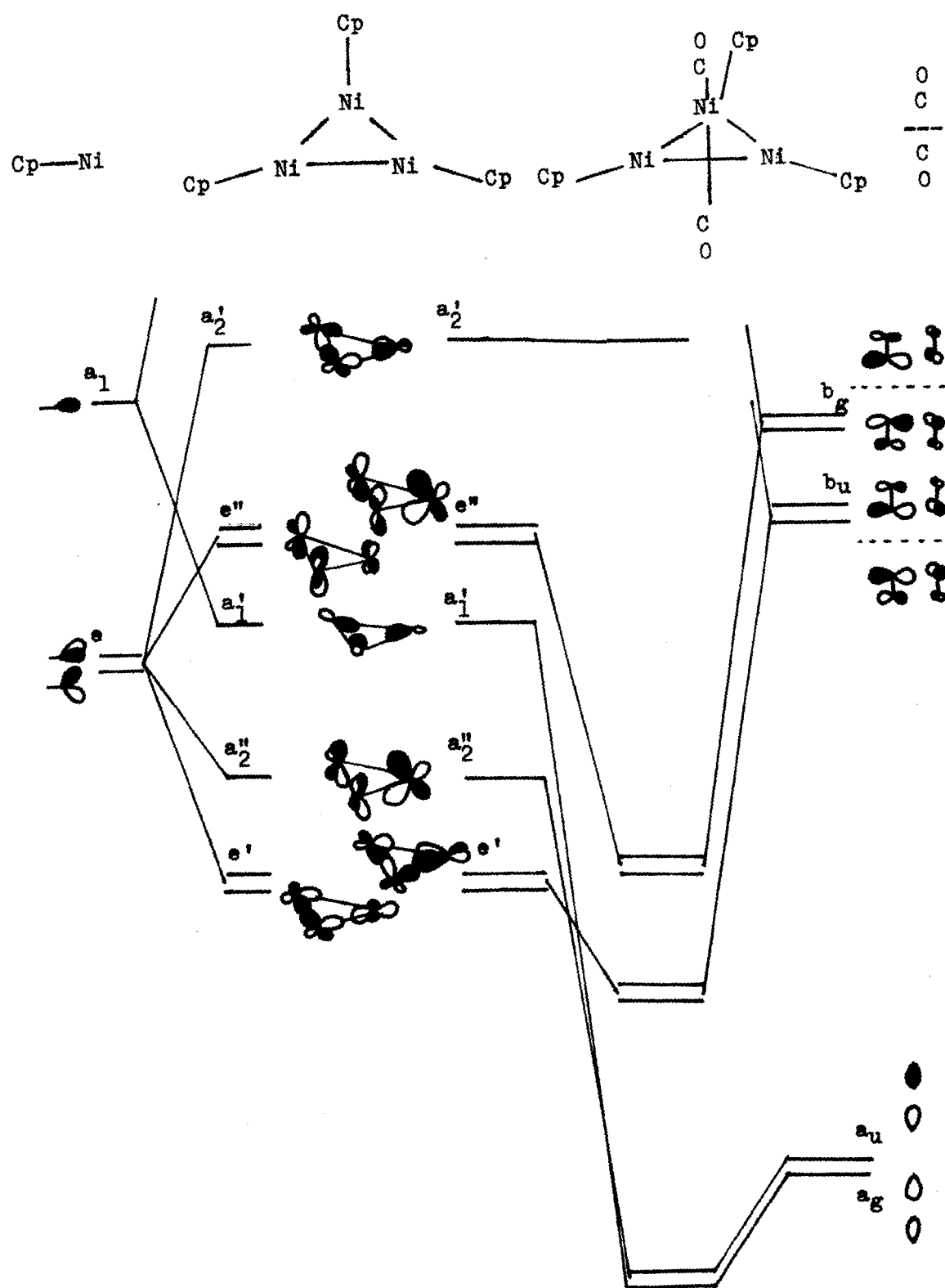
The structure and bonding in dimetal species may be extended to polynuclear metal species, as the larger polynuclear complexes contain the same types of bonding elements seen in the dimetal systems. The structures of the complexes $\text{Fe}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Co}_4(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{12}$ are shown in figure 14. It can be seen that (xiii) and (xv) contain only metal carbonyl terminal structural units. Structure (xii) contains the doubly bridged unit (ii) and structure (xiv) contains three singly bridged carbonyls around the basal edges. The bonding in $\text{Fe}_3(\text{CO})_{12}$ has been studied theoretically¹³⁶ as have some other polynuclear complexes, but no additional information can be gained from the bonding of ligands within these complexes, which is not available from dimetal species, apart from the triply bridging carbonyl ligand found in some polynuclear complexes,³⁸ the structure of which is shown in figure 3. The tendency for bridges in clusters containing metals of smaller atomic radius is noticeable.

Figure 14. Some Polynuclear Metal Carbonyl Complexes.



The complex $\text{Cp}_3\text{Ni}_3(\text{CO})_2$ contains two triply bridging carbonyl groups, and the bonding of these ligands is described below. The Cp_3Ni_3 cluster framework can be thought of as being formed from three CpNi fragments, and this is illustrated in figure 15. The addition of the two carbonyl groups is schematically represented on the RHS of figure 15. The build up of the orbitals are similar to those used by Hoffman in the structural analysis of the hypothetical molecule $\text{Cp}_3\text{Rh}_3(\text{CO})_2$.^{13d} The ligand a_g and a_u combinations again find suitable orbitals to interact with, from the Cp_3Ni_3 fragment as they did with the $\text{Cp}_2\text{Fe}_2(\text{CO})_2$ fragment discussed earlier. These molecular orbitals are mainly ligand in character. The b_u, b_g combinations of the ligand also find suitable orbitals to interact with in the Cp_3Ni_3 fragments,

Figure 15. Bonding in the $\text{Cp}_3\text{Ni}_3(\text{CO})_2$ Complex.



and are all fully occupied. Of these metal fragment orbitals, which are in effect the back bonding orbitals, two are metal-metal bonding and two are metal-metal antibonding, therefore nullifying any cluster bonding via metal-metal bonds. In fact the HOMO of the system which contains one electron, making the cluster paramagnetic, is clearly metal-metal antibonding. As with the case concerning doubly bridging carbonyls it would appear that triply bridging carbonyls form a multicentred delocalised bond with metal clusters.

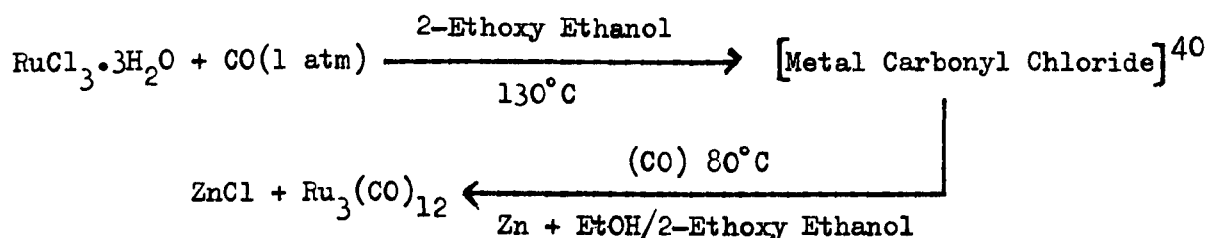
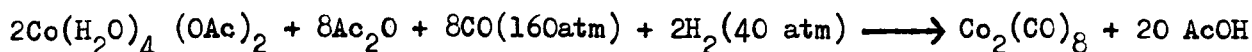
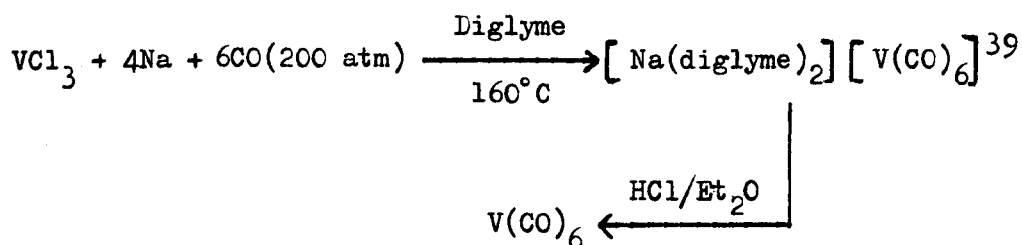
The triply bridging carbonyl is not unique as the only $2e^-$ donor to bond to clusters in this manner. Also known is the triply bridging CS ligand.³⁹ There is no reason why the isonitriles should not be able to triply bridge, but there are no reported complexes that contain a triply bridging isonitrile. The metal ligand bonding found in the polynuclear metal systems has been described and the various experimentally observed effects have tested the bonding theory quite thoroughly. The bonding picture explains well some observed effects, but has no answer for some observed effects like the influence of metal upon the structure. With increased research into this area the answer to this and other unexplained phenomena will surely result.

Now that we have some understanding of the structure and bonding of metal clusters it would now be useful to review the preparations of polynuclear metal complexes, and in particular the metal-isonitrile clusters, but first a brief description of metal carbonyl clusters will be undertaken.

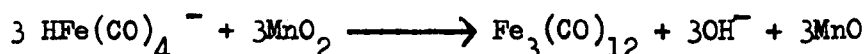
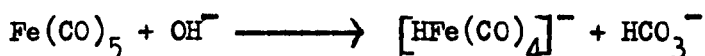
Many metal carbonyl clusters have been prepared, and they serve as good starting blocks for the preparation of numerous other metal complexes. Not only is carbon monoxide easily replaced by other ligands in a cluster, but it is useful as a probe for structural determination of the products.

Only nickel and iron will react with carbon monoxide directly using relatively mild conditions, to form $Ni(CO)_4$ and $Fe(CO)_5$ respectively. A much more widely used approach is the reductive carbonylation of metal salts. Various reducing agents have been employed, and conditions vary for the

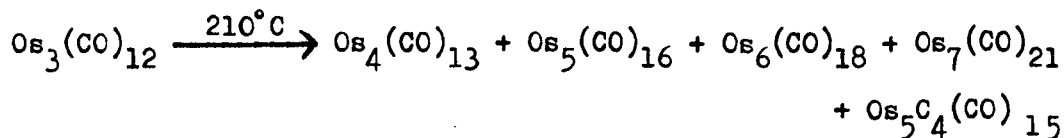
preparations of different metal carbonyl species. Some examples of these types of reaction are given below.



Higher nuclearity clusters can be prepared in a number of ways. For example uv irradiation of $\text{Fe}(\text{CO})_5$ in acetic acid produces a good yield of $\text{Fe}_2(\text{CO})_9$. Triironododecacarbonyl can be obtained from the oxidation of a solution of $[\text{HFe}(\text{CO})_4]^-$. The reaction sequence is shown below. Another



method for the preparation of higher nuclearity metal clusters is by the pyrolysis of smaller clusters. Pyrolysis of $\text{Os}_3(\text{CO})_{12}$ in a sealed tube at 210°C gives as products many polynuclear metal carbonyl species.⁴² Pyrolysis

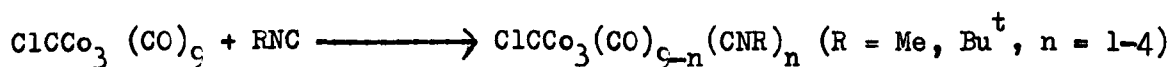
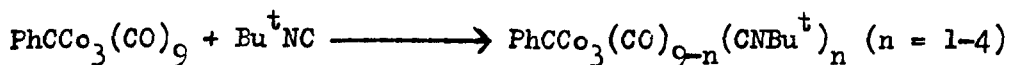
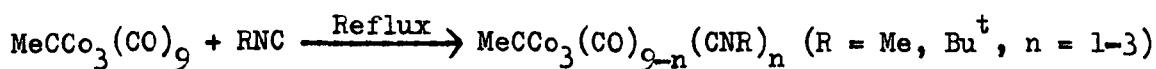
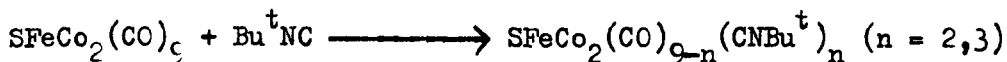
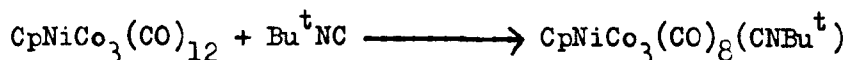
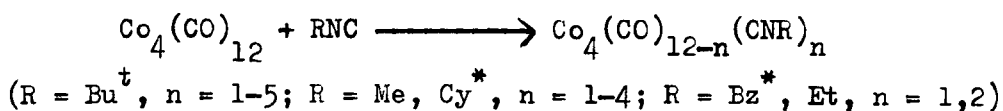


of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ in refluxing xylene gives as a product the iron tetramer $[\text{CpFe}(\text{CO})]_4$.³⁸ In this compound the carbonyls triply bridge the faces of the Fe_4 tetrahedron. Many homonuclear polynuclear metal carbonyl species have been prepared. Many mixed metal carbonyl species have been prepared,⁴³

but the preparations of these species are too diverse to comment on here. Using this legion of polynuclear metal carbonyl complexes it is now possible to prepare a vast number of metal complexes. A report is given below in the ways that isonitriles react with metal carbonyl clusters, and it extends into the regions of metal clusters containing solely isonitrile ligands.

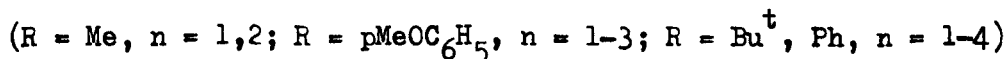
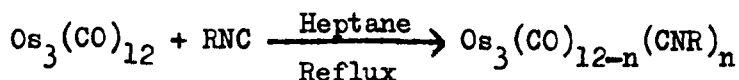
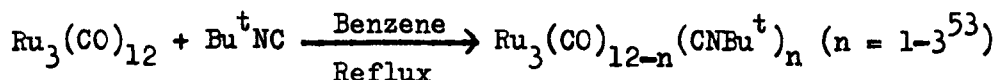
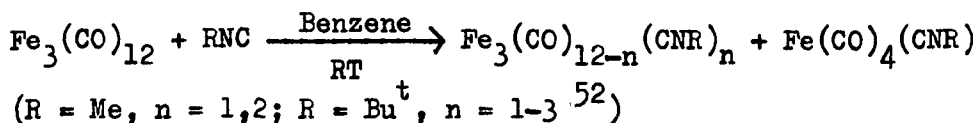
Isonitrile metal clusters have been prepared by a number of different routes, and different approaches can be used to form the same molecule. By far the most explored region of producing metal-isonitrile complexes is by the reaction of a neutral carbonyl species in the presence of isonitrile. In this way many complexes have been prepared. Amongst the first reported was the preparation of a dicyclopentadienyldiiron tetracarbonyl derivative $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNMe})$.⁴⁴ This was prepared by the reaction of the parent dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ with methyl isonitrile. Reported later were the preparations of many similar complexes, where various dienyl and isonitrile ligands were used.^{18, 19} The structure of the product was very dependent upon the dienyl ligand and the particular isonitrile used in the reaction, so that a crystal structure of $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNPh})$ ⁴⁵ reveals the isonitrile in a bridging position whilst that of $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNBu}^i)$ ⁴⁶ reveals the isonitrile to be in a terminal position. Prolonged reaction of the dimer with excess isonitriles produces the di and trisubstituted species $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNR})_2$ ($\text{R} = \text{Me}$,⁴⁷ Ph ,⁴⁸ Bu^t ⁴⁹) and $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNMe})_3$ ⁴⁷. Photolysis of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ in benzene solution with methyl isonitrile yields a small amount of the mono substituted complex $\text{Cp}_2\text{Mo}_2(\text{CO})_5(\text{CNMe})$ ⁵⁰, and the structure of this compound is similar to the parent dimer in that all of the ligands are co-ordinated terminally to the metal atoms.

The equations below show the reactions of polynuclear cobalt complexes with isonitriles in benzene at room temperature,⁵¹ unless shown otherwise. Replacement of carbonyl groups by isonitrile ligands in these complexes does not change the overall shape of the cluster, so the isonitriles all occupy terminal positions on metal atoms.



Photolysis of a toluene reflux of $\text{Mn}_2(\text{CO})_{10}$ in the presence of isonitrile produces the following species $\text{Mn}_2(\text{CO})_{10-n}(\text{CNR})_n$ (R=Me, n=1-4; R=Bu^t, n=1-3⁵²) all of which exhibit the same structure as $\text{Mn}_2(\text{CO})_{10}$. The reaction of $[(\text{PhO})_3\text{P}]_2\text{Mn}_2(\text{CO})_8$ with tert-butyl isonitrile produces $[(\text{PhO})_3\text{P}]_2\text{Mn}_2(\text{CO})_7(\text{CNBu}^t)_3$. Again no structural change is observed.

The iron group dodecacarbonyls all react with isonitriles and the reactions and conditions are given below. In all of these compounds no



structural changes are observed on the introduction of isonitriles into the systems, and the isonitriles occupy terminal positions. There is no

evidence to suggest that bridging isonitriles are present in any of the structures.

Addition of RNC to $\text{Mn}_2(\text{CO})_5(\text{dpm})_2$ produces $\text{Mn}_2(\text{CO})_5(\text{dpm})_2(\text{CNR})$ ($\text{R} = \text{pCH}_3\text{C}_6\text{H}_4, \text{Bz}, \text{Me}$).⁵⁵ The compound $\text{Mn}_2(\text{CO})_5(\text{dpm})_2$ contains a four electron donor carbonyl ligand, which becomes a two electron donor in the product. Heating of $\text{Mn}_2(\text{CO})_5(\text{CNC}_6\text{H}_4\text{CH}_3)(\text{dpm})_2$ in refluxing xylene produces the species $\text{Mn}_2(\text{CO})_4(\text{CNC}_6\text{H}_4\text{CH}_3)(\text{dpm})_2$ in which the isonitrile acts as a four electron donor.⁵⁶

All of the reactions mentioned so far have involved carbon monoxide substitution. There are limitations as to how far one can go with this method. Usually substitution of too many carbonyls leads to the breakdown of the cluster.^{51,52,53} Other methods must be employed to prepare metal isonitrile clusters that contain no carbonyl ligands. Of course there has to be an exception, and this is so with the reaction of $\text{Co}_2(\text{CO})_8$ with 2,6-xylylisocyanide in toluene at 80°C which yields $\text{Co}_2(\text{CNXyl})_8$.⁵⁷ It is structurally analogous to the bridged form of $\text{Co}_2(\text{CO})_8$. Sodium amalgam reduction of $[\text{Co}(\text{CNBu}^t)_5]^+\text{PF}_6^-$ yields $\text{Co}_2(\text{CNBu}^t)_8$.⁵⁸ This compound also has a structure similar to the bridged form of $\text{Co}_2(\text{CO})_8$. The reduction of metal salts in the presence of carbon monoxide proved to be a good route to the production of metal carbonyl species. Analogous reactions with modifications have been used to produce metal isonitrile species. For example the sodium amalgam reduction of iron(II)bromide in the presence of isonitrile in THF produces $\text{Fe}(\text{CNR})_5$ ($\text{R} = \text{Et}, \text{Pr}^i, \text{Bu}^t$).²¹ The sodium amalgam reduction of $\text{trans} - [\text{RuCl}_2(\text{CNBu}^t)_4]$ in the presence of isocyanide and dissolved in THF produces $\text{Ru}(\text{CNR})_5$, whilst a similar reaction with $\text{trans} - [\text{RuCl}_2(\text{CNPr}^i)_4]$ produces $\text{Ru}_2(\text{CNPr}^i)_9$.⁵⁹ Whilst $\text{Fe}(\text{CNR})_5$ is similar to $\text{Fe}(\text{CO})_5$, $\text{Ru}_2(\text{CNPr}^i)_9$ has the $\text{Fe}_2(\text{CO})_9$ structure. $\text{Ru}_2(\text{CO})_9$ is an unstable species which reverts to $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}(\text{CO})_5$.

When the clusters $\text{Os}_3(\text{CO})_{12-x}(\text{CNR})_x$ ($x = 1,2$) are pyrolysed in refluxing

octane, high nuclearity clusters result. The compounds formed are $\text{Os}_6(\text{CO})_{18-x}(\text{CNR})_x$ ($\text{R} = \text{Bu}^t$, $x = 1-5$).⁶⁰ This reaction is similar to the pyrolysis of $\text{Os}_3(\text{CO})_{12}$ mentioned earlier, which also produced higher nuclearity metal clusters. The isonitriles in this species are all terminally bound to the metal atoms.

Substitution of ligands other than carbonyls has also been looked at. In particular the substitution of $\text{M}(\text{cod})_2$ species ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) has been looked at. The reaction of $\text{Ni}(\text{cod})_2$ with isonitriles produces nickel cluster compounds containing only isonitrile ligands. When *t*-butyl isonitrile is used the complex formed is $\text{Ni}_4(\text{CNBu}^t)_7$. The nickel atoms in this cluster form a squat tetrahedron, with each Ni atom bonded to one terminal isonitrile. The other three isonitriles act as four electron donors about the basal plane, but the structure has still to be fully characterised.⁶¹ With isopropyl isocyanide a product formulated as $\text{Ni}_2(\text{CNR})_3$ is formed, which is thought to be $\text{Ni}_8(\text{CNR})_{12}$.⁶¹ Finally the reaction with benzyl isonitrile forms $\text{Ni}_4(\text{CNR})_4$ as the product.⁶¹ The complex $\text{Pt}(\text{cod})_2$ reacts with *t*-butyl isonitrile to form the complex $\text{Pt}_3(\text{CNBu}^t)_6$. In this complex the platinum atoms are triangularly arranged with one terminal isonitrile attached to each platinum. The three remaining isocyanides bridge the sides of the triangle of platinum atoms.⁶²

There remain just a few odd reactions that need to be presented. The reaction of nickelocene with $\text{Ni}(\text{CNPh})_4$ forms $\text{Cp}_2\text{Ni}_2(\text{CNPh})_2$ ⁶³ in which both isonitrile ligands bridge the two nickel atoms. The complexes $\text{Cp}_2\text{Ni}_2(\text{CNR})_2$ ($\text{R} = \text{CH}_3, (\text{CH}_3)\text{CHNC}, \text{CD}_3$)⁶⁴ have been prepared by the direct action of the isonitrile with nickelocene, although this reaction is thought to proceed via a $\text{Ni}(\text{CNR})_4$ intermediate.

The palladium complex $\text{Pd}_2(\text{dpm})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) reacts with isonitriles to form $\text{Pd}_2(\text{dpm})_2(\mu\text{CNR})\text{X}_2$ ($\text{R} = \text{CH}_3, \text{Cy}, \text{Ph}, \text{Xyl}$).⁶⁵ The product contains no metal-metal bond and the metals are bridged by the isocyanide. The compounds $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNR})$ ($\text{R} = \text{Bu}^t, \text{Ph}, \text{Cy}$) have been prepared from the

reaction of isothiocyanates with CpFe(CO)_2^- .⁶⁶ The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNBu}^t)$ has also been prepared by the reaction of $\text{CpFe(CO)}_2\text{H}$ and t-butyliisocyanate.⁶⁷ The compound $\text{Cp}_2\text{Mo}_2(\text{CO})_5(\text{CNMe})$ may be prepared in better yield by the reaction of CpMo(CO)_3^- with $\text{CpMo(CO)}_2(\text{CNCH}_3)\text{I}$.²⁴ A number of isonitrile clusters have been prepared to date, and their chemistry and structural properties have been found to be interesting. This work is but a start; a lot more work needs to be carried out in this field of rich and interesting chemistry, and this involves the preparation of further new isonitrile clusters.

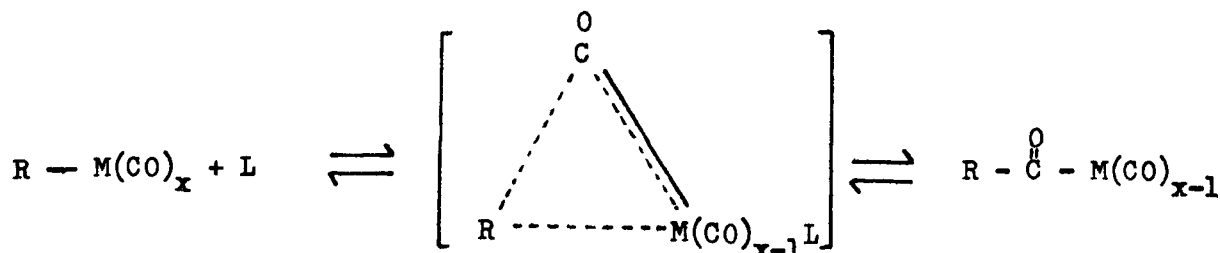
Much of the early work carried out with isonitrile clusters was performed with mononuclear species in which the metal was in a positive oxidation state. Today much interest is shown in the neutral polynuclear metal isonitrile complexes. This field is new and is at present under rapid development. The reactions of metal isonitrile clusters are wide and varied, and a brief account of metal isonitrile cluster chemistry is given below.

Having already explained the differences and similarities of bonding between isonitriles and carbon monoxide a brief account of their reactions when bonded in metal clusters will be given. The review by Triechel⁸ concerning metal-isocyanide complexes covers the types of reactions that metal isocyanide complexes undergo.

The insertion of CO into a metal-alkyl or aryl bond and decarbonylation of acyl complexes have been studied extensively both from the preparative and mechanistic viewpoint.⁶⁸ The proposed mechanism for these three processes is shown in figure (16). It would be reasonable to assume that isonitriles would undergo a similar reaction. Yamamoto initiated research into this reaction and in 1969 reported the reaction between $\text{CpNi(PPh}_3)_3\text{Me}$ and various isonitriles.⁶⁹ The product obtained $\text{CpNi(CNR) [C(Me)NR]}$ is presumably formed by phosphine substitution of $\text{CpNi(PPh}_3)_3\text{Me}$ followed by methyl migration and addition of a second isonitrile. The intermediate was not isolated in this reaction however. Much work has been carried out

on the reactions of square planar Ni, Pd and Pt isonitrile complexes. The oxidative addition of methyl iodide to $\text{Ni}(\text{CNBu}^t)_4$ results in the oligomerisation of the isonitrile to give (xvi).⁷⁰ This product is believed to arise through the sequential insertion of three isonitrile ligands into a metal-carbon bond. Upon treatment with further isonitrile at 60°C a polymer $(\text{RNC})_x$ is produced probably through multiple isonitrile insertions into the nickel carbon bond. More recently it has been shown that $\text{Fe}(\text{CNBu}^t)_5$ undergoes an analogous reaction with methyl iodide forming (xvii).⁷¹

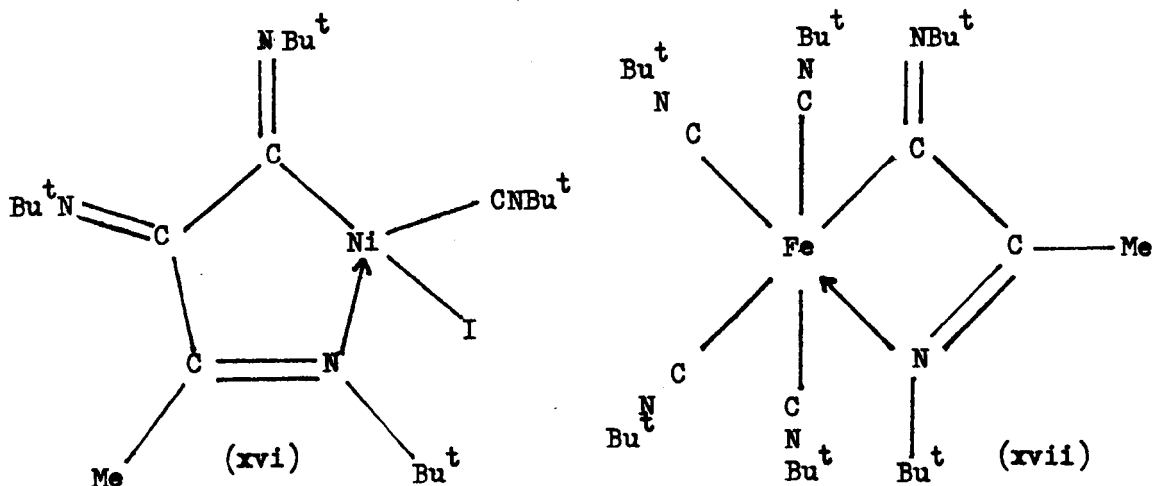
Figure 16. Carbonyl Insertion and Decarbonylation.



Nucleophilic reactions involving metal isonitrile complexes can lead to a variety of products formed by three routes. These are ligand substitution, reactions involving attack at a ligand and reduction of the metal complex. Early reactions of this type carried out by Pauson and Stubbs gave the complex $\text{CpMn}(\text{CNPh})_3$ from NaCp and $\text{Mn}(\text{CNPh})_6^+$.⁶³ Sodium borohydride and $\text{CpFe}(\text{CO})(\text{CNPh})\text{I}$ gave $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNPh})$ although in poor yield.⁴⁵ N-acyl amino groups and N-alkyl imino groups are very susceptible to proton attack, which is a property not common for acyl groups. Particularly important in this respect is the bridging isonitrile ligand. This is probably due to the inherent basicity of the nitrogen atom in these groups, which increases with increased back donation from the metal orbitals. For bridging isonitriles not only protonation, but alkylation may be observed

and Manning has prepared many protonated and alkylated derivatives of $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNR})$.^{72,73} Protonation or alkylation of terminal isonitrile groups has been observed in trans $[\text{Mo}(\text{CNMe})_2(\text{dpe})_2]$ the metal complex is electron rich and extensive $d\pi \rightarrow p\pi^*$ back bonding is responsible for the observed CNR angle in the complex.²⁰

Other classes of reactions that metal isonitrile complexes undergo are additions of protonic compounds to co-ordinated isonitriles, and the reactions of isonitrile metal clusters with hydrogen. The metal complex $\text{Ru}(\text{CO})_{11}(\text{CNBu}^t)$ reacts with dihydrogen to form as the major product (xviii).⁷⁴ It can be seen that partial reduction of the CN bond has occurred, and some



insight to hydrogenation of isonitriles by metal clusters can be seen. More dramatic, is the $\text{Ni}_4(\text{CNBu}^t)_7$ cluster. Its catalytic activity in hydrogenating acetylenes and isonitriles has been studied.^{1,61} In acetylene hydrogenation only cis-olefins are produced in over 95% yield. Reaction of $\text{Ni}_4(\text{CNBu}^t)_7$ and $\text{Ni}(\text{CNBu}^t)_4$ in toluene at 90°C in the presence of hydrogen produces N-methyl t-butylamine, and this reaction has been extended to other isonitriles with some success.

The bonding, preparations and reactions of some isonitrile metal cluster compounds has been described. The methods by which these metal clusters are characterised today were not generally available as little as ten years ago, the main difference in instrumentation being the availability

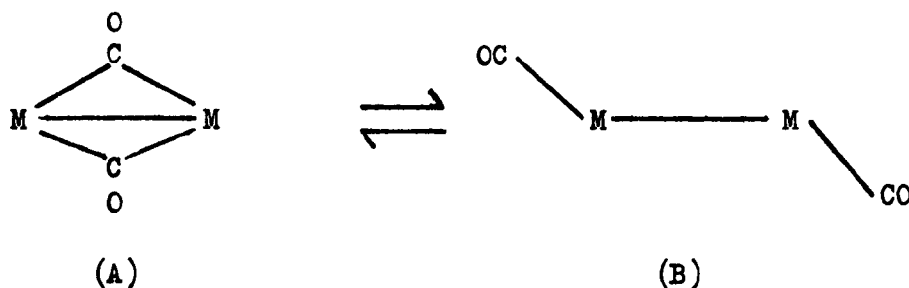
of Fourier Transform nmr spectrometers.

One of the major problems encountered with metal carbonyl complexes, before the advent of nmr spectroscopy, was that of structure determination. Infrared studies would reveal the presence of bridging and/or terminal carbonyl groups within a complex, but a time consuming X-ray structure determination was the best way of obtaining definite information. Nmr spectroscopy like organometallic chemistry was a relatively new field of activity thirty years ago and have developed hand in hand. Today commercially available instruments are able to use many nuclei as a probe in structure determination. For detailed description of nmr theory and applications there are many good books,⁷⁵ and ref. 75c is concerned with dynamic nuclear resonance spectroscopy. The commonly used nuclei are ^1H , ^{13}C , ^{19}F , ^{31}P , all of which have spin $\frac{1}{2}$. The proton was the ideal nucleus for nmr studies, because it has spin $\frac{1}{2}$, natural abundance approximately 100%. Other nuclei are only a fraction as sensitive as the proton, although ^{19}F and ^{31}P have natural abundances of 100% their relative sensitivity as compared to the hydrogen nucleus are 0.83 and 0.07 respectively. For ^{13}C which is only approximately 1% in natural abundance the relative sensitivity is approximately 0.01. Before FT nmr machines became available several techniques were used to enhance the ^{13}C nmr spectra. One method frequently used, and still used today, was that of isotopic enrichment. This was generally kept below levels of 30% to prevent spin-spin coupling between adjacent carbon atoms overcomplicating spectra. Another method used was by increasing the amount of sample, and this of course has certain physical restrictions, but increasing the amount of sample in the magnetic field does help increase the sensitivity.

Fourier transform techniques were by far the greatest aid to sensitivity but this method of obtaining spectra had problems with metal bonded carbonyl carbons. These have unusually long relaxation times, and this property

partially undermines the advantages of FT methods, because of the long recycle time needed between successive pulses. This problem was solved by the discovery of a shiftless relaxation agent $\text{Cr}(\text{acac})_3$. This paramagnetic compound is kinetically inert, is soluble in many organic solvents, and allows pulse intervals of 0.5 to 2 seconds.

Another problem encountered with polynuclear metal carbonyl complexes is that of limited solubility in most solvents and this problem is overcome by the use of isotopic enrichment and FT techniques. Many of these complexes are stereochemically non-rigid over the temperature range -100°C to $+100^\circ\text{C}$ and have an important effect on the nmr line shapes. Useful kinetic information may be obtained from these line shapes. A simple case to illustrate the point, is one in which carbonyl groups exchange between the two sites shown below, which are occupied for equal lengths of time. If the lifetime in each site is long on the nmr time scale, then two separate



signals will be obtained, each with a chemical shift that corresponds to the shielding of the carbon at the appropriate site. As the rate of exchange increases (e.g. by raising the temperature) so that lifetimes become shorter, it is found that the two signals broaden, approach one another, and finally coalesce to a broad single peak that sharpens at the fast exchange limit. The chemical shift of the singlet is the mean of those of the two lines obtained in the slow exchange situation. If the two sites are not equally populated the behaviour will be similar to the above case, but the two lines will coalesce to a point whose chemical shift is the weighted mean of the two chemical shifts found in the slow exchange limit. The position

where two separate peaks just merge into one is called the coalescence point. At this point the lifetime of a nucleus in a discrete state is given by

$$\tau = \sqrt{2} / \pi \delta\nu \text{ secs}$$

where $\delta\nu$ is the separation in frequency between the two separate signals. For ^1H $\delta\nu$ is of the order 0 - 100 Hz and therefore τ is approximately 10^{-2} secs at coalescence; for ^{13}C , the chemical shifts are larger and therefore the lifetimes smaller at coalescence; a 50ppm separation, typical for terminal, bridging carbonyl species, (1250 Hz at 25.2 MHz) requires a lifetime of approximately 5×10^{-4} secs for coalescence. The rate constant (k) for the process $A \rightarrow B$ is given by

$$k = 1/\tau$$

and the free energy of activation ΔG^\ddagger from the coalescence point and temperature (T_c)

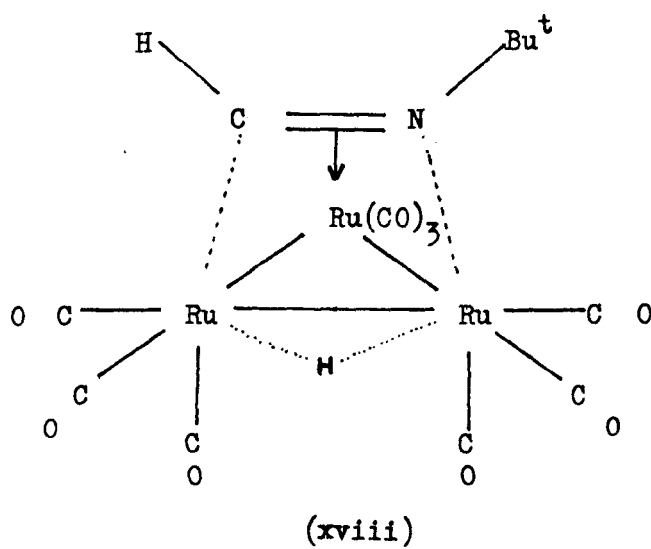
$$\begin{aligned} \Delta G^\ddagger / RT_c &= \log_e (\sqrt{2} R / \pi N h) + \log_e (T_c / \delta\nu) \\ &= 22.96 + \log_e (T_c / \delta\nu) \end{aligned}$$

This equation is only valid for the case where the populations of A and B are equal with no coupling, but can be used for more complex cases to obtain approximate values of ΔG^\ddagger .

Nmr is a useful tool for obtaining structural information and kinetic information, which for organometallic compounds has proved to be of vital importance, and in the following chapters more detail will be given as to the exchange mechanisms that take place within metal cluster compounds.

The work presented in the remainder of the thesis is mainly concerned with the effects that 2 electron donor ligands have upon the structures of the dimetal complexes $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ upon substitution. The ligands employed in substitution are a variety of phosphines, phosphites, isonitriles and bidentate isonitriles. The preparation of these complexes, their structural determination and study of stereo-chemical non-rigidity in solution are presented with some of the reactions that these types of

cluster undergo.



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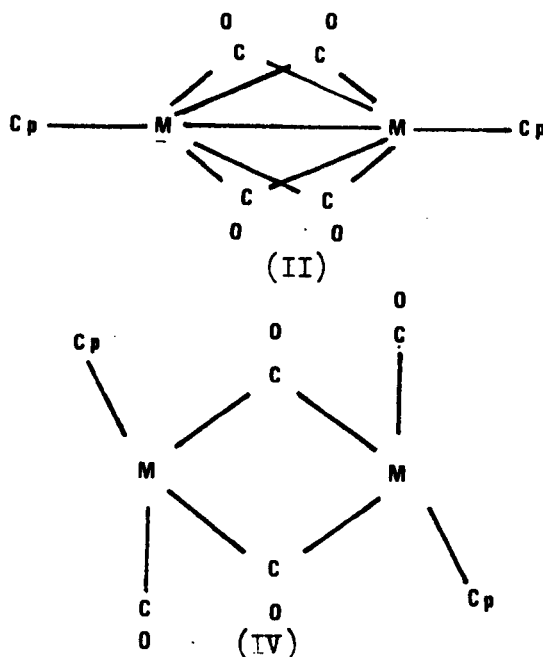
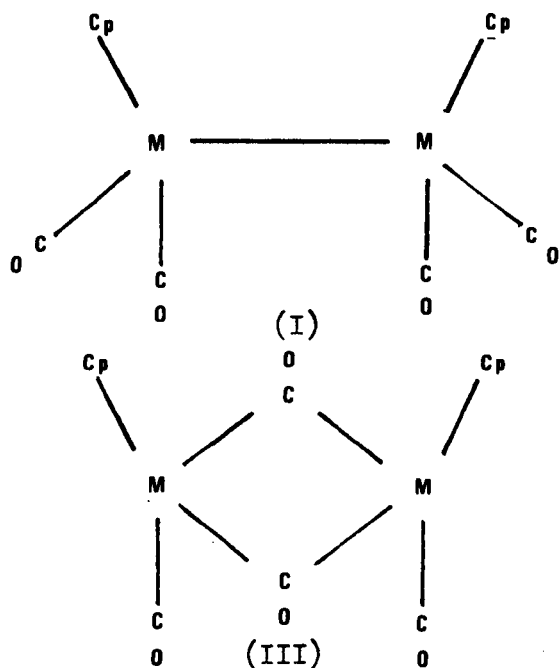
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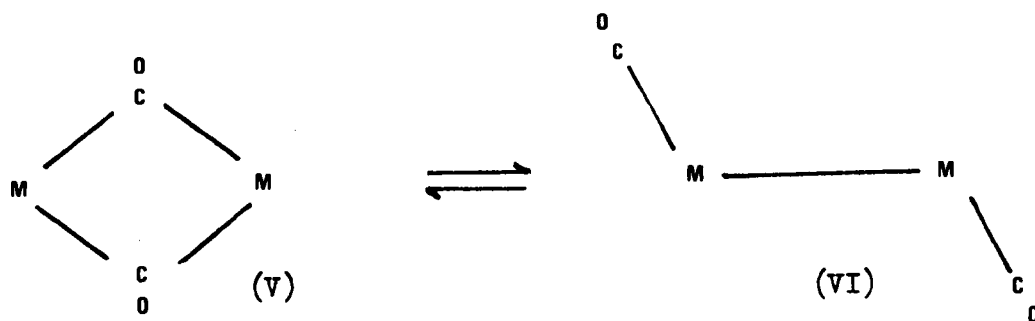
CHAPTER 2

Complexes of the type $\text{Cp}_2\text{M}_2(\text{CO})_4$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) can in principle exist as one or more of the isomers (I - IV). The nb isomer (I) is drawn in the cis configuration, but there are a number of possible rotamers. Experimentally it is observed that $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (1) exists as a mixture of (III) and (IV) in solution,^{1,2} and (III) and (IV) have been identified by the means of X-ray crystallography in the solid state.^{3,4} The ruthenium analogue $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (2) exists in solution as a mixture of the isomers (I), (III) and/or (IV).^{5,6} Although Manning¹⁰ has proposed that cis and trans rotamers of the nb species are probably present in solution, as yet only (IV)⁷ has been identified in the solid state. The osmium complex $\text{Cp}_2\text{Os}_2(\text{CO})_4$ (3) exists solely as a non bridged isomer in the solid state⁸ and in solution a similar spectrum to that of the nb ruthenium analogue is identified⁸ (vide infra). Thus again, using Manning's argument,¹⁰ it is probable that both cis and trans rotamers are present in solution. The quadruply bridged isomeric form (II) has not been observed in the species (1 - 3).



The fluxional properties of (1) and (2) have been studied by variable temperature nmr techniques,^{2,6} and it was observed that isomers (III) and (IV) undergo rapid intramolecular bridged-terminal carbonyl interconversions of the type (V) \rightleftharpoons (VI) as well as cis-trans structural interchange. At least for bimetallic species containing doubly bridging carbonyl groups (e.g. III, IV), the mechanism which has received most experimental support is that proposed by Adams and Cotton⁹ involving symmetric bridge opening followed, if necessary, by internal rotation about the M-M bond of the non-bridged intermediate (I). Simultaneous bridge closing then regenerates a doubly bridging isomer which has undergone bridge-terminal carbonyl exchange and/or geometric isomerism [e.g. (III) \rightleftharpoons (IV) interconversion for $\text{Cp}_2\text{Fe}_2(\text{CO})_4$].

The populations of the isomers (I - IV) in solution are not only dependent upon the metal employed, but are dependent upon solvent and temperature also.^{6,10} The ligands bound to the cluster also affect the equilibrium between various species in solution, and reported in this chapter are the results on the preparation and fluxional behaviour of the related

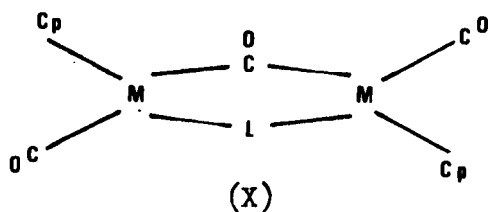
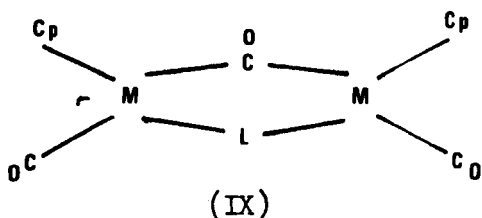
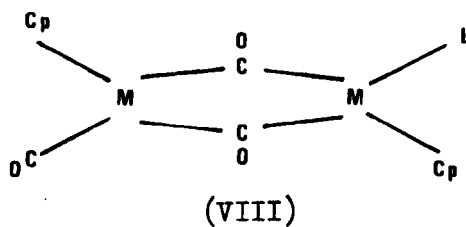
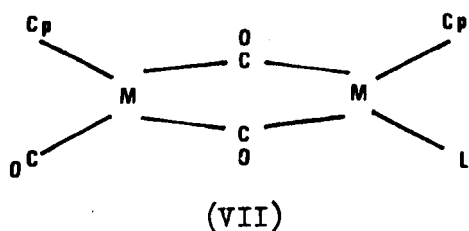


isonitrile complexes $[\text{Cp}_2\text{M}_2(\text{CO})_3(\text{CNR})]$ [(1a) - (1e) $\text{M} = \text{Fe}$, $\text{R} = \text{CH}_3$, C_2H_5 , $\text{CH}(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$ and Ph ; (2a) - (2d) $\text{M} = \text{Ru}$, $\text{R} = \text{CH}_3$, C_2H_5 , $\text{CH}(\text{CH}_3)_2$ and $\text{C}(\text{CH}_3)_3$], together with results on the complexes $[\text{Cp}_2\text{M}_2(\text{CO})_3(\text{CNHR})][\text{PF}_6]$ [(4a) - (4e) $\text{M} = \text{Fe}$, $\text{R} = \text{CH}_3$, C_2H_5 , $\text{CH}(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$ or Ph ; (5) $\text{M} = \text{Ru}$, $\text{R} = \text{C}_2\text{H}_5$] and $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNRR}')][\text{PF}_6]$ [(6a) - (6b) $\text{R} = \text{CH}_3$ or $\text{CH}(\text{CH}_3)_2$, $\text{R}' = \text{C}_2\text{H}_5$] formed from electrophilic attack by H^+ or C_2H_5^+ on the neutral isonitrile derivative.

While this work was proceeding, the preparation and infrared data of the complexes (1a) - (1e) were reported.¹¹ The preparation involves reacting

a slight excess of the isonitrile with the parent dimer (1) in benzene. Complex (1e) has previously been prepared by tetrahydroborate reduction of $[\text{CpFe}(\text{CO})(\text{CNPh})\text{I}]$,¹² and complex (1d) has been prepared from the hydride $\text{CpFe}(\text{CO})_2\text{H}$ by reaction with t-butylisocyanate.¹³ The complex $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (2) undergoes substitution slowly in refluxing xylene, and under the reaction conditions described only mono substitution is observed to yield the complexes (2a) - (2d). Rapid decomposition of the ligand prevented the preparation of $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CNPh})$. The complex $\text{Cp}_2\text{Os}_2(\text{CO})_4$ (3) did not undergo substitution under these conditions. The analytical data are shown in Table (1).

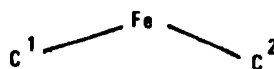
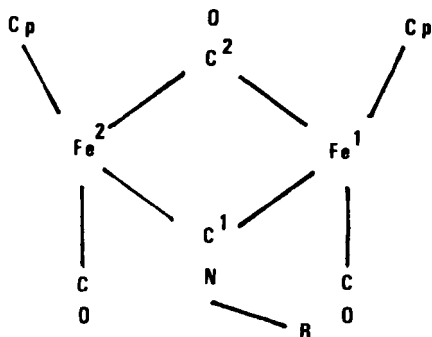
The infrared spectral data of complexes (1a) - (1e), (2a) - (2d) are shown in Table (2). Since an isonitrile may function as a terminal or bridging ligand, the four isomers (VII) - (X) are possible in principle. The infrared spectra of the complexes (1a) - (1e) and those of (2a) - (2d) may be assigned on the same basis. Thus bands (A) and (B) are due to the terminal CN vibration of (VII) and (VIII); band (C) may be assigned to the



symmetric terminal CO vibration of (IX), while band (D) is due to the coincident asymmetric terminal CO vibrations of (IX) and (X), and the terminal CO vibrations of (VII) and (VIII). Bands (F) and (G) are due to the coincident bridging CO vibrations of (IX), (X), and (VII), (VIII) respectively, while bands (H) and (I) may be assigned to the bridging CN vibrations of (IX) and (X). The origin of the remaining terminal CO

vibration band (E) is ambiguous, but a reasonable assignment is to the symmetric terminal CO vibration of (X). Although inactive for (1), it is well known that, both in solution¹⁴ and the solid state^{12, 15, 16} bridging isonitriles adopt a non-linear CNR linkage ($\hat{\text{CNR}} 125\text{--}130^\circ$), coupled possibly with a slight twist of the R group out of the plane defined by the Fe (μCO) (μCN) Fe moiety, as is seen for $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{CNPh})_2$.¹⁵ Thus the symmetric terminal CO vibration of (X) may be allowed, although perhaps weakly.

The infrared spectra indicate an increasing proportion of isomers (IX) and (X) in the order $\text{C}(\text{CH}_3)_3$, $\text{CH}(\text{CH}_3)_2$, C_2H_5 , CH_3 , Ph, in agreement with the nmr results shown below. The order of the alkyl substituted derivatives is consistent with the expected degree of steric interaction and electronic character of the isonitrile in a bridging position. The steric interaction is self evident. The σ electron donating ability of the isonitrile increases with the increasing size of the alkyl group within the isonitrile, and this will have the effect of destabilizing the bridged isonitrile form, (the strong σ donor properties of phosphorus (III) ligands are probably responsible for the lack of observed bridging tertiary phosphorus (III) ligands in polynuclear metal complexes), to a terminal isonitrile isomer. Thus the steric and electronic effects reinforce one another in the case of alkyl isonitriles. The totally bridged isonitrile structure adopted by (1e) is undoubtedly a consequence of electronic rather than steric factors.¹¹ The greater π acceptor facility, (in a sense π stability) of Ph-NC is brought about by the phenyl group being able to conjugate with the NC π system. It is usually found that good π acceptors will preferentially take up available bridging positions. The solid state geometry of (1e) has been described.¹² The structure is similar to cis - $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, with the isonitrile group replacing one of the bridging carbonyls. The $\text{C}_1\text{--Fe}_1\text{--C}_2\text{--Fe}_2$ ring is puckered away from the Cp groups, the fold being along the metal-metal axis, consistent with the bonding described for these types of complexes. The isonitrile group is non linear forming an angle of 131° at the nitrogen atom. At the same time



the phenyl group is rotated out of the $\text{Fe}_1 - \text{Fe}_2 - \text{C}_1 - \text{N}$ plane by 50° . The rotation away from the adjacent Cp group prevents short non-bonded contacts between this group and the phenyl group. The relative importance of the steric and electronic effect has been investigated in the isonitrile series $\text{CNCH}_2\text{C}_6\text{H}_5\text{X}$ -p ($\text{X} = \text{H}, \text{Me}, \text{OMe}, \text{Cl}$) for $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNR})$. In the complexes containing $\text{CNC}_6\text{H}_5\text{X}$ -p ligands it may be assumed that steric interactions are virtually constant, and that changes observed are due mainly to electronic effects. The importance of the isonitrile bridged isomers increases along the series $\text{X} = \text{OMe}, \text{Me}, \text{H}, \text{Cl}$. This correlates well with the total electron withdrawing power of X, as measured by the Taft constant σ_p , which increases along the same series.³⁷ By comparison with (1a) - (1d) it can be seen that the ruthenium complexes show a much greater tendency towards occupation of the bridged position by isonitrile. Presumably the need to bridge a longer M-M bond (12.4 vs 13.6nm in the parent dimers)^{3,7} is more than compensated for by relief of steric interaction between the cyclopentadienyl ligand and the alkyl substituent of the isonitrile. It should be noted that the infrared spectrum of (2) in hexane reveals significant concentrations of both bridged [$\nu(\text{CO})$ at 2011, 1964 and 1794 cm^{-1}] and non-bridged forms [$\nu(\text{CO})$ at 2021, 1972, 1943 cm^{-1}].⁵ Bands of very low intensity at ca. 1920, 1930 and 1964 cm^{-1} may possibly be assigned to very small concentrations of non-bridged isomers of (2a) - (2d), although no non-bridged isomers of (2a) - (2d) are evident in the nmr studies. The equilibrium between the non-bridged and bridged forms is very sensitive to ligand; thus, $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PR}_3$,¹⁷ $(\text{C}_5\text{Me}_4\text{Et})_2\text{Ru}_2(\text{CO})_4$,¹⁸ $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CS})$ and $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{CS})_2$ ¹⁹

all adopt a totally bridged structure in solution, with thiocarbonyl functioning exclusively as a bridging ligand in the latter two complexes. These bridged - non bridged structural preferences for dimetal clusters have been discussed in the introduction. The table below outlines the infrared absorptions in the region 2050 - 1700 cm^{-1} for some substituted ruthenium dimer (2) complexes.

<u>Complex</u>	<u>νCot</u>	<u>νCob</u>	<u>Solvent</u>
$\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu\text{CO})_2$	2004 1960	1785	CS_2
$\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu\text{CS})_2$	2012 1976	-	CS_2
$\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu\text{CO})(\mu\text{CS})$	2008 1969	1813	CS_2
$\text{Cp}_2\text{Ru}_2(\text{CO})(\mu\text{CO})_2\text{PR}_3$	1943	1762	Hexane
$(\text{Et Me}_4\text{C}_5)_5\text{Ru}_2(\text{CO})_2(\mu\text{CO})_2$	1933	1748	
$\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu\text{CO})_2$	2010 1965	1794	Hexane

The ligands PR_3 and $\text{C}_5\text{Me}_4\text{Et}$ are more powerful electron donors than CO (in the case of PR_3) and the cyclopentadienyl ligand (in the case of $\text{C}_5\text{Me}_4\text{Et}$). PR_3 is also a poorer π -acceptor ligand than CO; thus for the clusters $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{PR}_3)$, $(\text{Me}_4\text{EtC}_5)_2\text{Ru}_2(\text{CO})_4$ the build up of negative charge on the cluster from ligand donation, as compared with $\text{Cp}_2\text{Ru}_2(\text{CO})_4(2)$, is reduced by increasing back donation to the remaining carbonyl ligands. A carbonyl ligand accepts more back donation in the bridged position compared to the terminal position, and the conversion of non-bridged $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ into a totally dibridged structure upon substitution with $\text{C}_5\text{Me}_4\text{Et}$ or PR_3 seems reasonable. Investigation of the infrared νCO stretching frequencies for the compound $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PR}_3$ show a reduction in CO bond strength for both Cot and Cob as compared to Cot and Cob in $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu\text{CO})_2$, indicative of increased back donation of charge in the former complex. The complexes $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{CS})_2$ and $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CS})$ are found to be totally bridged. The CS ligand is a more powerful π -acceptor than CO and forms a weaker $\text{CS}\pi$ -bond than CO. In a bridged position ligand bond order is reduced to compensate for increased back donation from the metal cluster orbitals into the ligands π -acceptor orbitals as compared to the back donation experienced in a terminal position. For CS this loss of ligand π -bonding energy would be less than for CO, because of

weaker π -bonding in CS. It seems reasonable therefore that the CS bridged structure would be more energetically favourable than the CS terminal structure, because the increased metal ligand interaction is gained at the loss of little CS π bonding energy in the CS ligand migrating from a terminal to a bridging position. Investigation of the infrared of the complexes $\text{Cp}_2\text{Ru}_2(\mu\text{CO})_2(\text{CO})_2$, $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu\text{CO})(\mu\text{CS})$ and $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\mu\text{CS})_2$ shows the effect on the remaining CO ligands upon CS substitution of CO. Note that the increased back donation to CS reduces the back donation to the remaining CO ligands as reflected in the increased strength of the COt, COb infrared stretches of $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{CS})_2$, $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CS})$ compared to $\text{Cp}_2\text{Ru}_2(\text{CO})_4$.

Finally it should be noted that both cis : trans ratios (VII) : (VIII) and (IX) : (X) and the ratio of bridged to terminal isonitrile isomers are solvent dependent,^{11,20} the proportion of the more polar isomers, (VIII) and (IX), increasing with increasing solvent polarity. Thus direct comparison of isomer distributions derived from the infrared spectra (hexane solution) with those obtained from nmr spectra (dichloromethane or toluene solutions) is therefore not valid.

The proton nmr data of (1a) - (1e) and (2a) - (2d) are given in table (3). The spectra of (1a) - (1e) were run in both d^8 -toluene solutions and d^2 dichloromethane solutions. Since high temperature limiting spectra were obtained for the iron complexes only at 60-80°C, spectra were run in toluene solutions; ^1H spectra in CD_2Cl_2 at the low temperature limit are included in the table to enable comparison with ruthenium derivatives and to confirm conclusions drawn from the ^{13}C studies.

Figures (1.) - (5) show the low temperature limiting spectra in CD_2Cl_2 solution obtained for the complexes (1a) - (1e) respectively. The proton spectrum of (1b) is shown at four different temperatures. In the cyclopentadienyl region at -40°C the single peak at 4.826 is assignable to the equivalent Cp ligands of (IX), (X) (assuming rapid nitrogen inversion), while the larger resonances of 4.78 and 4.576 may be assigned to the non-

equivalent Cp ligands of (VII), (VIII). On the basis of intensities and decoupling experiments the triplet and quartet resonances at 0.95 δ may be assigned to the CH₃ and CH₂ resonances respectively of (VII), (VIII), while those at 1.32 and 3.89 δ may be assigned to (IX), (X). Although the apparent presence of only two isomers might be explained by depopulation of one bridging and one terminal isomer beyond the limits of detection, results on the analogous ruthenium complex indicate the true reason to be a coincidence of cis and trans signals.

Figures (6) - (9) show the low temperature limiting spectra of the complexes (2a) - (2d) respectively. The proton spectrum of (2b) is shown at four different temperatures. At -85°C complex multiplets at 3.5 and 1.1 δ are assignable to CH₂ and CH₃ resonances respectively. Irradiation of the CH₃ multiplet reduces the CH₂ multiplet to a set of four singlets; the two at lowest field may be assigned to the cis and trans isomers of the bridging isonitrile isomer, and the two at higher field to cis and trans isomers of the terminal isonitrile isomer. No cis, trans distinction is, however, observed in the cyclopentadienyl region where the resonances at 5.09 and 5.19 δ may be assigned to the (VII), (VIII) mixture and the resonance at 5.25 δ to the Cp ligands of (IX), (X). For the iron complexes, only in the case of the phenyl derivative (1e) are separate resonances for (IX) and (X) observed.

As can be seen in Figures (2) and (7) warming results in cyclopentadienyl site exchange in the resonances assigned to (VII), (VIII) and bridge-terminal isonitrile exchange to yield finally the high temperature limiting spectrum. The broadening and coalescence of resonances due to (IX) and (X) in the spectra of (1e) also demonstrates the presence of (IX) \rightleftharpoons (X) interconversion.

The low-temperature spectra of (1a), (1c), (1d) and (2a), (2c), (2d) may be interpreted similarly and show similar changes with temperature. The ratios of terminal : bridged isomers listed in table (3) were derived from intensities of the cyclopentadienyl resonances in the low temperature limiting spectrum, and the order is in agreement with the conclusions reached from the

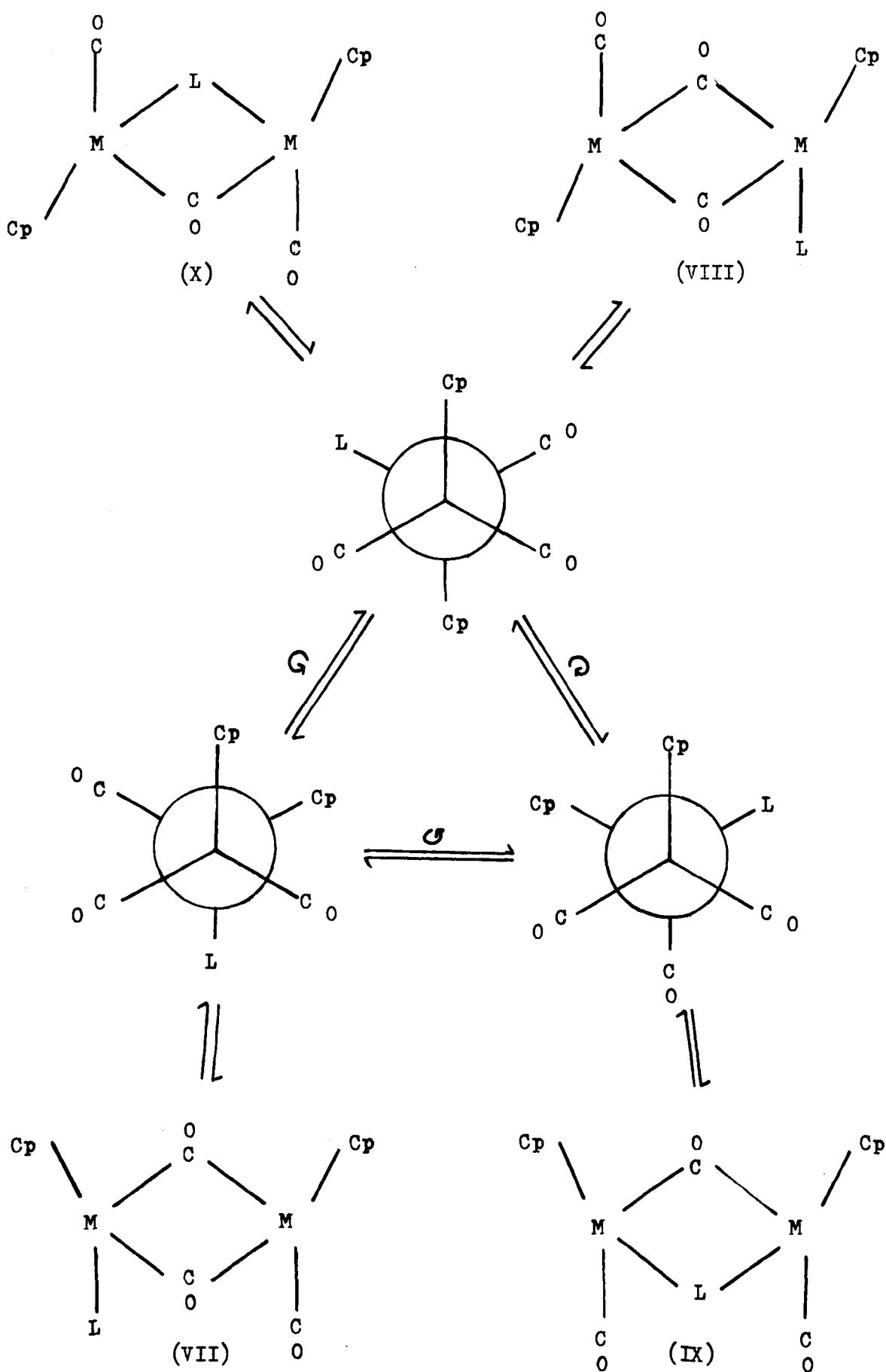
infrared studies.

The ^{13}C nmr data are given in Table (4). Figures (10) - (14) show the low temperature limiting ^{13}C spectra of the complexes (1a) - (1e) respectively. Assignment of (1b) at -20°C follows from chemical shifts and intensities, and is consistent with a mixture of bridged and terminal isonitrile isomers in which cis, trans differentiation is not observed. The only exception is (1e) where separate resonances due to (IX) and (X) are found.

Values of 272.9 and 210.0 ppm have been found for the bridging and terminal resonances of cis - $[\text{Cp}_2\text{Fe}_2(\text{CO})_4]^{21}$ in CH_2Cl_2 ; the only consistent variation found for (1a) - (1d) is a downfield shift of ca. 6ppm for the bridging CO resonance attributed to (VII), (VIII). The average chemical shift difference between bridging and terminal CO ligands for (1a) - (1e) (ca. 65 ppm) is quite similar to that observed for the parent dimer (62 ppm); the ruthenium complexes show on average a smaller chemical shift difference between bridging and terminal positions (ca. 50ppm). The downfield shift of the isonitrile resonance on bonding as a bridging ligand is much larger (ca. 80 ppm for both iron and ruthenium complexes).

The figures (15) - (18) show the low temperature limiting spectra of the ruthenium complexes (2a) - (2d). Warming results in the onset of bridge-terminal carbonyl and isonitrile exchange while changes in the alkyl and cyclopentadienyl regions are consistent with those observed in the ^1H spectra. High temperature limiting spectra were not obtained for the iron complexes due to limited solubility in toluene and slow decomposition at elevated temperatures. However, the high temperature limiting spectra of (2a) - (2d) are obtained at 0°C , and the spectrum of (2b) is shown in figure (19). The ^{13}C spectrum of $[\text{Cp}_2\text{Ru}_2(\text{CO})_4]^{21}$ in CH_2Cl_2 (34°C) shows only one resonance at 216.9 ppm which does not broaden down to -80°C . Assuming values of 250 ppm and 200 ppm respectively for the bridging and terminal Ru-CO resonances, the position of this averaged value corresponds approximately to a 1 : 1 mixture of bridged and non-bridged isomers in solution, in agreement with the infrared

SCHEME 1 : The Mechanism of Exchange between The Isomers (VII) - (X).



L = Isonitrile ligand.

results. The nmr spectral parameters (0°C , CD_2Cl_2) of $\text{Cp}_2\text{Os}_2(\text{CO})_4$ are [^{13}C , CO 185.3, Cp 82.5; ^1H , Cp 5.39 ppm] and no dependence on temperature down to -80°C is observed in either proton or carbon spectrum. The CO resonance is quite clearly in a position associated with a terminal Os - CO moiety²², and is consistent with the infrared spectrum [hexane (relative intensities given in parentheses) : 2010 (15), 1967 (93), and 1931 (100) cm^{-1}] which shows that the osmium complex exists solely as non-bridged isomer(s).

In the low temperature limiting spectra of (2a) - (2c), two cyclopentadienyl resonances are observed for the (IX), (X) mixture (although only a single peak in the ^1H spectrum). Since the two peaks are of equivalent intensity for all three complexes, assignment to cis and trans isomers seems unlikely, and it appears that at this temperature nitrogen inversion is slow on the nmr time scale, thus creating inequivalent cyclopentadienyl ligands. Even at temperatures down to -110°C ($\text{CH}_2\text{Cl}_2/\text{CCl}_3\text{F}$ solution), the cyclopentadienyl resonances of the iron complex (1e) show no sign of splitting and since the slowing of nitrogen inversion in the complex $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNMe})_2$ ⁹ can be easily seen, it is probable that, in complexes (1a) - (1c), nitrogen inversion is still fast at -80°C and has a lower activation energy than the nitrogen inversion in the ruthenium complexes. The nitrogen in the isonitrile ligands in a bridged position can be thought to be sp^2 hybridised. The inversion process is dependent upon the nitrogen atom becoming sp hybridised in the transition state. For ammonia in which the nitrogen is sp^3 hybridised, the inversion process is dependent upon the nitrogen becoming sp^2 hybridised. It would seem therefore that the energy difference between the sp^2 and sp states for the ruthenium complexes (2a - 2d) is greater than that for the iron complexes (1a - 1e).

The CO and CN resonances in the high temperature limiting spectra of (2a) - (2c) are not in the positions calculated from chemical shift differences and relative isomer populations in the low temperature spectra. The results indicate an increase in population of the terminal isonitrile isomer with increasing temperature. In the absence of high temperature limiting spectra

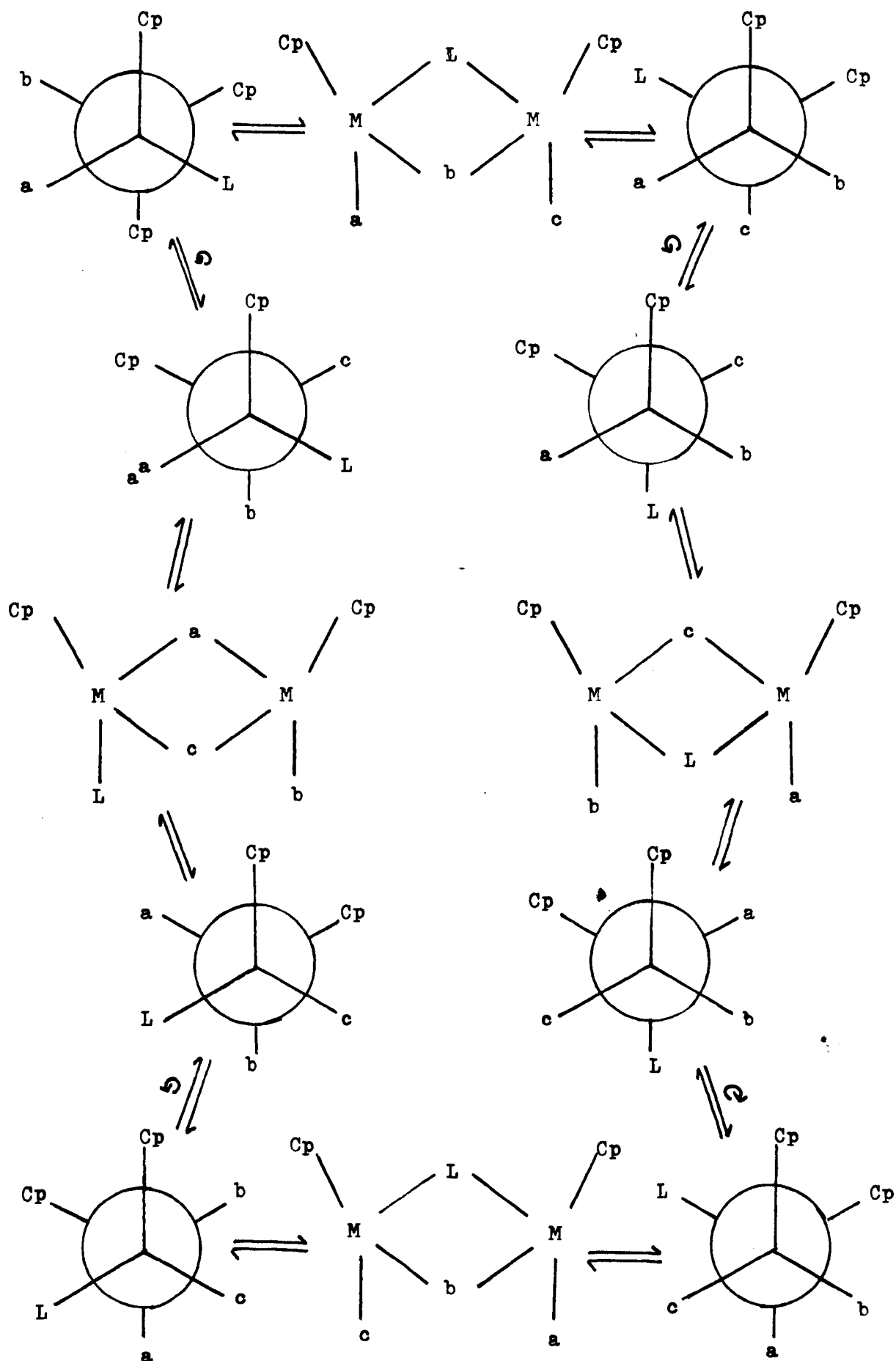
for (1a) - (1c), the change in isomer populations has been studied using variable temperature infrared spectroscopy. For (1b), (1c) in cyclohexane [(1a) is too insoluble at low temperatures] a decrease in temperature (+20°C to -50°C) results in an increase in the intensity ratio of band (G), due to the coincident bridging CO vibrations of (IX) and (X), to band (F), due to the coincident bridging vibrations of (VII) and (VIII), thus indicating an increasing proportion of terminal isonitrile isomer with decreasing temperature.

Finally the results from the nmr studies can be compared with predicted behaviour from the Adams - Cotton mechanism. Scheme (1) shows that all the isomers (VII) - (X) may be interconverted by bridge opening - bridge closing. Only for the interconversion (VIII) \rightleftharpoons (X) may this be done without bond rotation of the unbridged intermediate, which is a requirement for the other five interconversions capable in principle of observation [(VII) \rightleftharpoons (VIII), (VII) \rightleftharpoons (IX), (VII) \rightleftharpoons (X), (VIII) \rightleftharpoons (IX), (IX) \rightleftharpoons (X)].

For any of the six possible exchange processes, a closed cycle may be drawn as shown in Scheme (2) for (VII) \rightleftharpoons (IX) exchange. It can be shown for all six cycles that cis - trans isomerism or bridge - terminal isonitrile exchange must be accompanied by bridge - terminal carbonyl exchange, and that where bridge - terminal isonitrile exchange occurs, this must be accompanied by cyclopentadienyl site exchange in the terminally bound isonitrile isomer (see Scheme 2). Although drawn as a closed loop, linking to other cycles occurs by one or more of the unbridged rotamers. All possible permutations have not been shown, since in the absence of labelling of the metal atoms and/or the cyclopentadienyl ligands they are indistinguishable from those drawn.

It might therefore be expected that (VIII) \rightleftharpoons (X) interconversion would proceed with a lower activation energy, and that resonances assigned to these isomers would broaden and coalesce at a lower temperature, as observed for $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ ¹. For the parent dimer the difference between ΔG^\ddagger for the process involving M - M bond rotation and ΔG^\ddagger for the process simply

SCHEME 2 : The Mechanism for Cis (μ L) \rightleftharpoons Cis (tL) Exchange [(VII) \rightleftharpoons (IX)].



involving bridge opening and bridge closing is at least 4.5 Kcal mol⁻¹.^{41a,b} In contrast, the difference in ΔG^\ddagger between processes involving and not involving M - M bond rotation in $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNMe})_2$ is only 1.4 Kcal mol⁻¹ (the values are also much higher, being 17.5 and 18.9 Kcal/mol⁻¹ respectively). The monosubstituted complex might be expected to fall at intermediate values. Examination of both iron and ruthenium ¹³C spectra reveals an equivalent collapse of both CO and CN resonances, perhaps as expected in view of the anticipated small difference in ΔG^\ddagger between the two processes, and in view of the probable low population of isomer (VIII).

It is qualitatively obvious from the spectra that activation energies for exchange in the ruthenium complexes are lower. Perhaps the most meaningful comparison of ΔG^\ddagger values is for the cyclopentadienyl site exchange of (1d) and (2d) respective where calculations⁴⁰ give values of 14.2⁴² and 10.9 Kcal mol⁻¹ respectively. It is apparent from comparison of infrared spectra for the parent dimers that the bridged and non-bridged forms of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ are of more comparable stability and the lower activation energy observed for the isomer interconversion and site exchange are consistent with this.

The mass spectra of the complexes (1b) - (1e) and (2a) - (2d) are presented in Table (5). Complex (1a) has been studied²⁴ and the fragmentations for (1b) - (1e) are similar. The molecular ions of all the compounds were observed with reasonable intensities. Generally fragmentation consists of the sequential loss of the monodentate ligands to leave the Cp_2M_2^+ fragment, which probably fragments to give the CpM^+ fragment, which for iron is usually the most abundant ion in the spectrum under the conditions used. There is a marked preference for the initial loss of carbonyl relative to isonitrile. Methyl isonitrile is a better σ donor but poorer π acceptor than carbon monoxide,²³ and so the positive charge upon the molecular ion which is likely to weaken the back bonding to the attached ligands, (carbon monoxide being more strongly affected than the isonitrile), should result in carbonyl loss in preference to isonitrile. Also strong in the spectra are the mono-nuclear fragments $\text{CpM}(\text{CO})(\text{CNR})^+$ indicating fragmentation of the metal-metal

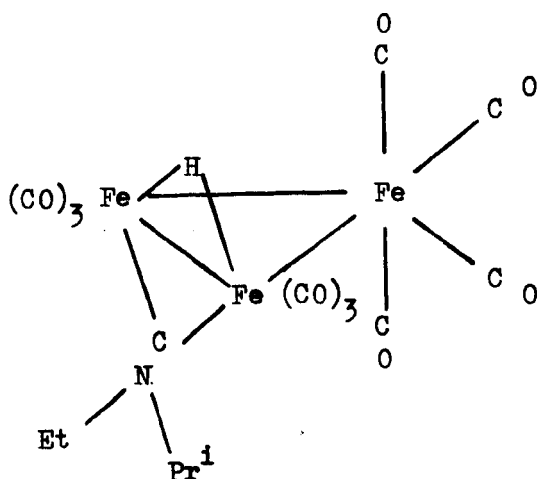
bond before all the monodentate ligands have been stripped off the dimetal framework. Other characteristic fragmentations include the loss of the alkyl group from the isonitrile.

Complexes (4a) - (4e), (5) and (6a), (6b) were prepared by electrophilic attack by acid or alkylation on the nitrogen of the corresponding neutral derivatives (1a) - (1e), (2b). Protonation of (1a) was first observed by Treichel et al.²⁵ While protonation of terminally co-ordinated isonitrile has been observed,²⁶ all results indicate that protonation or alkylation results in isolation of only the bridged iminium derivative. Some of the complexes have been previously prepared by Manning and Willis.^{27,28} Although the infrared spectra are similar, the salts prepared by the method described below do not contain solvent of crystallisation. Protonation of (1d) also yields the bridged iminium derivative (4d) in which the isonitrile has migrated from a terminal position. Previous unsuccessful attempts at preparing this compound have been attributed to the steric hindrance of a Bu^t group in a bridging position. It has been demonstrated, however, that in the complex $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNBu}^t)_2$ there is a small but significant concentration of the $(\text{CO})(\text{Cp})\text{Fe}(\mu\text{CO})(\mu\text{CNBu}^t)\text{Fe}(\text{Cp})(\text{CNBu}^t)$ isomer.²⁹

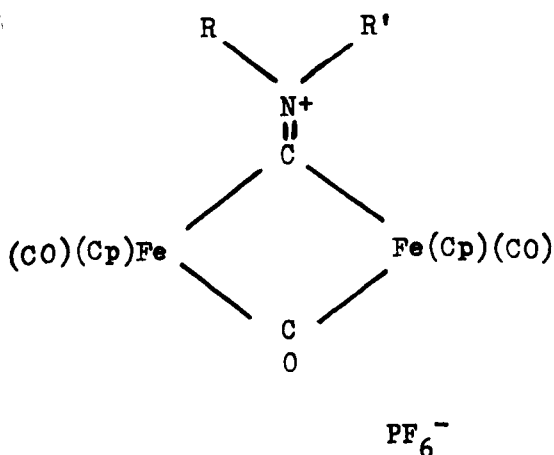
Proton and ¹³C spectral data are given in Tables (6) and (7). Slight decomposition even at -10°C results in broadening of resonances in the ¹H spectra (particularly for (4d) for which a spectrum could not be obtained) which is undoubtedly responsible for the observation of only one cyclopentadienyl resonance for (4a) - (4c), (4e). Of particular interest is the doublet of doublet resonances associated with the $\text{CH}(\text{CH}_3)_2$ groups of (4c) and (6b), and the AB resonances associated with the CH₂ groups of (5) and (6a). The ABX₃ system associated with (6a) was matched by a computer simulation. The ¹H nmr spectrum together with the computer simulation are illustrated in figures (20) and (21).

The most obvious feature of the ¹³C spectra is the large deshielding (ca 75 ppm) of the CN carbon compared to values for the neutral bridging isonitrile. A similar, although smaller, deshielding (35 ppm) of the bridging

carbonyl resonance of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ has been observed on adduct formation with BCl_3 to yield $(\text{CO})(\text{Cp})\text{Fe}(\mu\text{CO}\cdot\text{BCl}_3)_2\text{Fe}(\text{Cp})(\text{CO})$.³⁰ Inequivalence of the two iron atoms is evident only in the two cyclopentadienyl resonances observed for (4d) and the two terminal CO resonances of (6a). Although it would appear that the complexes (4a - 4e) and (6a,b) are non fluxional at room temperature, at elevated temperatures it is conceivable that CN bond rotation may occur. Recent work has shown that the complex $\text{Fe}_3(\text{CO})_{10}(\text{H})-(\text{CNEt}(\text{Pr}^i))$ (shown below) undergoes CN bond rotation, which is fast on the nmr time scale at room temperature, although it can be "frozen out" at -50°C



Reaction of the neutral isocyanide complexes (1a), (1c), (1e) with iodine results in metal-metal bond cleavage to yield $\text{CpFe}(\text{CO})_2\text{I}$ and $\text{CpFe}(\text{CO})-(\text{CNR})\text{I}$ [(7a) - (7c) ; $\text{R} = \text{Me}, \text{Pr}^i, \text{Bu}^t$] in fair yield. The parent dimer (1) reacts similarly to yield $\text{CpFe}(\text{CO})_2\text{I}$.³¹ Interestingly only poor yields of $\text{CpFe}(\text{CO})(\text{L})\text{I}$ are obtained from cleavage of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{L}$ by I_2 where $\text{L} = \text{P}(\text{OR})_3$, PR_3 ³⁸ and CS .³⁹ Spectral data of the complexes (8a) - (8d) are given in Table 7.



(4a). $\text{R} = \text{H}, \text{R}' = \text{Me}$

(4b). $\text{R} = \text{H}, \text{R}' = \text{Et}$

(4c). $\text{R} = \text{H}, \text{R}' = \text{Pr}^i$

(4d). $\text{R} = \text{H}, \text{R}' = \text{Bu}^t$

(4e). $\text{R} = \text{H}, \text{R}' = \text{Ph}$

(6a). $\text{R} = \text{Me}, \text{R}' = \text{Et}$

(6b). $\text{R} = \text{Et}, \text{R}' = \text{Pr}^i$

Experimental

The isonitriles,³²⁻³⁴ $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ ¹⁹ and $(\text{OEt})_3(\text{BF}_4)$ ³⁵ were prepared by literature methods; other chemicals were purchased. Reactions were carried out under nitrogen in purified solvents.

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer using 0.1mm NaCl cells, variable temperature spectra using a Beckman-RIIC VLT-2 cell equipped with an automatic temperature controller. Proton and ^{13}C nmr spectra were obtained using a JEOL FX-100 spectrometer, ^{13}C spectra in the presence of $\text{Cr}(\text{acac})_3$ (acac = acetylacetonate) as relaxation agent.

Preparations

- (a) $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNBu}^t)$. The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (3.54 g / 10 mmols) and Bu^tNC (1.66g / 20 mmols) were stirred in refluxing benzene (100 cm³) for ca. 8 hrs until reaction was complete as judged by infrared spectroscopy. The solvent was removed under reduced pressure and the residue was chromatographed on grade (II) alumina using a 3 : 1 mixture of dichloromethane : pet-ether (40/60) as eluent. The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ was eluted first, followed by the product as a purple band. Recrystallisation from CH_2Cl_2 - pet-ether (40/60) gave 3.1 g (75%) of dark purple crystals.
- (b) $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNCH}(\text{CH}_3)_2$. The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (3.54g / 10 mmols) were stirred in benzene (100 cm³) at RT for ca. 24 hrs until reaction was complete as judged by infrared spectroscopy. The solvent was removed under reduced pressure and the residue chromatographed on grade (III) alumina (350 g) using dichloromethane as eluent. The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ eluted first, followed by the product as a purple band. Recrystallisation from CH_2Cl_2 - pet-ether (40/60) gave 3.5 g (90%) of purple crystals. Complexes 1(a) and 1(b) were prepared similarly.
- (c) $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNPh})$. The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (3.54 g / 10 mmols) and PhNC (2.1g / 20 mmols) were stirred in benzene at 50°C for

ca. 8 hrs until partial monosubstitution had occurred as judged by infrared spectroscopy. (If the reaction is carried out at higher temperatures or over a long period the work up is more difficult because extensive decomposition occurs and the disubstituted complex $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNPh})_2$ is formed). The solvent was removed under reduced pressure and the residue chromatographed on grade (III) alumina (350 g) using 1 : 1 dichloromethane : pet-ether (40/60) as eluent. The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ is eluted first, followed by the product as a purple band. Recrystallisation from CH_2Cl_2 - pet-ether (40/60) gave 2.2 g (50%) of deep purple crystals.

- (d) $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CNMe})$. The complex $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (0.5 g / 1.13 mmols) and CH_3NC (1.00 g / 2.2 mmols) were stirred in refluxing xylene (10 cm^3) for ca. 24 hrs until reaction was complete as judged by infrared spectroscopy. The solvent was removed under reduced pressure and the residue was chromatographed on grade (II) alumina using dichloromethane as eluent. The complex $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ was eluted first, followed by the product as a yellow band. Recrystallisation from CH_2Cl_2 : pet-ether (40/60) gave 0.25 g of orange crystals. Complexes (2b) - (2d) were prepared similarly.

- (e) $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNHMe})](\text{PF}_6)$. The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNMe})$ (1.0 g / 2.5 mmols) was stirred in diethyl ether (25 cm^3) and enough dichloromethane added dropwise to bring it into solution. Hexafluorophosphoric acid (75% aqueous) was added dropwise until precipitation ceased. The deep red precipitate of (3a) was filtered off, washed with diethyl ether, and dried in vacuo, giving (1.4 g). Complexes (4b) - (4e) and (5) were prepared similarly. [(4a), $\nu(\text{CO})$ at 2015, 1995 and 1835 cm^{-1} , $\nu(\text{CN})$ at 1600 cm^{-1} ; (4b), $\nu(\text{CO})$ at 2020, 1985 and 1825 cm^{-1} , $\nu(\text{CN})$ at 1580 cm^{-1} ; (4c) $\nu(\text{CO})$ at 2020, 1985 and 1830 cm^{-1} , $\nu(\text{CN})$ at 1563 cm^{-1} ; (4d), $\nu(\text{CO})$ at 2020, 1985 and 1825 cm^{-1} , $\nu(\text{CN})$ at

- 1530 cm^{-1} ; (4e), $\nu(\text{CO})$ at 2030, 1992 and 1830 cm^{-1} ; $\nu(\text{CN})$ at 1525 cm^{-1} (nujol mull)].
- (f) $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNMeEt})(\text{PF}_6)$. To a stirred solution of $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNMe})$ (1.0 g / 2.6 mmol) in diethyl ether (25 cm^3) was added an excess of $(\text{OEt})_3(\text{BF}_4)$. After 30 min, the red precipitate was filtered off, dissolved in the minimum of acetone and added to a stirred aqueous solution of $(\text{NH}_4)(\text{PF}_6)$. The resultant red precipitate was filtered off, washed with a small amount of cold ethanol followed by diethyl ether, and dried in vacuo (yield 1.1 g). Complex (5b) was prepared similarly. [(5a), $\nu(\text{CO})$ at 2010, 1985 cm^{-1} , $\nu(\text{CN})$ at 1575 cm^{-1} ; (5b) $\nu(\text{CO})$ at 2015, 1985, and 1820 cm^{-1} , $\nu(\text{CN})$ at 1595 cm^{-1} (nujol mull)].
- (g) $\text{CpFe}(\text{CO})(\text{CNMe})\text{I}$. The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNMe})$ (0.5g / 1.3 mmols) and iodine (0.5g / 2 mmols) were stirred in chloroform at room temperature for ca. 2 hours until reaction was complete as judged by infrared spectroscopy. Excess iodine was removed by extraction with an aqueous solution of sodium thiosulphate (40 g / 100 cm^3). The solvent was then removed under reduced pressure, and the residue chromatographed on grade (II) alumina using dichloromethane : pet-ether (40/60) (50 : 50) as eluent. The complex $\text{CpFe}(\text{CO})_2\text{I}$ eluted first, followed by the product as a dark green band. Crystallisation from dichloromethane : pet-ether (40/60) followed by sublimation (0.1mm/90°C) gave dark green crystals (0.3g). Complexes (7b) and (7c) were prepared similarly. [(7a) (ir), $\nu(\text{CN})$ at 2165 cm^{-1} , $\nu(\text{CO})$ 1989 cm^{-1} , (^1H nmr), Cp 4.67 δ , Me 3.54 δ ; (7b) (ir) $\nu(\text{CN})$ at 2134 cm^{-1} , $\nu(\text{CO})$ at 1987 cm^{-1} , (^1H nmr), Cp 5.71 δ , $\text{CH}^*(\text{CH}_3)_2$ 4.11 δ (sept J = 6.5 Hz), $\text{CH}(\text{CH}_3)_2$ 1.42 δ (doublet); (7c) (ir) $\nu(\text{CN})$ at 2132 cm^{-1} , $\nu(\text{CO})$ at 1987 cm^{-1} , (^1H nmr), Cp 4.71 δ , Me 1.48 δ).
- (h) $[\text{Cl}_2\text{Os}(\text{CO})_3]_2$. The salt $\text{Na}_2(\text{OsCl}_6)$ (5g) was refluxed in formic acid for seven days. The resulting pale yellow solution was

passed through a cationic exchange resin in the acid form. The resulting solution was decomposed into the crude product $[\text{Cl}_2\text{Os}(\text{CO})_3]_2$ by evaporation of the solvent under reduced pressure. The infrared spectrum of the crude product was in agreement with published results,³⁶ and further purification of the product was not necessary.

- (i) $\text{Cp}_2\text{Os}_2(\text{CO})_4$: The complex $[\text{Cl}_2\text{Os}(\text{CO})_3]_2$ (345mg) and thallium cyclopentadienyl (2.7 g) were suspended in toluene (30ml) in an autoclave under an atmosphere of carbon monoxide. The reaction was heated to 200°C and allowed to react for 3 hours. The solvent was removed under reduced pressure, and the residue chromatographed upon alumina grade (IV) using methylene chloride as eluent. The pale yellow band that developed was collected, and the solvent evaporated to leave a yellow oil. The oil was a mixture of the product $\text{Cp}_2\text{Os}_2(\text{CO})_4$ and $\text{CpOs}(\text{CO})_2\text{Cl}$ as judged by infrared spectroscopy. Further chromatography upon alumina grade (III) using a (50/50) mixture of (40/60) petroleum - ether and methylene chloride resulted in separation to yield first $\text{Cp}_2\text{Os}_2(\text{CO})_4$ (150 mg, 48%) as pale yellow crystals followed by $\text{CpOs}(\text{CO})_2\text{Cl}$ (50mg, 15%).

TABLE 1
Analytical Data (%)

<u>Compound</u>	<u>Found</u>			<u>Calculated</u>		
	<u>C</u>	<u>H</u>	<u>N</u>	<u>C</u>	<u>H</u>	<u>N</u>
(1a)	49.0	3.6	3.8	49.1	3.6	3.8
(1b)	50.7	3.8	3.6	50.4	3.9	3.7
(1c)	51.6	4.3	3.5	51.6	4.3	3.5
(1d)	52.9	4.6	3.1	52.8	4.6	3.4
(1e)	56.0	3.5	3.5	55.9	3.5	3.3
(2a)	40.3	3.1	3.3	39.4	2.8	3.1
(2b)	41.2	3.2	3.3	40.8	3.2	3.0
(2c)	42.0	3.5	3.2	42.1	3.5	2.9
(2d)	44.2	3.6	3.5	43.3	3.8	2.8
(4a)	34.9	2.7	2.8	35.1	2.7	2.7
(4b)	36.1	3.0	2.8	36.4	3.0	2.7
(4c)	37.7	3.0	2.7	37.5	3.3	2.5
(4d)	38.5	3.6	2.7	38.9	3.6	2.5
(4e)	42.1	2.7	2.8	41.7	2.8	2.4
(5)	31.7	2.6	2.7	31.1	2.6	2.3
(6a)	37.6	3.1	2.5	37.7	3.3	2.6
(6b)	39.7	3.5	2.7	40.1	3.9	2.5
(7a)	30.9	2.5	4.7	30.3	2.5	4.4
(7b)	34.3	3.3	4.1	34.8	3.5	4.1
(7c)	37.2	4.0	4.3	36.8	3.9	3.9

TABLE 2 Infrared Data for (1a - 1e) and (2a - 2d)

<u>Compound</u>	<u>Band</u>								
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>
$\text{Cp}_2\text{Fe}_2(\text{CO})_4^a$	-	-	2007 (52)	1964 (100)	-	1797 (86)	-	-	-
(1a)	2137 (10)	2115 (sh)	1998 (80)	1953 (100)	-	1802 (35)	1774 (65)	1737 (35)	-
				1958 (sh)					
(1b)	2129 (30)	2099 (sh)	1996 (80)	1951 (100)	1961 (5)	1801 (50)	1773 (95)	1741 (40)	1713 (10)
				1959 (sh)					
(1c)	2111 (50)	2083 (sh)	1996 (85)	1952 (100)	1967 (10)	1801 (55)	1774 (85)	1741 (35)	1711 (20)
				b					
(1d)	2111 (30)	2077 (sh)	-	1953 (85)	-	-	1774 (100)	-	-
(1e)	-	-	1998 (95)	1955 (100)	1972 (30)	1806 (90)	-	1705 (70)	
				1959 (sh)					
(2a)	c	2060 (5)	2003 (95)	1958 (100)	-	1808 (70)	1772 (20)	1729 (70)	-
				1964 (sh)					
(2b)	2124 (3)	c	2004 (75)	1958 (100)	1975 (10)	1809 (55)	1774 (15)	1735 (25)	1706 (15)
				1963 (sh)					

cont'd over.....

TABLE 2 (Cont'd)

<u>Compound</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>
(2c)	2110 (10)	2090 (sh)	2000 (95)	1955 (100)	1971 (10)	1807 (80)	1771 (35)	1734 (20)	1708 (50)
				1961 (sh)					
(2d)	2120 (30)	2075 (sh)	1999 (5)	1955 (70)	1973 (15)	1804 (5)	1775 (100)	-	-

b

68

^a Reference 12.

^b CO vibration asymmetric, but assignment of shoulder not possible.

^c CN vibration asymmetric, but assignment of shoulder not possible.

* Hexane solution; values in cm^{-1} with relative intensities in parentheses .

TABLE 3

Variable temperature ¹H nmr spectra of (1a) - (1e) and (2a) - (2d)

<u>Compound</u>	<u>θc/°C</u>	<u>Solvent</u>	<u>Type of Proton</u>				<u>Ratio of bridged: terminal Isomers</u>
			<u>Cp</u>	<u>CH₃</u>	<u>CH₂</u>	<u>CH</u>	
(1a)	-40	CD ₂ Cl ₂	4.81	4.60			
			4.67 } 4.54 }	2.85			1 : 7
	-30	CD ₃ C ₆ D ₅	4.27 } 4.28 }	1.69			1 : 4
			4.13	3.44			
(1b)	80	CD ₃ C ₆ D ₅	4.31	2.55			
	-61	CD ₂ Cl ₂	4.82	1.32 (t,7.3)	3.89 (q)		
			4.78 } 4.57 }	0.95 (t,7.3)	3.22 (q)		1 : 16
	-48	CD ₃ C ₅ H ₅	4.29 } 4.27 }	0.36 (t,7.1)	2.19 (q)		1 : 7
			4.16	1.39 (t,7.1)	3.71 (q)		
	80	CD ₃ C ₅ H ₅	4.32	0.72 (t,7.1)	2.79 (q)		

Cont'd over.....

TABLE 3 (Cont'd)

<u>Compound</u>	<u>$\theta_c/^{\circ}\text{C}$</u>	<u>Solvent</u>	<u>Type of Proton</u>				<u>Ratio of bridged: terminal Isomers</u>
			<u>Cp</u>	<u>CH₃</u>	<u>CH₂</u>	<u>CH</u>	
(1c)	-40	CD ₂ Cl ₂	4.81	1.19 (d,6.5)		a	1 : 30
			4.68 } 4.56 }	1.01 (d,6.5)		3.58 (5)	
	-30	CD ₃ C ₆ D ₅	4.27 } 4.28 }	0.53 (d,6.5)		2.73 (5)	1 : 13
			4.16	1.59 (d,6.5)		a	
(1d)	64	CD ₃ C ₆ D ₅	4.31	0.73 (d,6.5)		3.04 (5)	
	-20	CD ₂ Cl ₂	4.67 } 4.55 }	1.02			b
	-40	CD ₃ C ₆ D ₅	4.30 } 4.27 }	1.72			b
	30	CD ₃ C ₆ D ₅	4.31	1.77			
(1e) ^c	-22	CD ₂ Cl ₂	4.66 ^d 4.73				e
	-28	CD ₃ C ₅ D ₅	4.24 ^d 4.11				e

Cont'd over.....

TABLE 3 (Cont'd)

<u>Compound</u>	<u>θc/°C</u>	<u>Solvent</u>	<u>Type of Proton</u>				<u>Ratio of bridged: terminal Isomers</u>
			<u>Cp</u>	<u>CH₃</u>	<u>CH₂</u>	<u>CH</u>	
(1e) ^c	50	CD ₃ C ₆ D ₅	4.23				
(2a)	-90	CD ₂ Cl ₂	5.26	3.20			
			5.18 } 5.08 }	2.94			3.4 : 1
	22	CD ₂ Cl ₂	5.28	3.27			
(2b)	-85	CD ₂ Cl ₂	5.27	0.95 - } 5.20 } 5.10 }	3.15 - } 3.77 (m) }		2.3 : 1
	22	CD ₂ Cl ₂	5.26	1.24 (t,7.3)	3.53 (q)		
(2c)	-90	CD ₂ Cl ₂	5.25	1.11 (m) }		3.75 (s,br)	
			5.19 } 5.09 }			3.35 (s,br)	
	20	CD ₂ Cl ₂	5.24	1.25 (d,6.4)		3.65 (s)	

cont'd over.....

TABLE 3 (Cont'd)

<u>Compound</u>	<u>$\theta_c/^\circ\text{C}$</u>	<u>Solvent</u>	<u>Type of Proton</u>				<u>Ratio of bridged: terminal Isomers</u>
			<u>Cp</u>	<u>CH₃</u>	<u>CH₂</u>	<u>CH</u>	
(2d)	-90	CD ₂ Cl ₂	5.20	1.02			b
			5.18				
		CD ₂ Cl ₂	5.16	1.13			

^a Septet not detected due to low abundance

^b No bridging isomer detected

^c Aromatic multiplet at δ 7.05 - 7.49

^d Two cyclopentadienyl peaks assignable to (III), (IV) in the ratio 1 : 4 and 1 : 2.5 in CD₂Cl₂ and CD₃C₆D₅ respectively.

^e No terminal isomer detectable

* δ relative to SiMe₄; multiplicities and coupling constant in parentheses

TABLE 4

Carbon - 13 nmr spectra of the complexes (1a) - (1e) and (2a) - (2d)

<u>Complex</u>	<u>θc/°C</u>	<u>CO_b</u>	<u>CN_b</u>	<u>CO_t</u>	<u>CN_t</u>	<u>Cp</u>	<u>CH₃</u>	<u>CH₂</u>	<u>CH</u>	<u>C</u>
(1a)	-24	278.8		211.8	158.4	85.9	29.3			
						84.9				
		272.6	246.6	209.9		86.9	34.8			
(1b)	-20	278.2		212.0	159.9	86.1	14.2	38.8		
						85.3				
		272.1	24.20	210.2		86.9	15.3	40.8		
(1c)	-20	278.5		211.8	158.4	85.8	21.9		47.4	
						84.0				
		272.8	239.7	210.1		86.9	23.0		a	
(1d)	-20	278.1		211.6	157.8	85.5	28.6			b
						84.7				
(1e) ^c	-20	270.1	252.6	209.7		86.4				147.9
		275.7		211.1		87.9				147.2

cont'd over.....

TABLE 4 (Cont'd)

Complex	$\theta_c/^\circ\text{C}$	CO_b	CN_b	CO_t	CN_t	Cp	CH_3	CH_2	CH	C
(2a) ^d	-70	247.7	227.0	197.8		89.0 } 87.2 }	46.9			
(2b)	-70	247.4	224.0	197.7		88.6 } 87.5 }	14.8	a		
		253.1		200.0	142.9	e	13.3	28.2		
(2c)	-70	247.7	220.4	197.8		88.6 } 86.8 }	22.5		63.5	
		252.9		200.6	142.6	e	21.2		44.3	
(2d)	-70	252.8		200.8	142.5	87.6 } 86.6 }	28.2			b

a Not detected

b Probably under solvent resonance; chemical shift for quaternary carbon of free ligand is 51.2ppm (benzene solution)

c Two sets of resonances due to (IX) and (X); those of higher intensity quoted first. Para and (ortho and meta) resonances at 112.0 and (119.0 + 127.8)ppm.

d Resonances due to terminal isomers not detected

e Resonances due to terminal isomers obscured by bridging isomer resonances

* $\text{CD}_2\text{Cl}_2 - \text{CH}_2\text{Cl}_2$ solvent; chemical shifts in ppm relative to SiMe_4

TABLE 5

Mass spectra of (1b) - (1e) and (2a) - (2d)

Most probable ion	Complex							
	<u>1b</u>	<u>1c</u>	<u>1d</u>	<u>1e</u>	<u>2a</u> ^a	<u>2b</u> ^a	<u>2c</u> ^a	<u>2d</u> ^a
$[\text{Cp}_2\text{M}_2(\text{CO})_3 (\text{CNR})]^+$	381 (51)	395 (10)	409 (14)	429 (50)	459 (47)	473 (73)	487 (43)	501 (54)
$[\text{Cp}_2\text{M}_2(\text{CO})_2 (\text{CNR})]^+$	353 (29)	367 (7)	381 (7)	401 (30)	431 (10)	445 (15)	459 (17)	473 (8)
$[\text{Cp}_2\text{M}_2(\text{CO})_1 (\text{CNR})]^+$	325 (30)	339 (8)	353 (7)	373 (47)	403 (41)	417 (73)	431 (41)	445 (27)
$[\text{Cp}_2\text{M}_2(\text{CO})_2]^+$	-	-	-	-	-	-	-	390 (73)
$[\text{Cp}_2\text{M}_2 (\text{CNR})]^+$	297 (96)	311 (37)	325 (14)	345 (98)	375 (62)	389 (76)	403 (45)	417 (7)
$[\text{Cp}_2\text{M}_2 (\text{CN})]^+$	268 (51)	268 (24)	268 (38)	-	-	360 (18)	360 (16)	360 (44)
$[\text{Cp}_2\text{M}_2]^+$	242 (25)	242 (5)	242 (39)	242 (28)	334 (63)	334 (68)	334 (76)	334 (88)
$[\text{CpM}(\text{CO}) (\text{CNR})]^+$	204 (42)	218 (13)	232 (11)	252 (33)	236 (31)	250 (53)	264 (30)	278 (92)
$[\text{CpM} (\text{CNR})]^+$	176 (100)	190 (60)	204 (38)	224 (88)	208 (100)	222 (100)	236 (100)	250 (23)
$[\text{Cp}_2\text{M}]^+$	187 (98)	187 (53)	187 (57)	187 (89)	-	-	-	232 (100)
$[\text{CpM}(\text{CO})]^+$	149 (49)	149 (60)	149 (48)	149 (15)	-	-	-	195 (71)
$[\text{CpM}]^+$	121 (93)	121 (100)	121 (100)	121 (100)	167 (44)	167 (71)	167 (29)	167 (88)

^a Calculated using ¹⁰²Ru isotope

TABLE 6

Proton nmr data for the complexes (4a) - (4c), (4e), (5), (6a), (6b)

Compound	R	R'	$\underline{\text{CH}}_3$	$\underline{\text{CH}}_2$	$\underline{\text{CH}}_3$	$\underline{\text{CH}}_2$	$\underline{\text{CH}}$	$\underline{\text{Cp}}$	$\underline{\text{NH}}$
(4a)	CH ₃	H			4.09			5.45	3.22 (br)
(4b)	CH ₃ CH ₂	H			1.54 (t, 7.3)	4.49 (q)		5.47	3.07 (br)
(4c)	CH(CH ₃) ₂	H			1.74 (d, 6.0)		4.77 (s)	5.45	3.17 (br)
					1.64 (d, 6.0)				
(4e) ^a	Ph	H						5.35	3.26 (br)
(5)	CH ₂ CH ₃	H			1.45 (t, 7.3)	4.23 (q)		5.87	3.03 (br)
						4.24 (q)		5.78	
(6a)	CH ₃	CH ₂ CH ₃	1.64 (t, 7.2)	4.66 (q)	4.28			5.54	
				4.68 (q)				5.52	
(6b)	CH(CH ₃) ₂	CH ₂ CH ₃	1.7 (t, 7.2)	4.57 (q)	1.48 (d, 6.8)		5.3 (s)	5.55	
					1.83 (d, 6.8)			5.53	

^a Aromatic multiplet at 7.71 δ * δ relative to SiMe₄; multiplicities and coupling constants in parentheses; C₂D₆CO solution -10°C

TABLE 7

Carbon - 13 nmr data for the complexes (4a) - (4e), 6a, 6b

<u>Compound</u>	<u>R</u>	<u>R'</u>	<u>CO_b</u>	<u>CN_b</u>	<u>CO_t</u>	<u>C_p</u>	<u>CH₃¹</u>	<u>CH₂¹</u>	<u>CH₃</u>	<u>CH₂</u>	<u>CH</u>	<u>C</u>
(4a)	CH ₃	H	255.5	320.6	208.2	89.9			43.3			
(4b)	CH ₂ CH ₃	H	255.4	318.6	208.4	89.9			14.3	54.8		
(4c)	CH(CH ₃) ₂	H	255.3	315.4	208.5	89.9			22.0		64.0	
(4d)	C(CH ₃) ₃	H	254.3	314.1	209.2	89.9 90.3	}		a			63.7
(4e)	Ph ^b	H	255.2	321.7	208.6	90.1						143.7
(6a)	CH ₃	CH ₂ CH ₃	255.2	315.9	208.7 208.3	90.3	13.0	63.0	56.6			
(6b)	CH(CH ₃) ₂	CH ₂ CH ₃	255.2	316.4	209.0	90.4	16.0	53.7	20.7		63.7	

^a Not detected, but may be under solvent resonance at 29.2 ppm

^b Para and (ortho + meta) resonances at 128.8 and (123.3 + 129.9) ppm

* (CD₃)₂CO solution, - 10°C; chemical shifts in ppm relative to SiMe₄

Figure 1

^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNMe}$ (1a)

Solvent : CD_2Cl_2

Temperature : -40°C

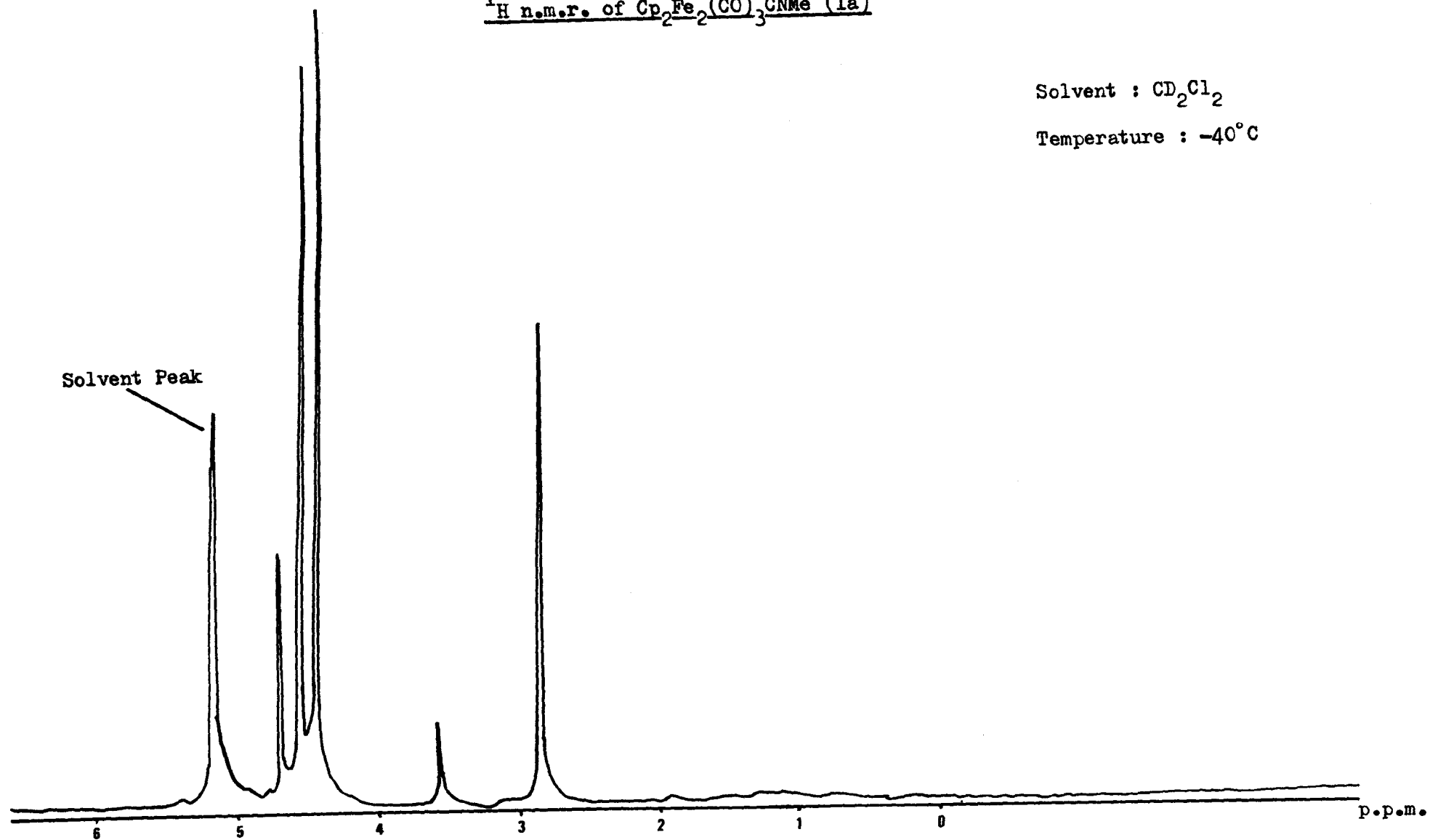


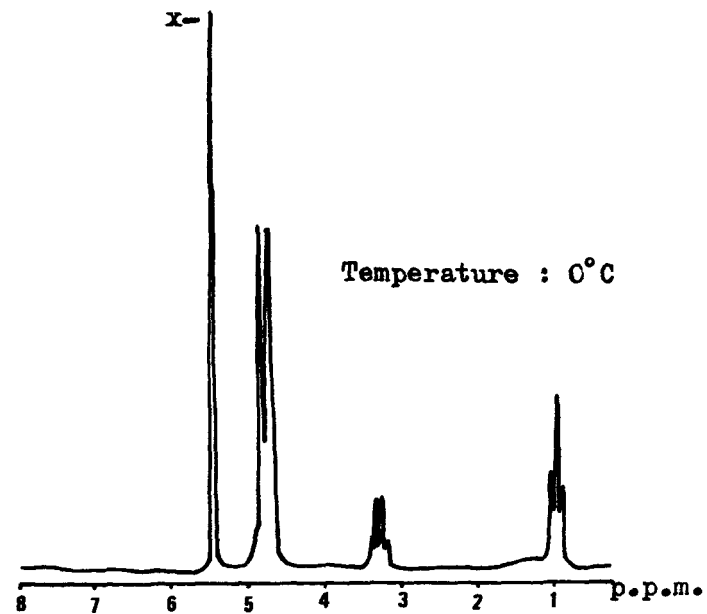
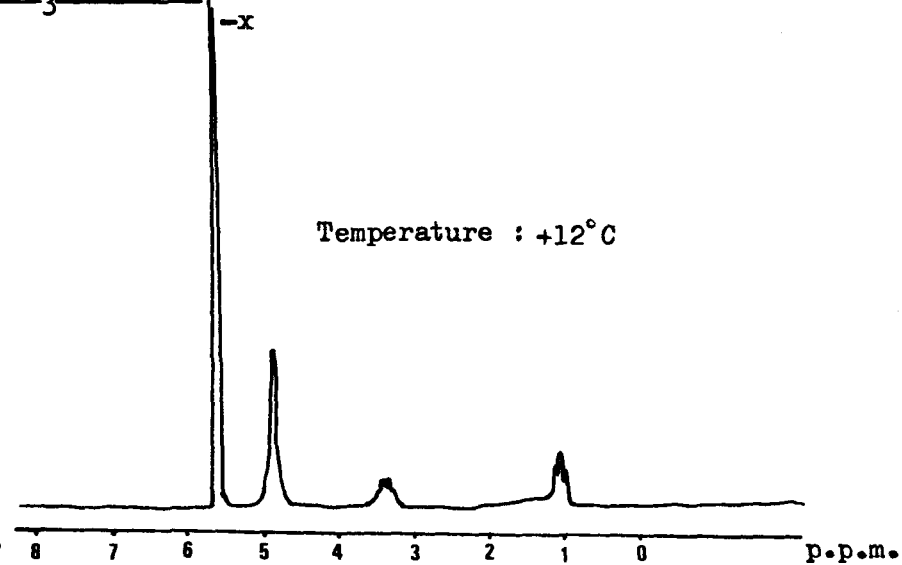
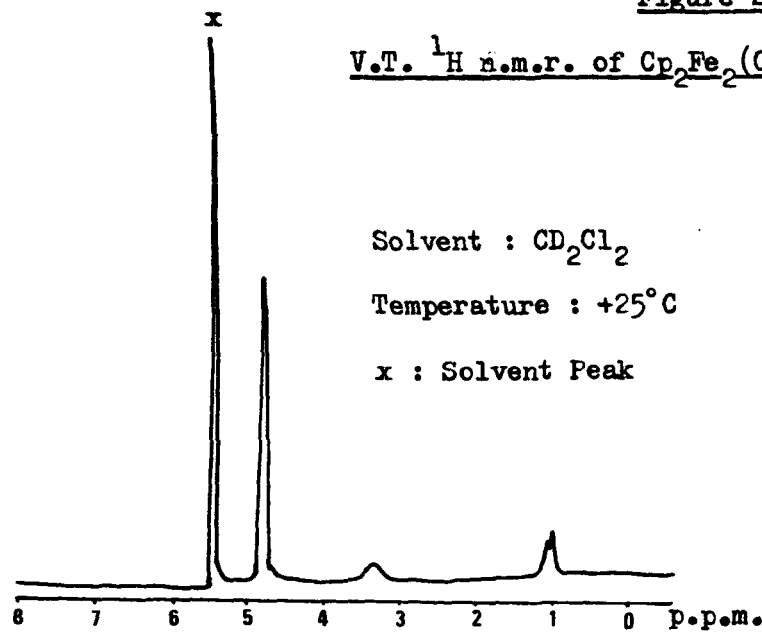
Figure 2

V.T. ^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNEt}$ (1b)

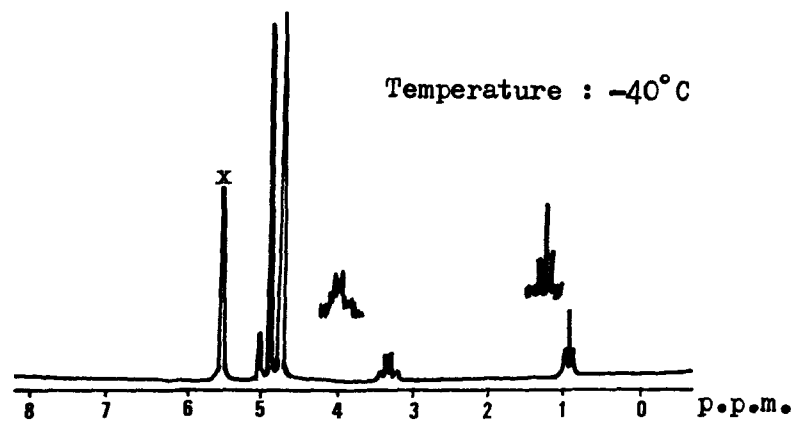
Solvent : CD_2Cl_2

Temperature : $+25^\circ\text{C}$

x : Solvent Peak



Temperature : 0°C



Temperature : -40°C

Figure 3

^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNPr}^1$ (lc)

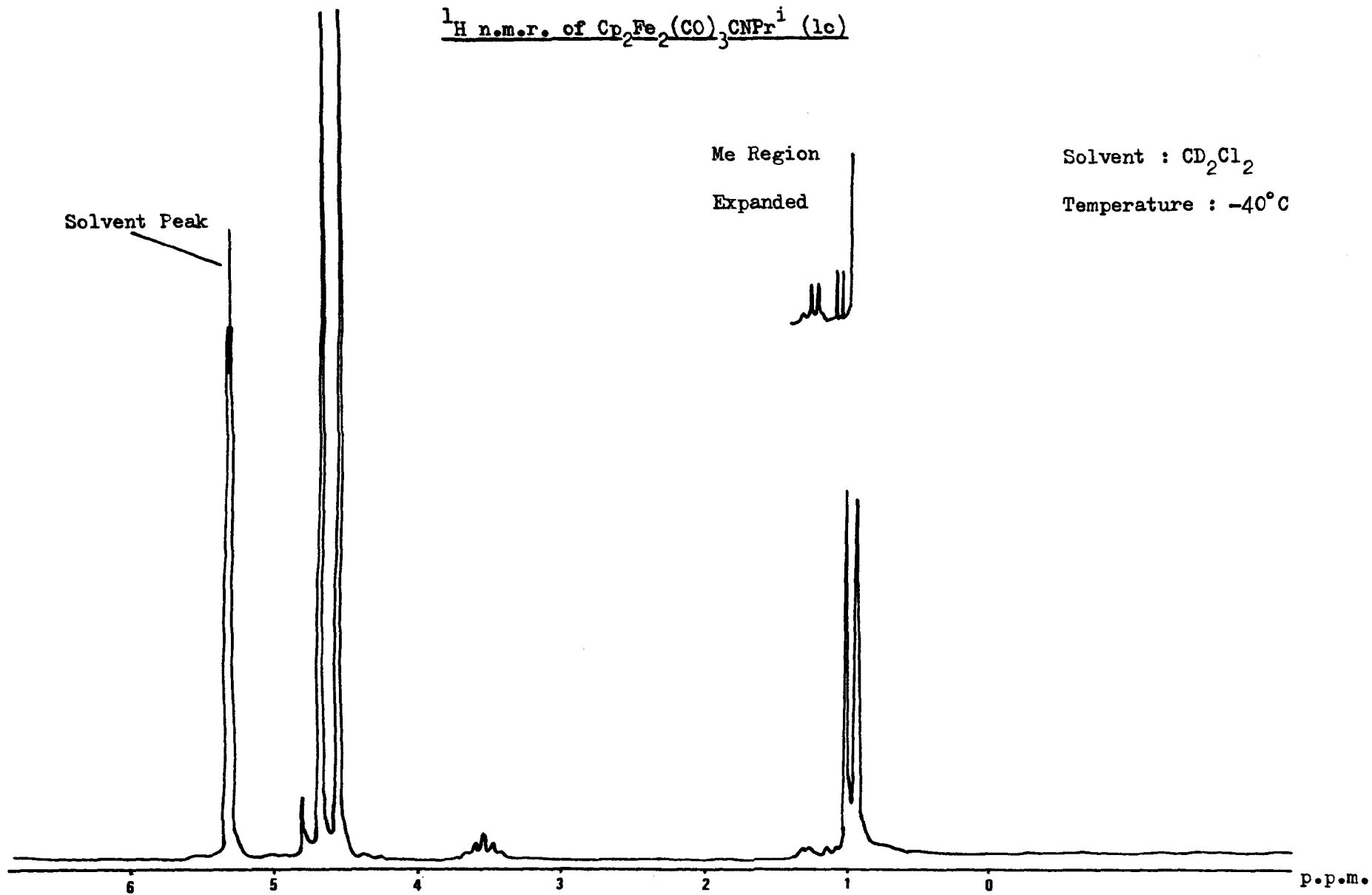


Figure 4

^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNBu}^t$ (ld)

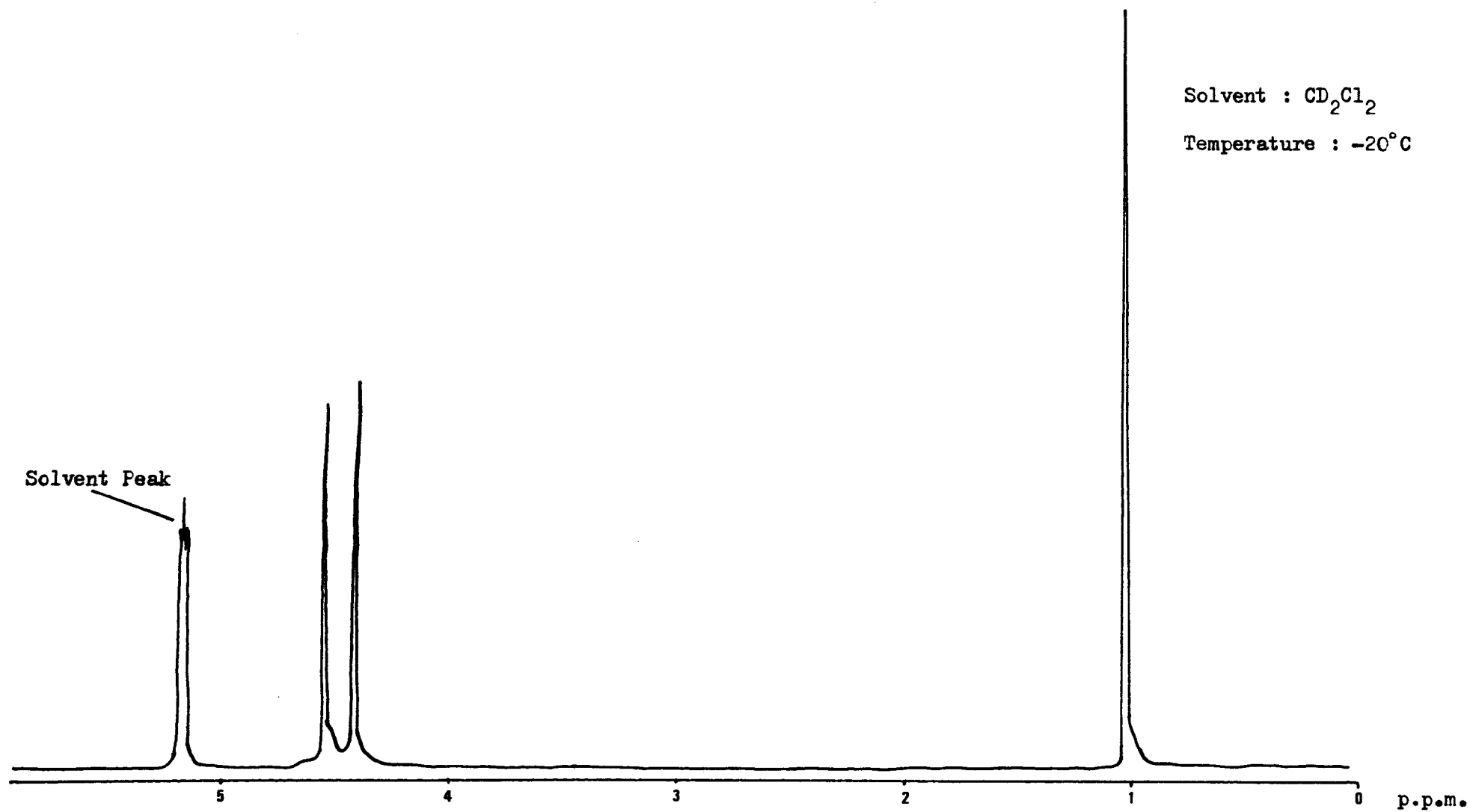


Figure 5

^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNPh}$ (1e)

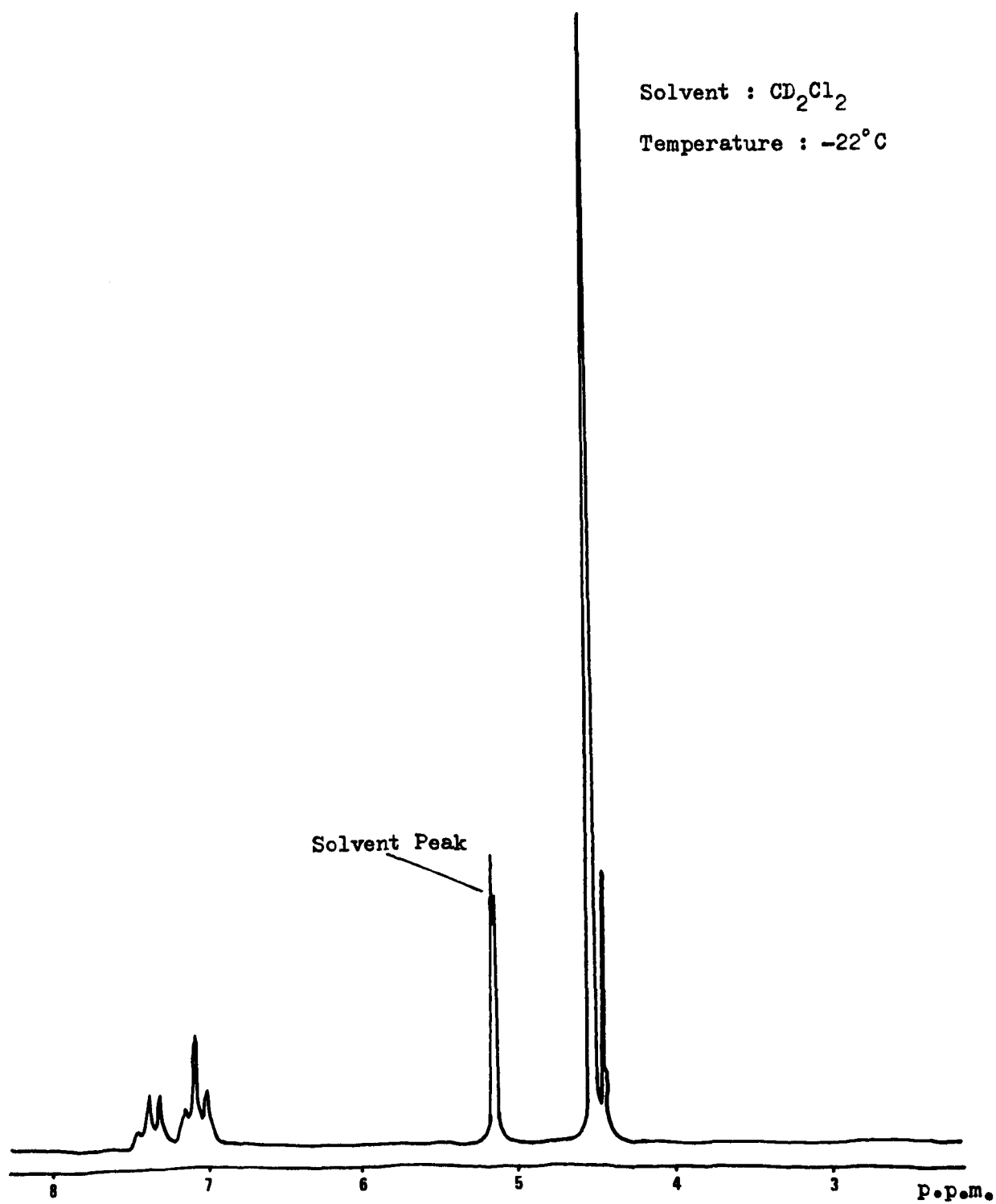


Figure 6

^1H n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{CNMe}$ (2a)

Solvent : CD_2Cl_2

Temperature : -90°C

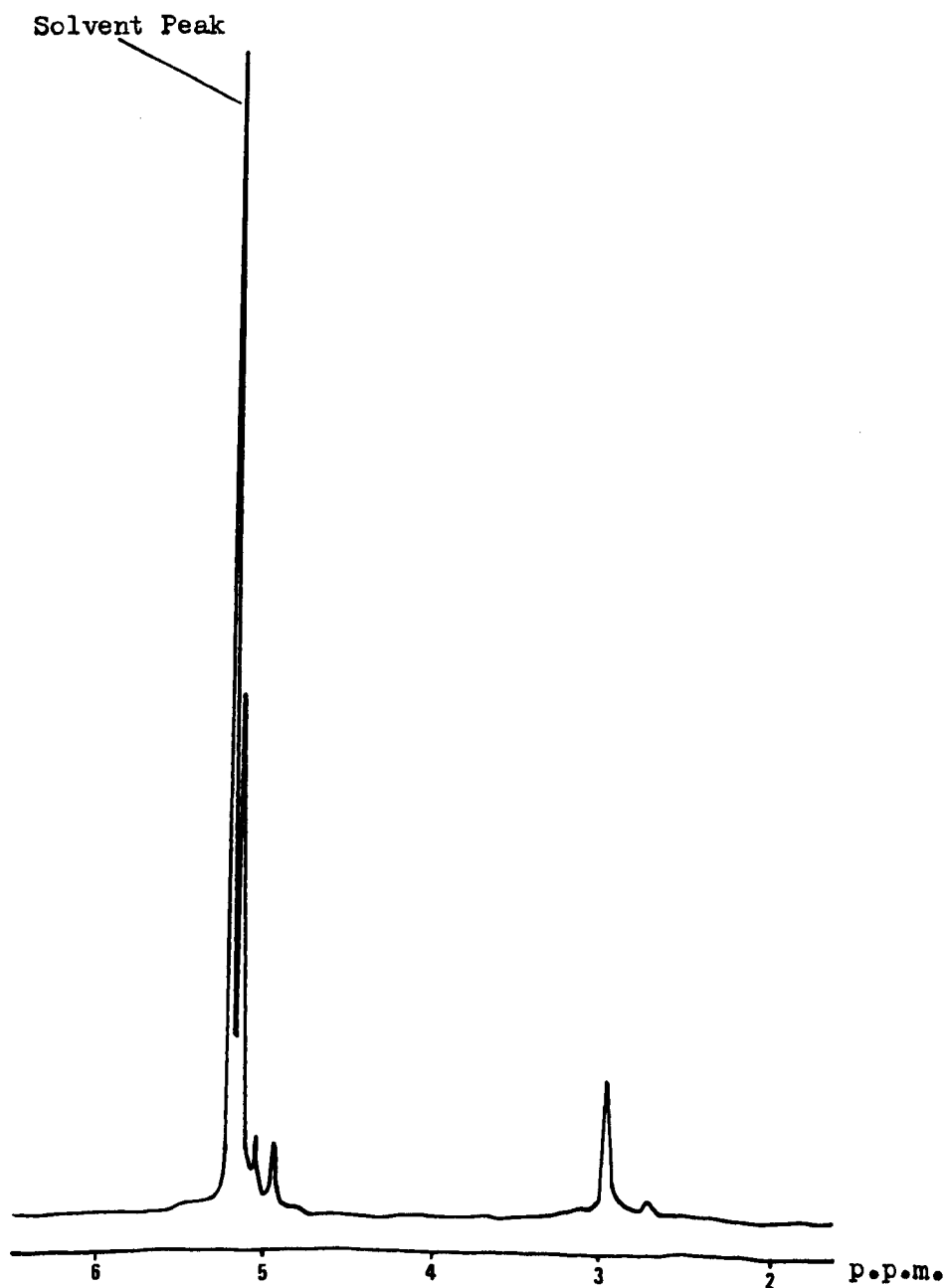


Figure 7

V.T. ^1H n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{CNEt}$ (2b)

Solvent : CD_2Cl_2

Temperature : 0°C

x : Solvent Peak

Temperature : -60°C

Temperature : -70°C

Temperature : -85°C

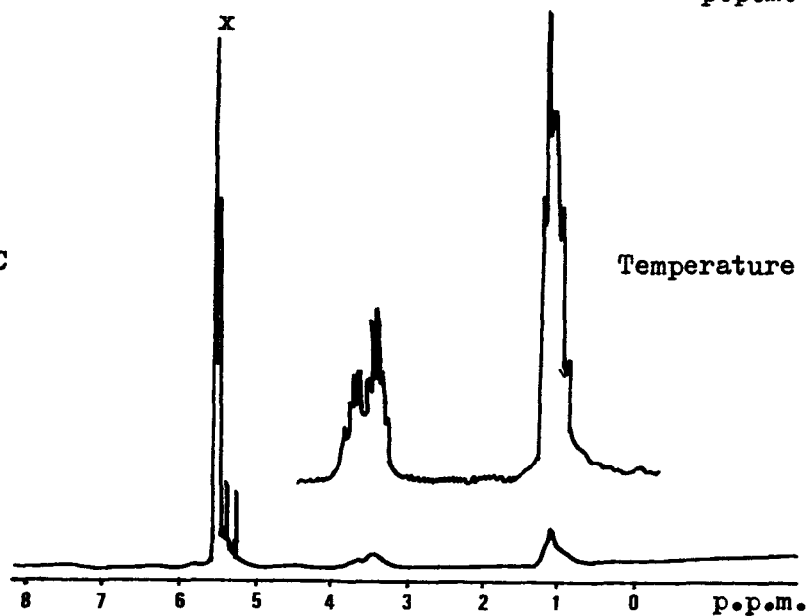
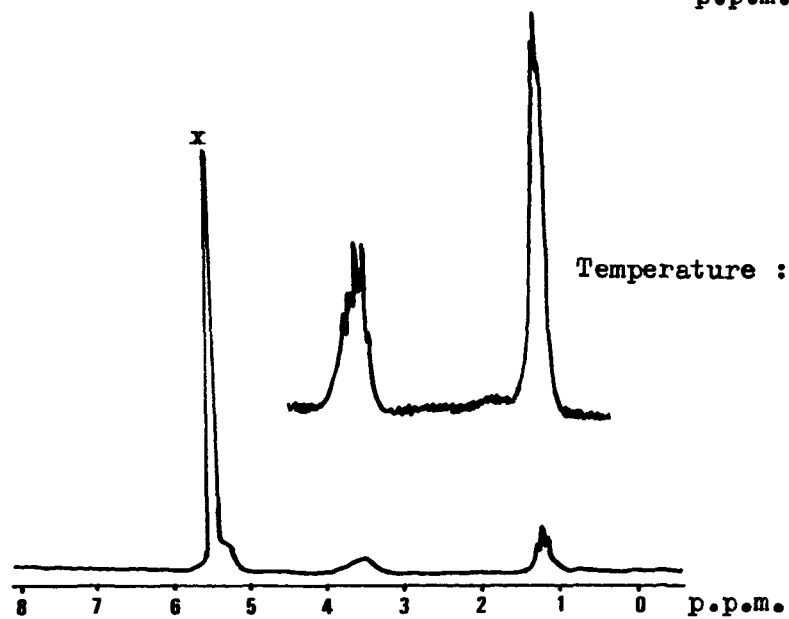
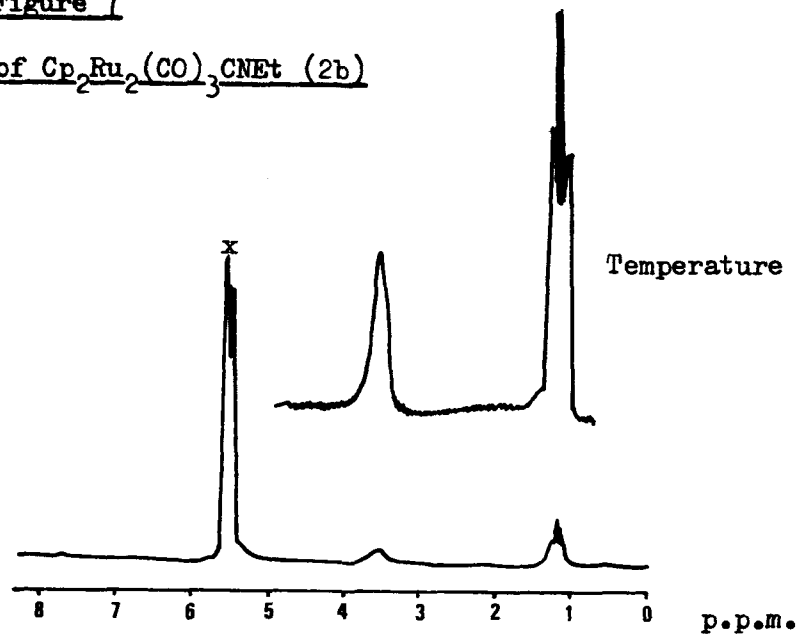
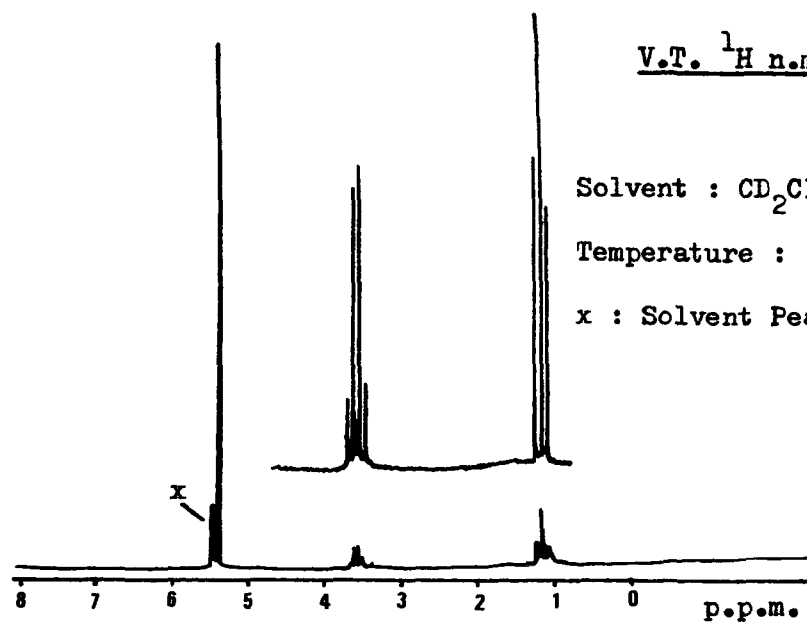


Figure 8

^1H n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{CNPr}^i$ (2c)

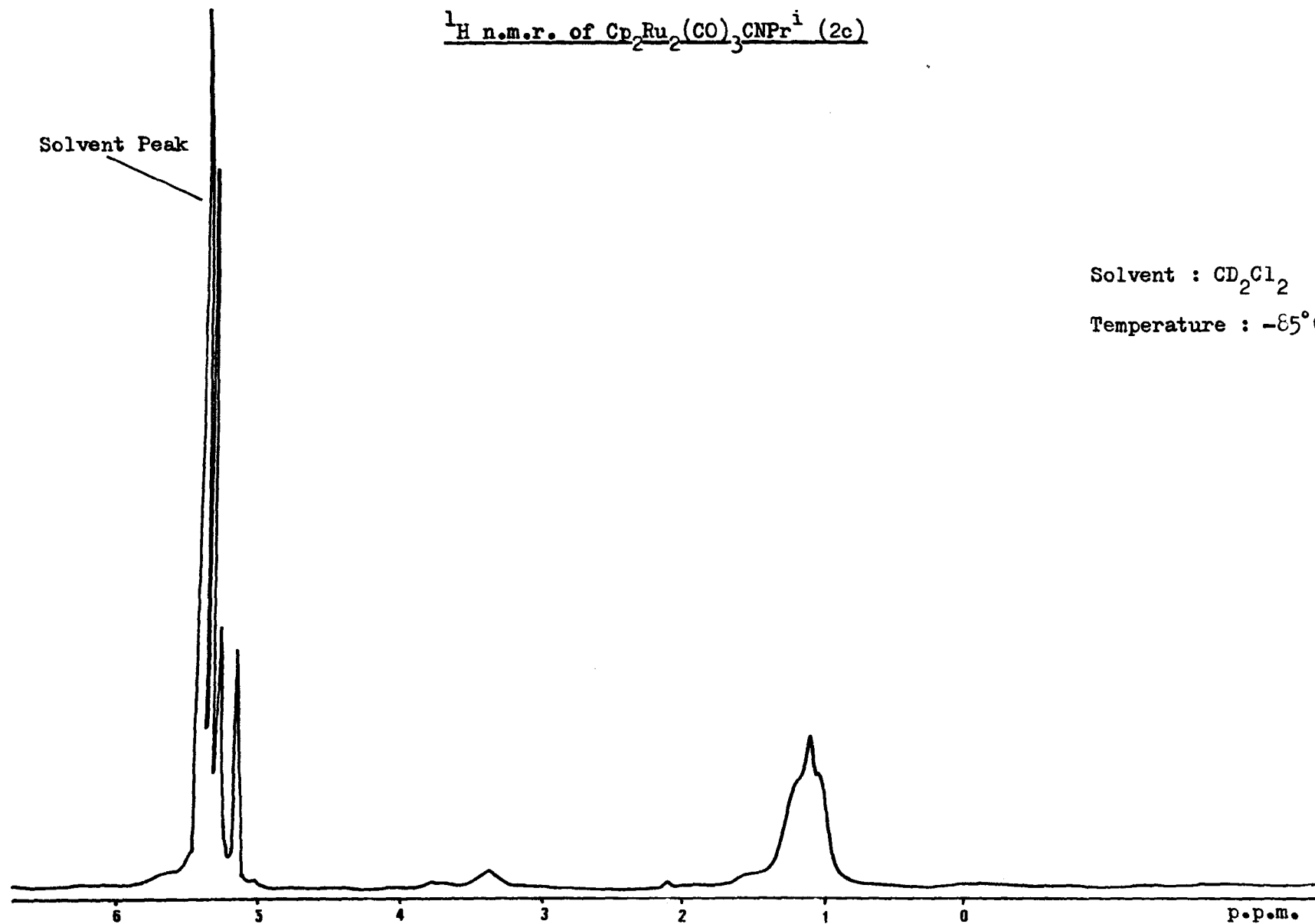


Figure 9

^1H n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{CNEt}^t$ (2d)

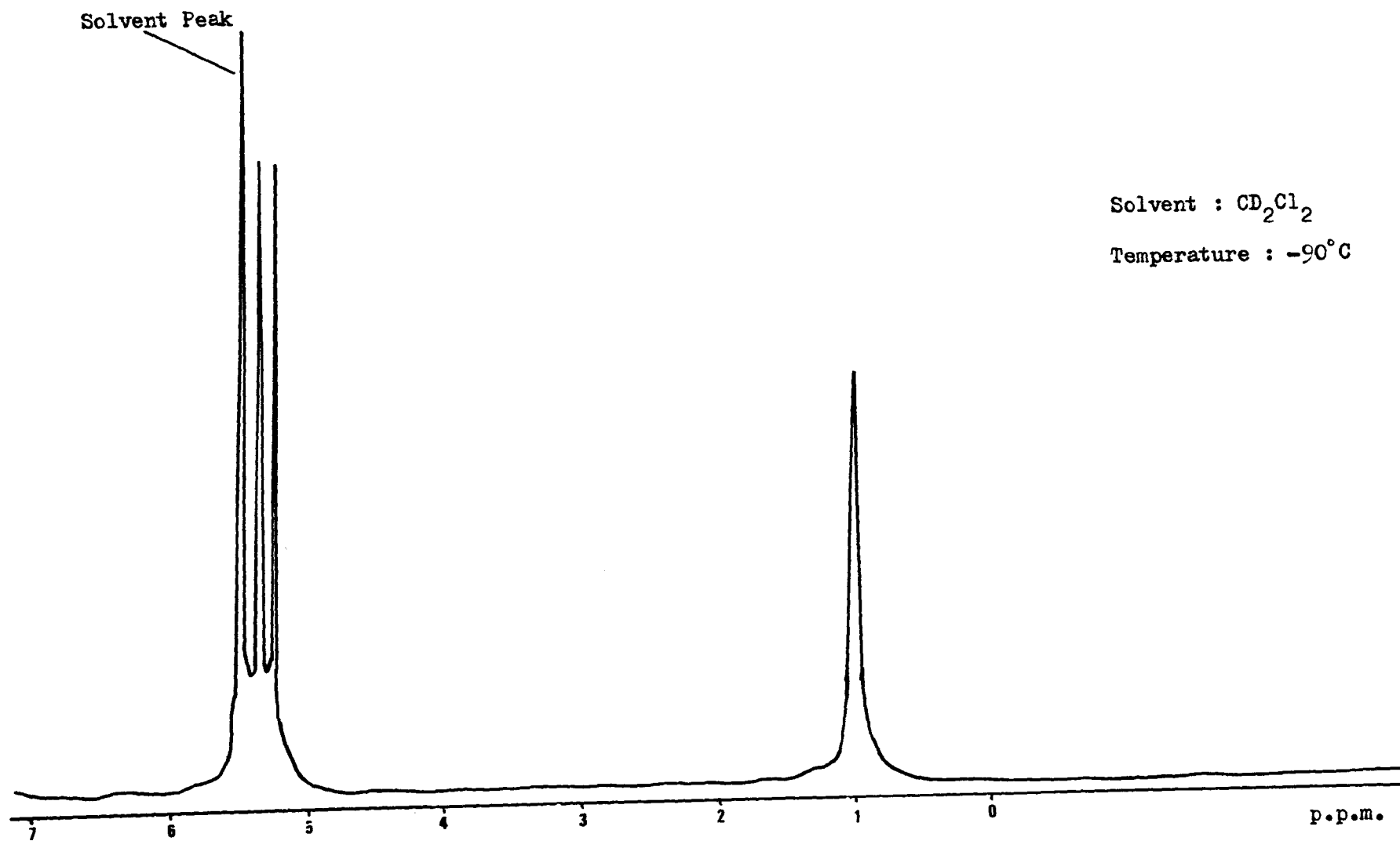


Figure 10

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNMe}$ (1a)

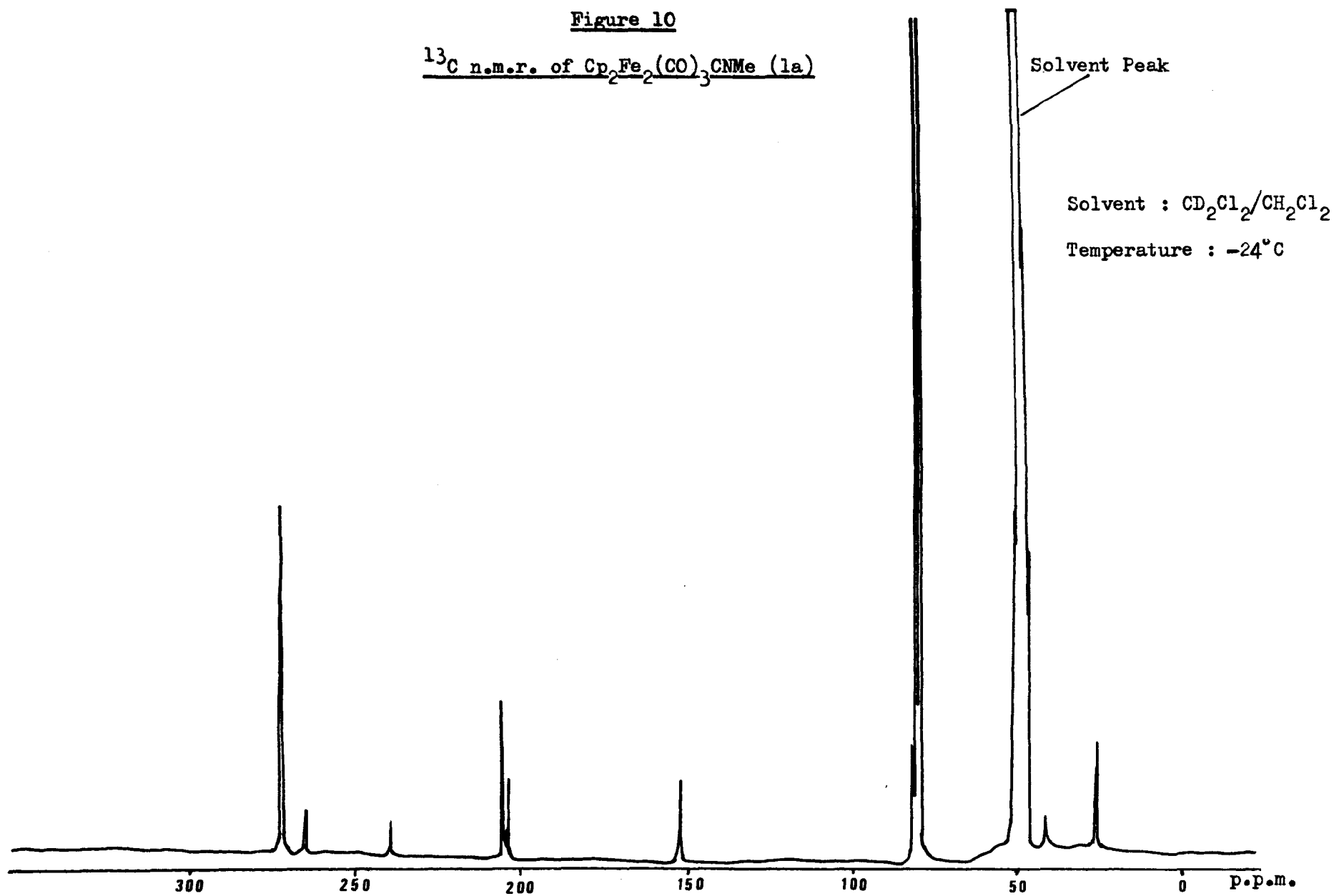


Figure 11

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNEt}$ (1b)

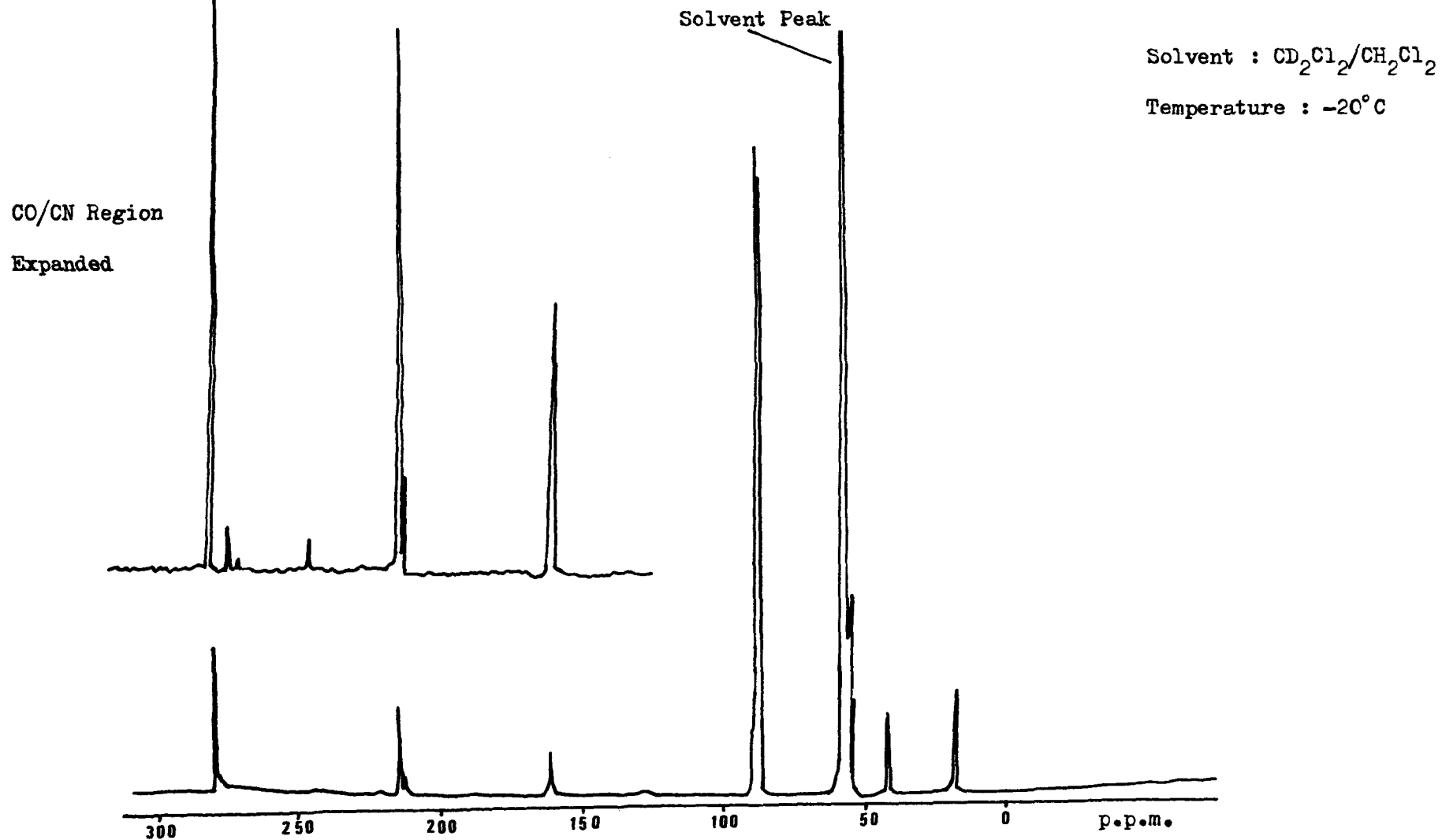


Figure 12

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNPr}^i$ (1c)

CO/CN Region
Expanded

Solvent Peak

Solvent : $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$

Temperature : -20°C

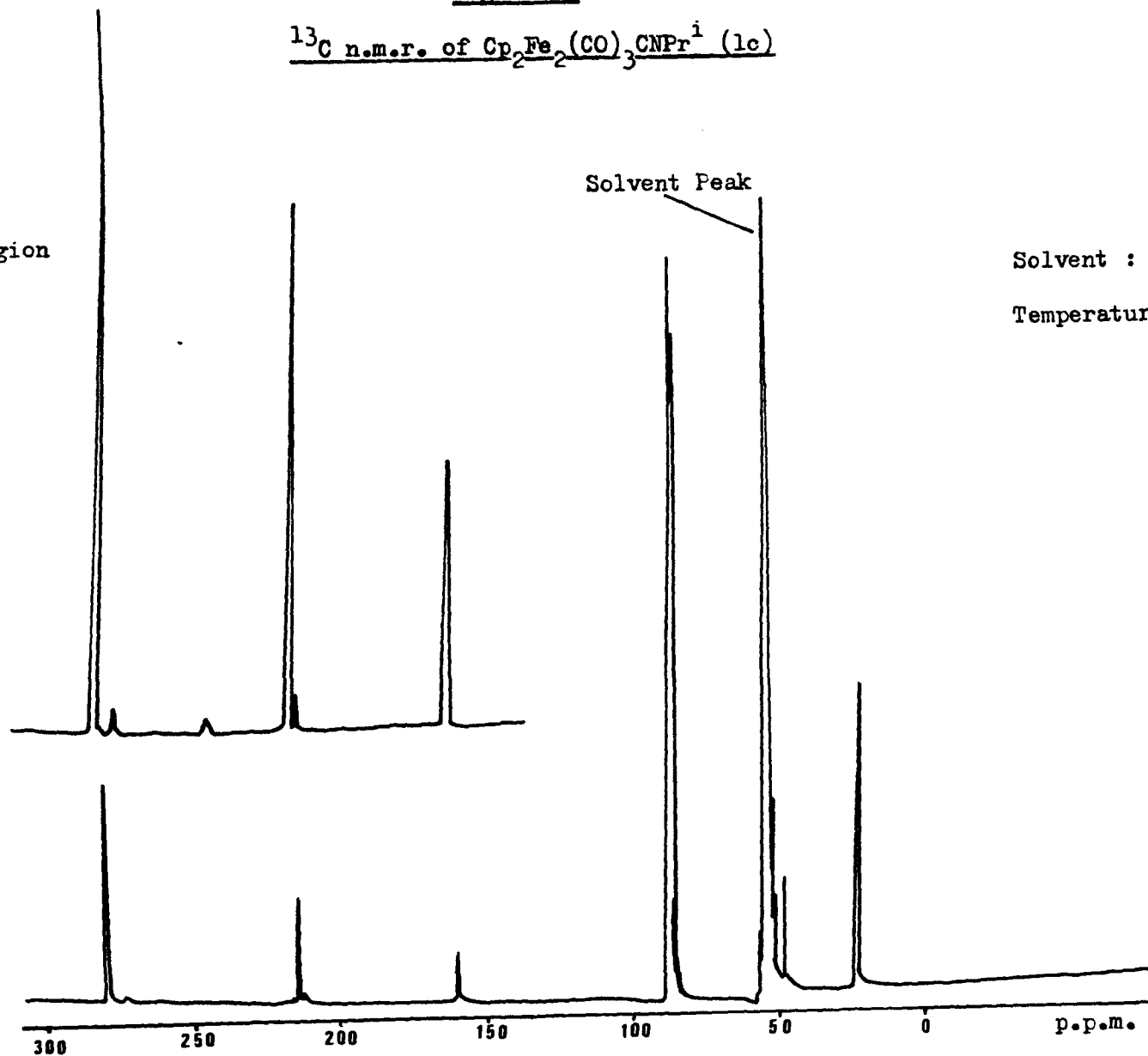


Figure 13

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNBu}^t$ (1d)

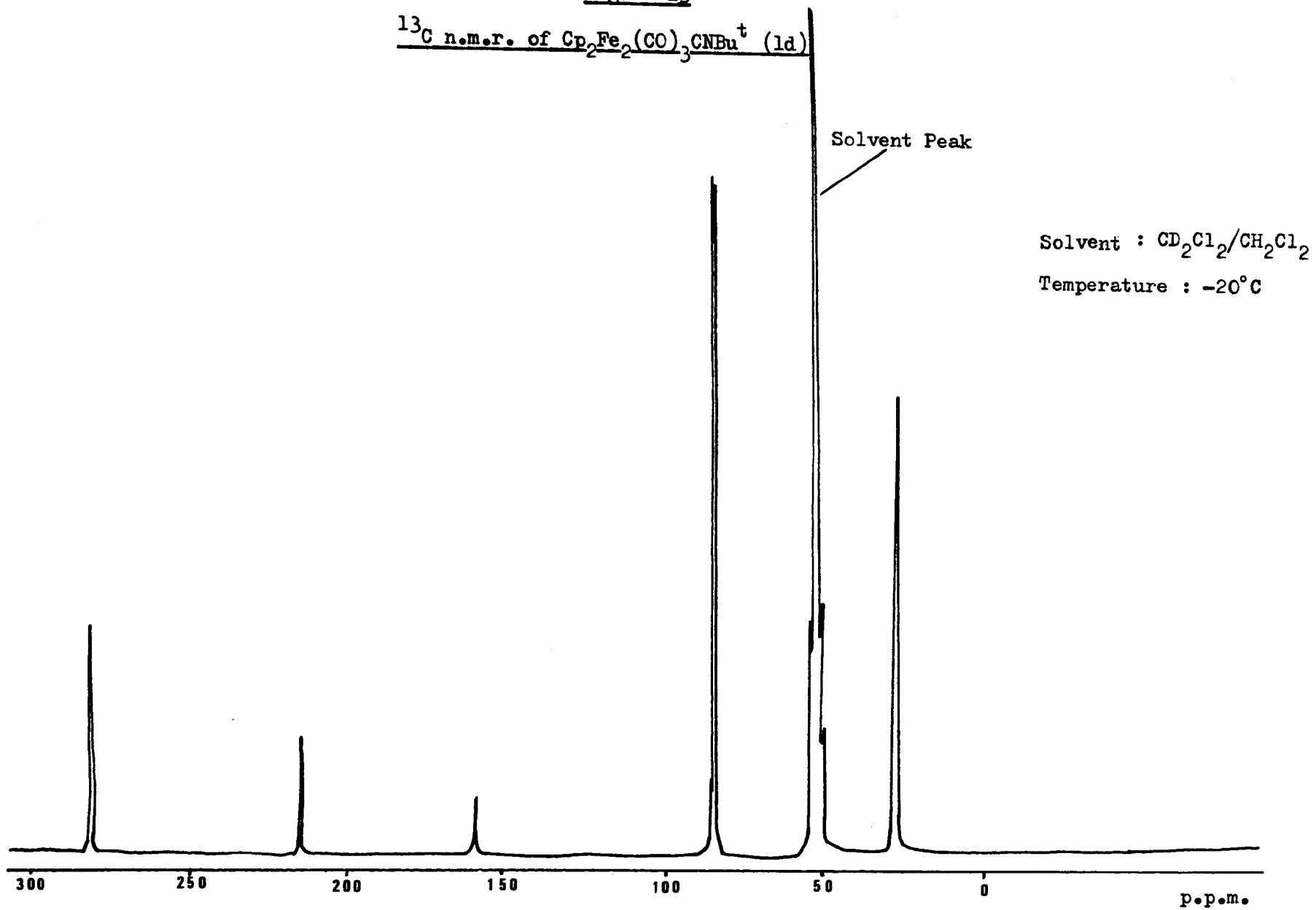


Figure 14

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNPh}$ (1e)

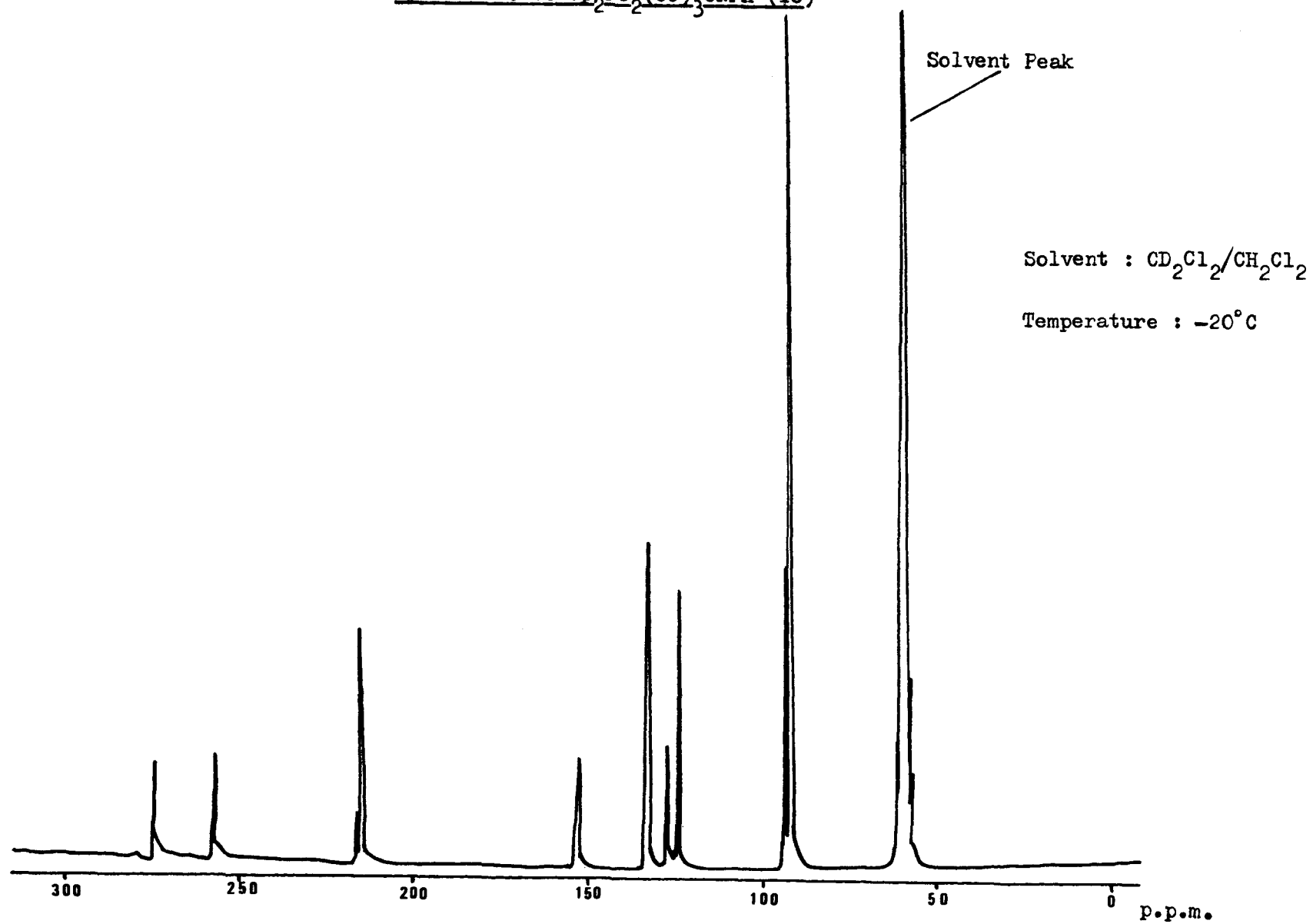


Figure 15

^{13}C n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{CNMe}$ (2a)

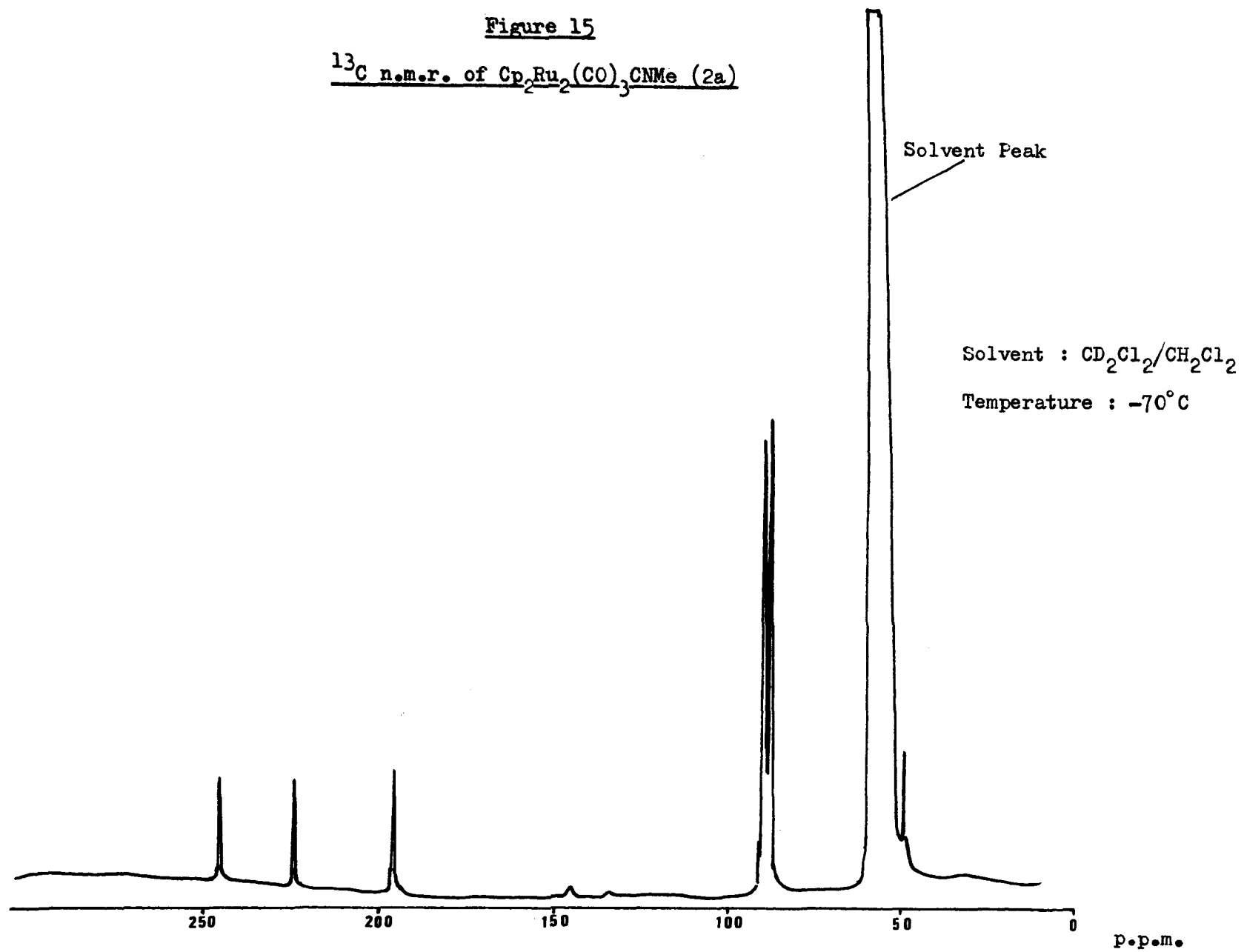


Figure 16

^{13}C n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{CNEt}$ (2b)

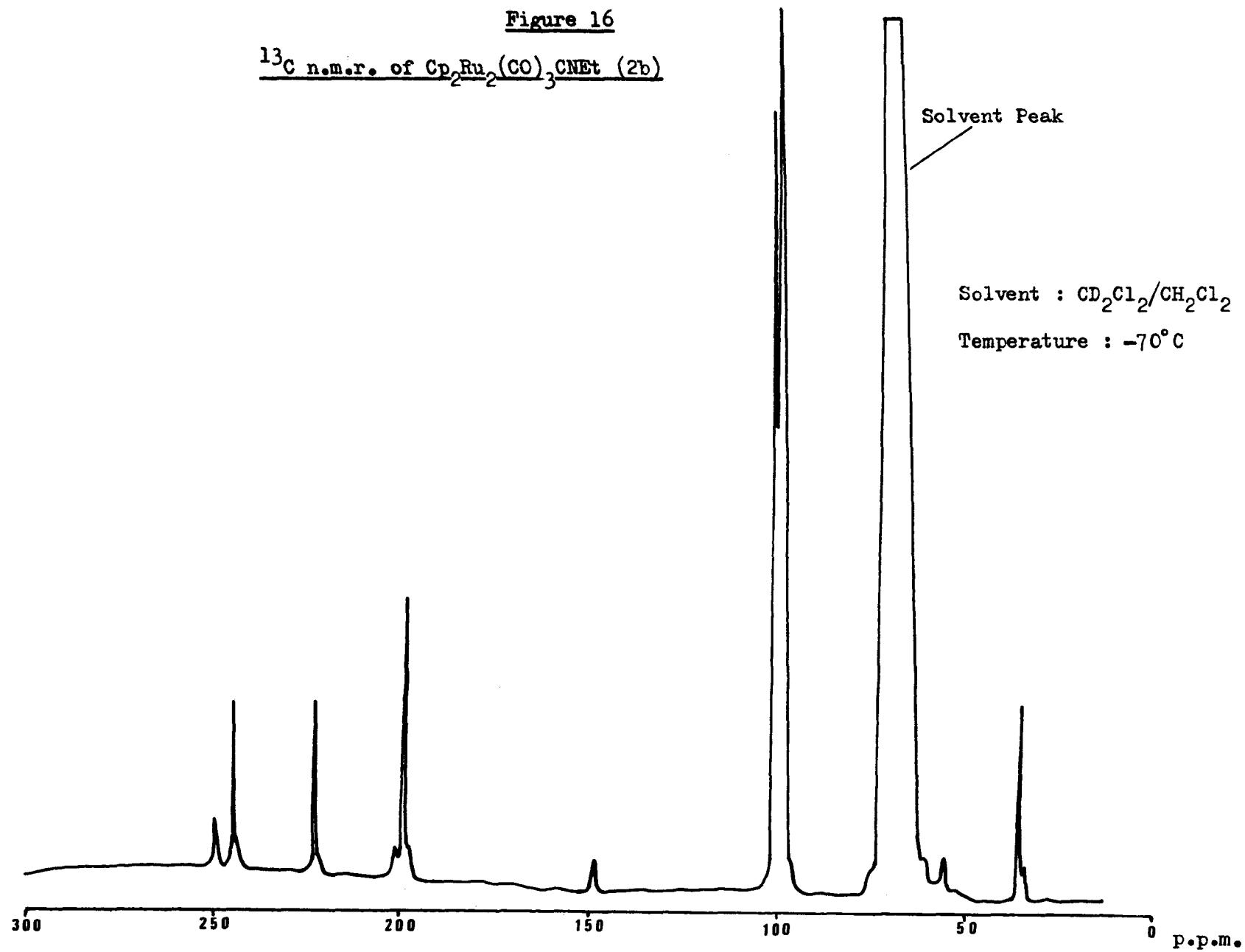


Figure 17

^{13}C n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{CNPr}^i$ (2c)

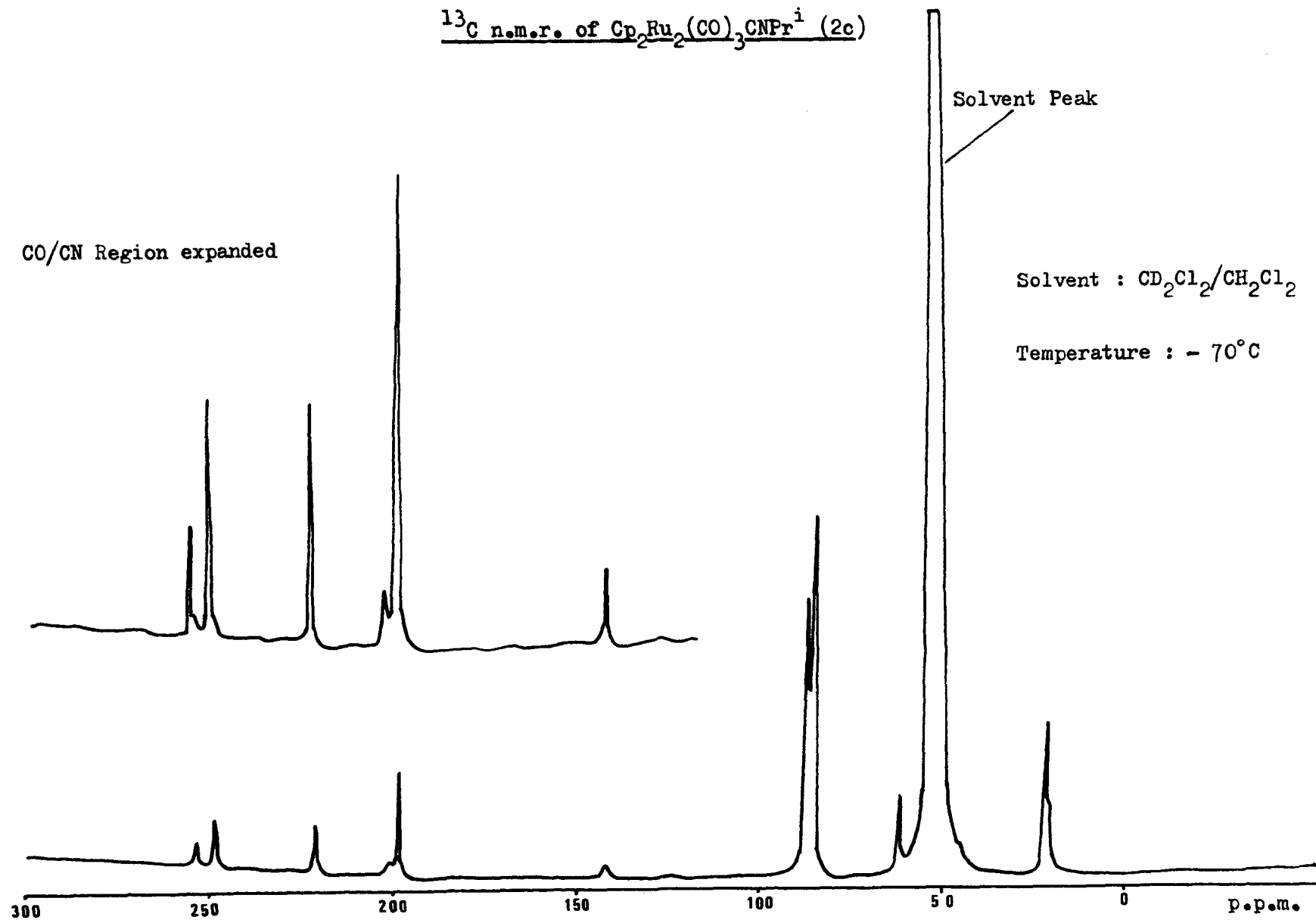


Figure 18

^{13}C n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{CNBu}^t$ (2d)

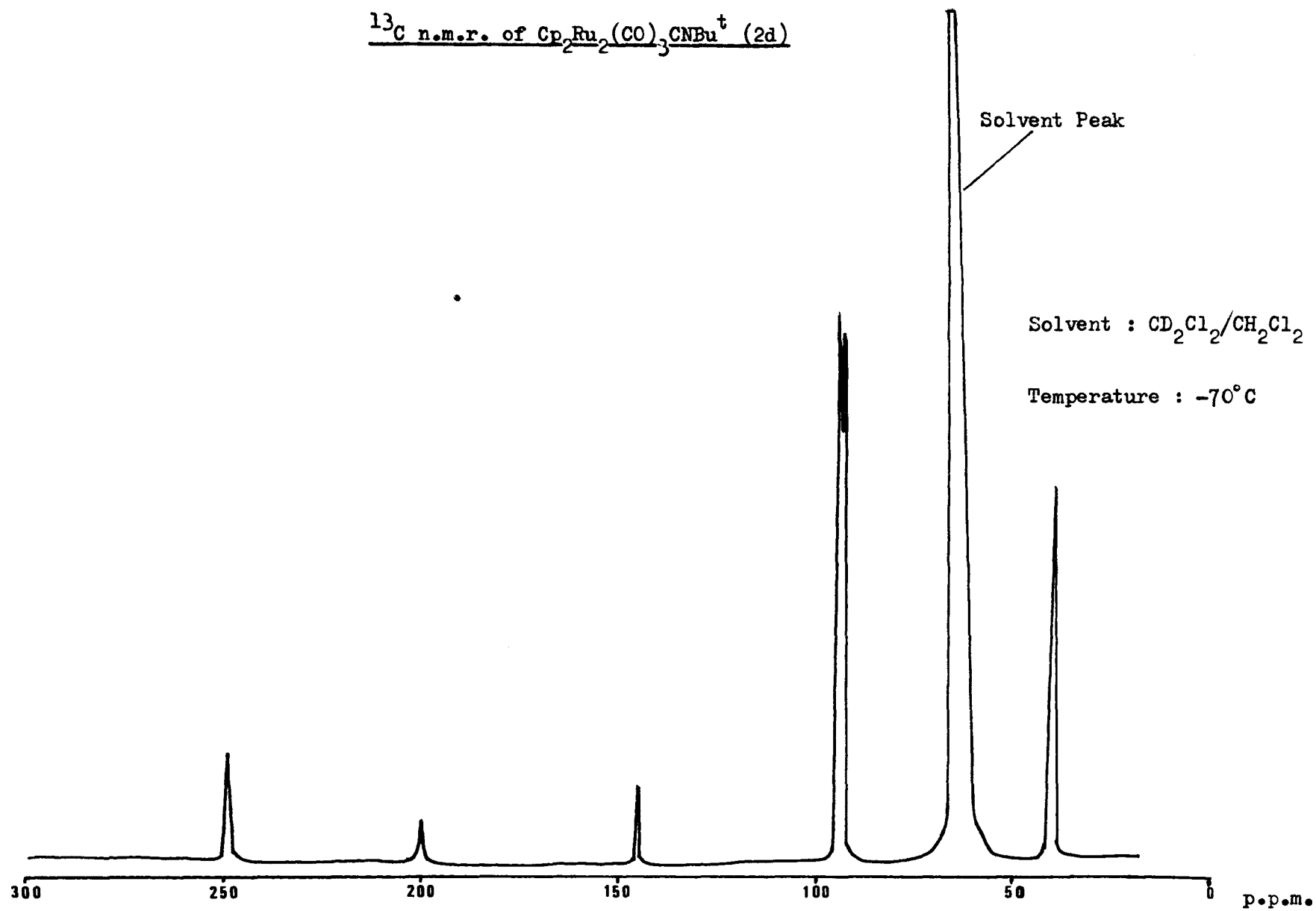


Figure 19

^{13}C n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{CNEt}$ (2b)

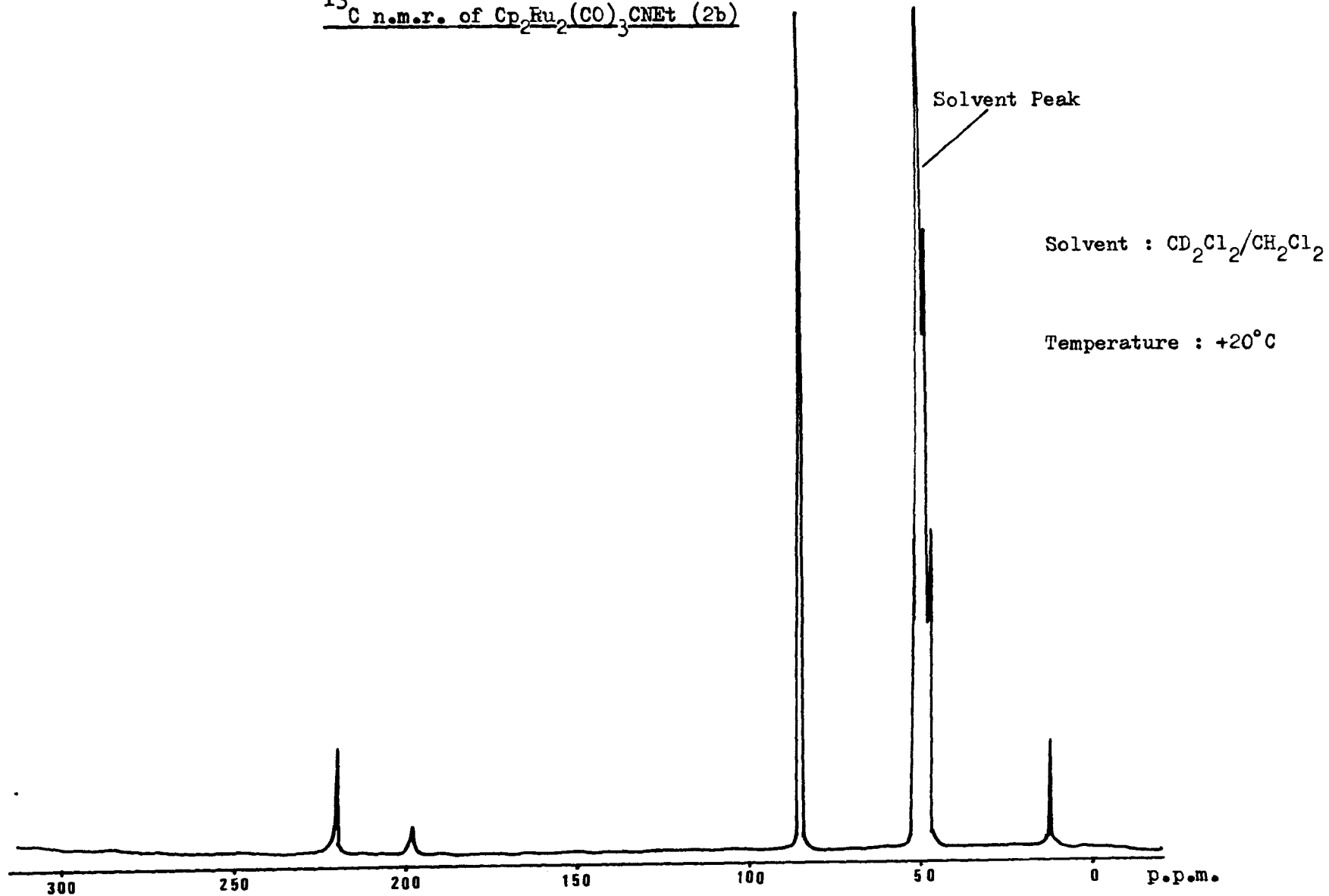


Figure 20

^1H n.m.r. of $[\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CN}(\text{Me})(\text{Et})]^+\text{PF}_6^-$ (6a)

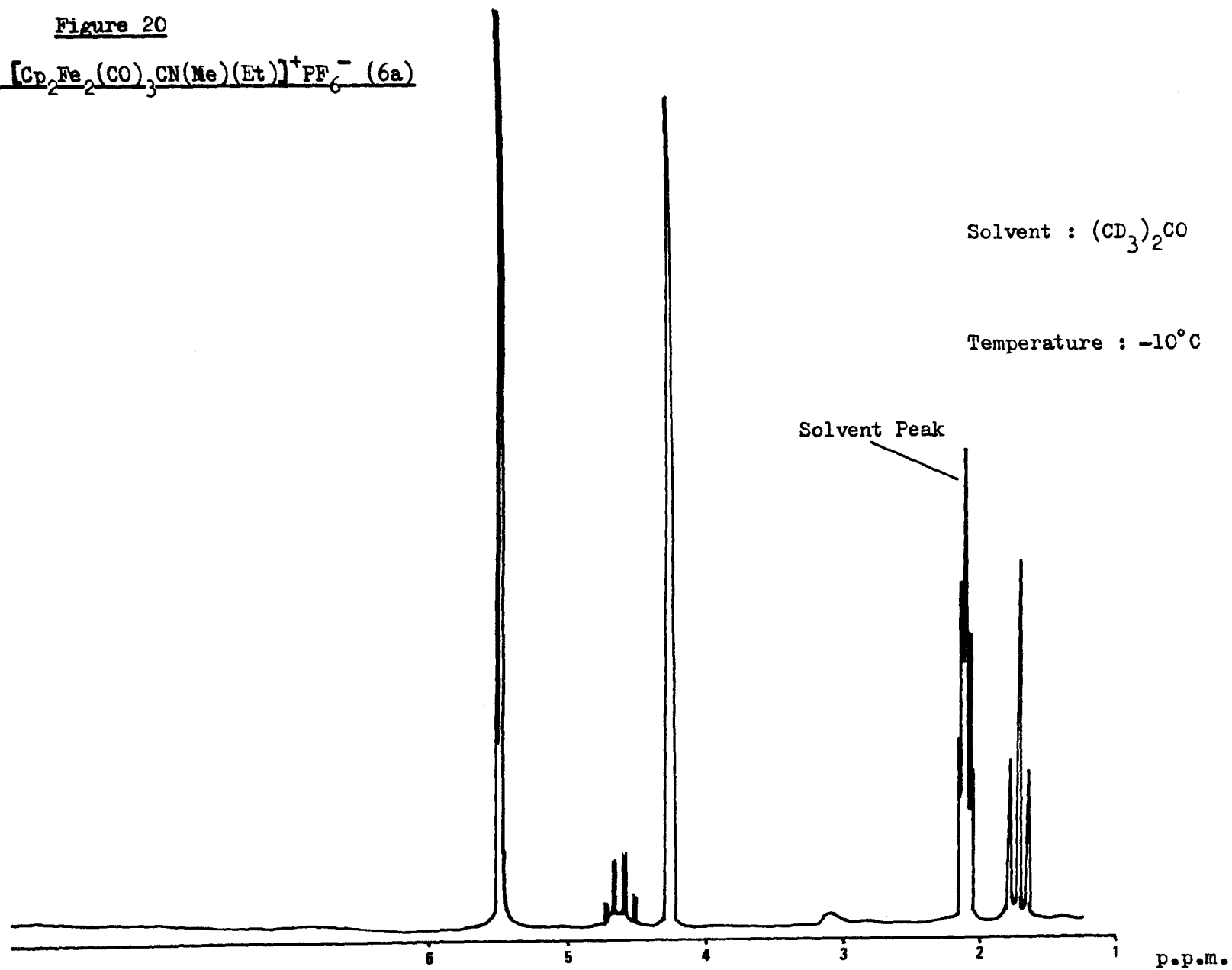
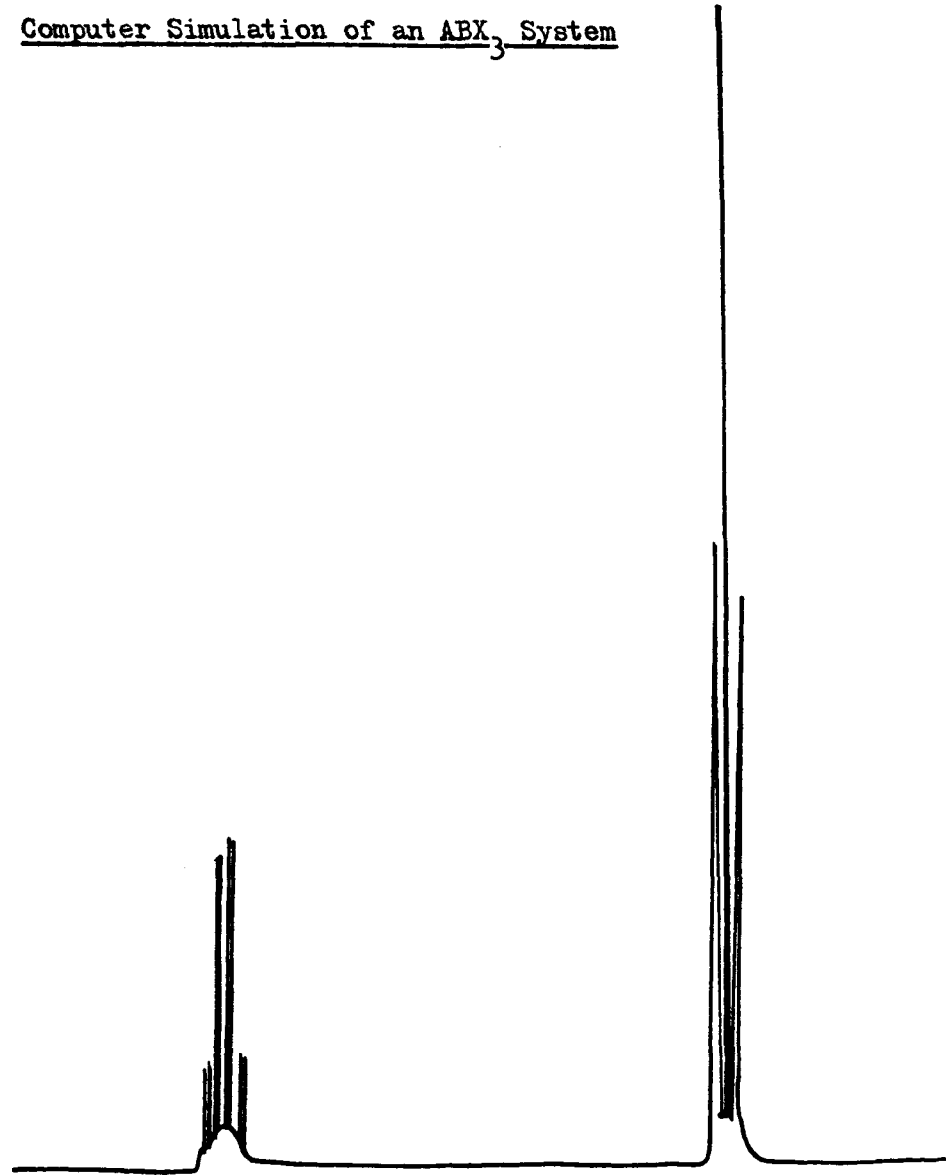


Figure 21

Computer Simulation of an ABX₃ System



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40. Calculated using T_c values of 283 and 218K for (1d) and (2d) respectively both in $CD_2Cl_2^*$
- 41.a. 1 cal = 4.184J.
- 41.b. Values for the two ΔG^\ddagger of 11.4 and 6.9 kcal mol⁻¹ may be calculated from the data of ref. 21 assuming T_c values of 273 and 193 K respectively. The ΔG value is a minimum difference since the coalescence temperature for the latter process is lower than 193K.*
42. An activation energy of 14.4 Kcal mol⁻¹ has been determined for this process in CS_2 solution (R.D. Adams, F.A. Cotton, and J.M. Troup, Inorg. Chem. (1974) 13, 257).

*

$$\Delta G^* = 2.303 RT_c \text{ Log } \frac{kT_c}{\pi h \Delta w}$$

k = Boltzmann constant.

h = Planck constant.

Δw = Chemical shift difference (Hz).

T_c = Coalescence temperature.

R = Gas constant.

CHAPTER 3

Complexes of the type $\text{Cp}_2\text{M}_2(\text{CO})_n(\text{CNR})_{4-n}$ ($\text{M} = \text{Ru}, \text{Fe}; n = 1 - 4$) are generally found as one isomer in the solid state,^{1 - 5} but as a interconverting equilibrium mixture in solution.^{6 - 9} In Chapter 2 the chemistry and fluxional processes of the monosubstituted dimers $\text{Cp}_2\text{M}_2(\text{CO})_3(\text{CNR})$ were studied, and in this particular case ($n = 3$). In this chapter the chemistry and fluxional processes of the di and trisubstituted complexes will be discussed, and in these cases $n = 2$ and 1 respectively.

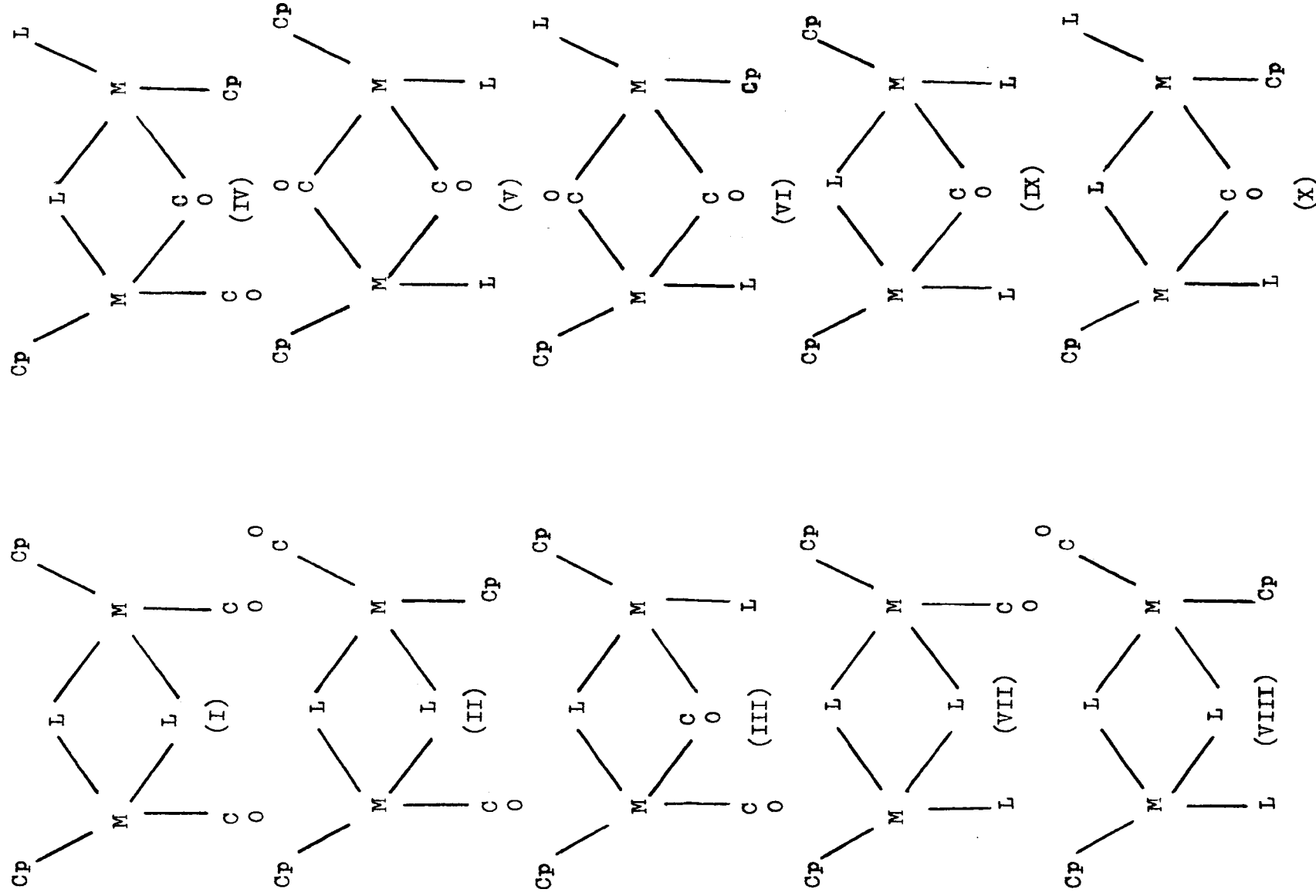
The solid state structure of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNMe})_2$ ¹ and $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNPh})_2$ ³ have been determined by x-ray crystallography. The fluxional processes of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNMe})_2$ (1a) and $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNMe})_3$ ^{6,7} (3a) have been studied previously. These results are now extended to include the complexes $\text{Cp}_2\text{M}_2(\text{CO})_2(\text{CNR})_2$ [$\text{M} = \text{Fe}; \text{R} = \text{Et}, \text{Pr}^i, \text{Bu}^t$ ⁹, (1b - 1d); $\text{M} = \text{Ru}; \text{R} = \text{Pr}^i$, (2) and $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNR})_3$ $\text{R} = \text{Et}, \text{Pr}^i$, (3b, c)].

The complexes (1a) - (1c), (3a) - (3c) were prepared by the reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ with excess isonitrile in refluxing benzene. Yields of the complexes were variable, dependent upon the molar excess of isonitrile, the isonitrile, and the duration of the reaction. Prolonged reaction results in increased decomposition of the products and isonitrile; thus the reactions were followed by infrared spectroscopy in order to obtain optimal yields of products. Complex (2) was prepared by the reaction of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ with excess isonitrile in refluxing xylene. Analytical data are given in Table 1.

Infrared spectra are presented in Table 2. Since isonitriles may function as bridging or terminal ligands, the six structural isomers (I) - (VI) are possible in principle for the complexes (1a) - (1d) and (2), while the four isomeric forms (VII) - (X) are possible for the complexes (3a) - (3c).

Infrared spectra of the complexes (1a) - (1c) and (2) in solution generally show five absorption bands in the region $1600 - 2200 \text{ cm}^{-1}$. Band (A) is attributed to the $\nu(\mu\text{CN})$, band (B) to $\nu(\mu\text{CO})$, band (B) to $\nu(\mu\text{CO})$, band (C)

Isomers of $\text{Cp}_2\text{M}_2(\text{CO})_2(\text{CNR})_2$ and $\text{Cp}_2\text{M}_2(\text{CO})(\text{CNR})_3$.



and (D) to $\nu(\text{Cot})$ and band (E) to $\nu(\text{Cnt})$ vibrations. With the exception of (B) and (D), absorption bands are not simple and clearly contain more than one component. Band (A) is broad and asymmetric with an envelope that varies with R. Band (C) is resolved into two or three well defined components for (1a) - (1c) and (2). Band (E) is very broad and asymmetric. For (1b) and (1c) a second resolved peak at lower frequency is present. These peaks appear genuine but the spectra of (1b) and (1c) also show a band at ca. 1725cm^{-1} which cannot be removed (eg by chromatography) but its intensity varies between different samples, and is thought to be due to an impurity.¹² There is no evidence in the spectra for detectable concentrations of non-bridged isomers.

It is well established that bridging isonitriles form a non-linear linkage. The $\hat{\text{CNR}}$ angle is found to be ca. 130° and the CNR group lies approximately in the Fe_2C , plane.³ Therefore there are two geometric isomers for each of (I) - (IV), which depend on the orientation of the μR group.

The absence of bands (B) and (E) in the spectrum of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNPh})_2$ indicates that this complex exists solely as a mixture of (I) and (II) in solution.¹¹ From the relative intensities of bands (C) and (D) a cis/trans ratio of 59:41 may be calculated.¹⁷ Analogous values for the $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNPh})$ complex, which exists solely as the $\mu\text{-CNR}$ isomer, and $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ of 49:51 and 43:57 respectively in CS_2 indicate an increasing proportion of cis isomer with increasing isonitrile substitution. For the complexes (1a) - (1c) and (2) the appearance of band (E) indicates the presence of isomers (III) and (IV). For (1d) only isomers (III) - (VI) are present as evidenced by the lack of band (D) and the presence of the (μCO) - at 1750cm^{-1} due to (V/VI). Only for (1d) can the isomers (V/VI) be detected in the infrared in significant concentration, and consistent with this, two (Cnt) absorption bands are observed. Although calculation of the (V/VI) ratio from these bands is not possible due to broadness, and a contribution from isomers (III) and (IV), n.m.r. results show that the cis/trans ratio in CH_2Cl_2 at -80°C is 66:33.⁹

Spectra of the other complexes are consistent with the proportion of (III/IV) increasing in the order Me, Et, Prⁱ .

Band (C) clearly consists of two components (1a) - (1c) , while band (E) is asymmetric and may actually be resolved into two components (1b), (1c) . This may be due to either

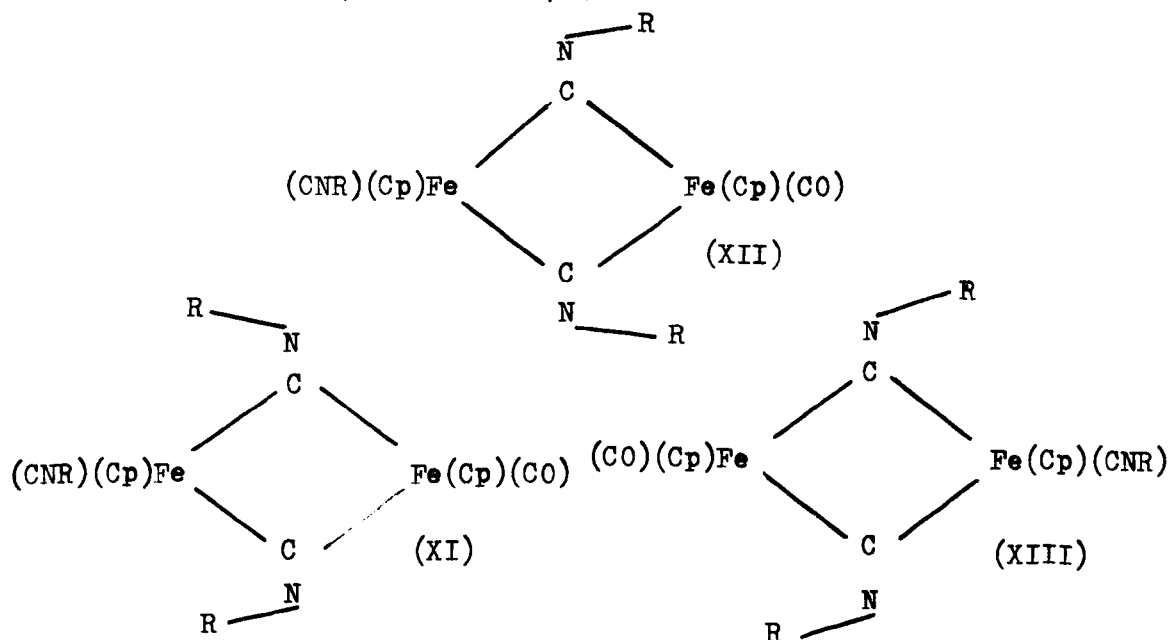
- (a) the resolution of the $\nu(\text{CO})$ absorption band of (III) from that of (IV) or
- (b) resolution of the (Cot) bands of the two forms of either (II) or (IV) (with one isomer being absent) or
- (c) a mixture (III) and (IV) in which the bands are coincident.

If (b) is correct, one might expect that the two forms of (I) would also have different (Cot) frequencies and that band (D) would have two resolvable components separated by an amount comparable to the splitting in (C) (ie, ca. 10 cm^{-1}). This is not observed, and while it is possible that only one form of (I) is present in solution, n.m.r. results on (2) indicates that both forms are present.

As with the mono-substituted complexes $\text{Cp}_2\text{Fe}_2(\text{CO})_3 (\text{CNR})^{10}$ an increase in bulk or electron denoting ability of the R group in the isonitrile results in site preference. Thus for the complex (1e) only (I) and (II) are present in solution, while for the complexes (1a) - (1d) increasing preference for terminal co-ordination is observed for the isonitrile. Comparison of (1c) with (2) shows that the proportion of isomers (I/II) in solution is greater for the ruthenium complex. A similar trend was observed in the $\text{Cp}_2\text{M}_2(\text{CO})_3 (\text{CNR})$ (M=Fe,Ru) series.¹⁰

The infrared spectra of the complexes (3a) - (3c) (Table 2) show only $\nu(\text{CNT})$, $\nu(\text{Cot})$ and $\nu(\mu\text{CN})$ absorptions, indicating that only isomers (VII/VIII) are present in solution. Both the (CNT) and (μCN) bands are broad, but the presence of more than one component is apparent, particularly in the Et and Prⁱ derivatives. A band of varying intensity at ca. 1725 cm^{-1} is also observed and is attributed to an impurity. The $\nu(\text{Cot})$ band is clearly

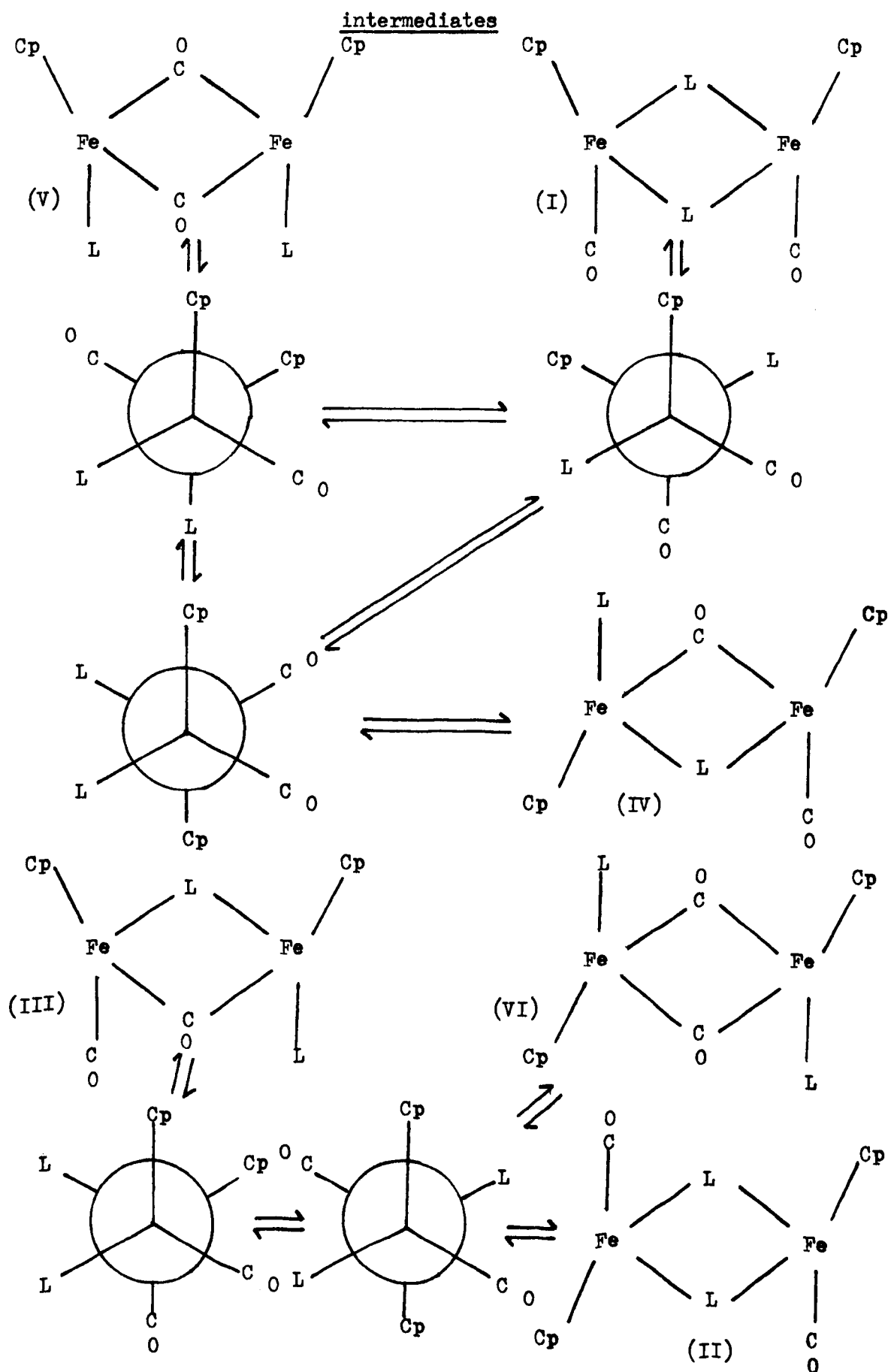
resolved into three components. The most likely explanation would seem to be resolution of the three isomeric forms (XI) - (XIII), shown in figure (2) below, as the relative intensities of the bands roughly parallel the distribution of (XI) - (XIII) determined by n.m.r. Either resolution of (VII) from (VIII) does not occur, or only one isomer is present in solution. In the spectrum of (3c), a weak band at 2044 cm^{-1} may be attributed to the (C≡N) band of (IX/X).



^1H and ^{13}C n.m.r. spectral data for the series of compounds (1a) - (1d) and (2) are summarised in tables (3) and (4). N.m.r. data for the complexes (1a),^{6,7} and (1d)⁹ have previously been reported. In terms of exchange between isomers (I) - (VI) limiting low temperature spectra are obtained at ca. -10°C for the iron complexes and -30°C for the ruthenium complex. With the exception of (1d), resonances due to cis or trans forms are not resolved (if indeed both are present in CH_2Cl_2 at low temperature). The limiting low temperature ^1H n.m.r. spectra of the complexes (1a)-(1c) and (2) are shown in figures (1 - 4) respectively. From integrations of the peaks assigned as shown a ratio of (I/II) to (III/IV) can be obtained. As (III/IV) are inherently chiral, the Pr^i and Et resonances of (1c), (1b) and (2) exhibit diastereotopic methyl and methylene protons. In addition a small resonance at ca. 4.45 δ is observed for all the iron

SCHEME 1

Isomer interconversion for the compounds (I - VI) involving symmetrical



L = Isonitrile.

complexes, The chemical shift by comparison with (1d) and lack of temperature dependent behaviour at lower temperature is consistent with an assignment to the equivalent cyclopentadienyl protons of (V/VI), but because of the low intensity (less than 5% of the integrated intensity), an impurity may be responsible. Warming to + 80°C in d⁸ - toluene results in coalescence to yield cp and alkyl resonances indicative of both isomer interconversion and bridge - terminal isonitrile exchange.

This interconversion is thought to proceed via non-bridged intermediates, and has been discussed in detail by Adams and Cotton.⁶ If the mechanism is restricted to symmetrical non-bridged intermediates of the type Cp (CO)(CNR) M - M (CO)(CNR)Cp then

- (a). The six isomers (I) - (VI) are divided into two groups [(I)(IV)(V)] and [(II)(III)(VI)]. Scheme (1) shows the interconversions of isomers within the two separate groups.
- (b). Interconversion of isomers within a group is possible via a bridge opening and closing mechanism.
- (c). It is not possible for the two groups to interconvert.

Following this argument we may say that if the single cp resonance at ca 4.8δ in the ¹H n.m.r. spectra of (1a) - (1c) is due to isomer (I), then it follows that the cp signals at ca. 4.7 and 4.5δ for the complexes (1a) - (1c) are due to isomer (IV), and the only other isomer likely to be present is (V). Since separate cp signals are not observed for (cis/trans) isomers, in the ¹H n.m.r. spectra of the complexes (1a) - (1c) and (2) this may indeed be the case.

However study of the interconversion processes for (1d)⁹ indicate that the formation of only symmetrically substituted intermediates seems unjustified.

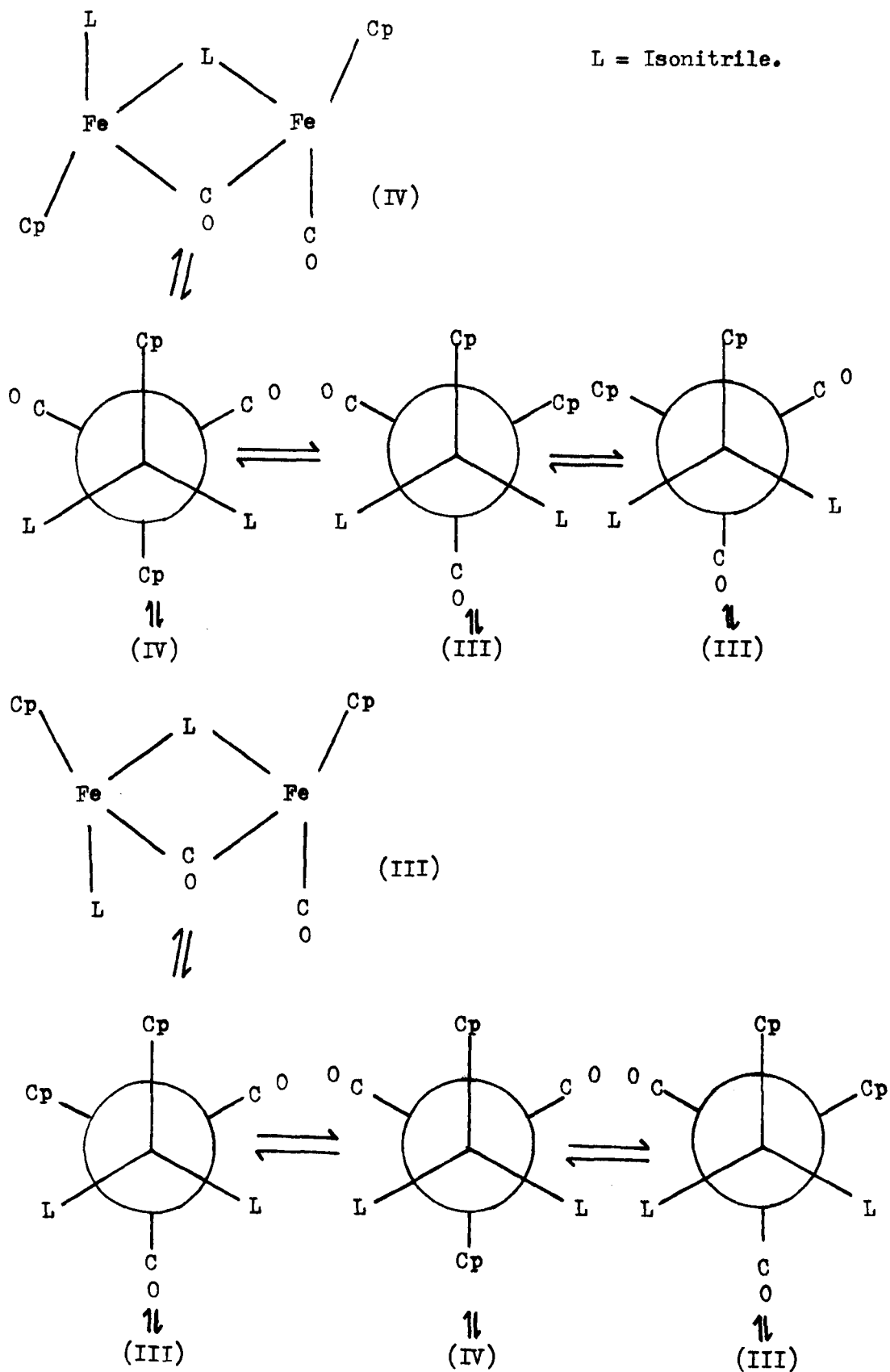
Consideration of the

variable temperature spectra show that two fluxional processes are occurring

- (a). at lower temperature, both bridge - terminal isonitrile and

SCHEME 2

Isomer interconversion for the compounds (I - VI) involving unsymmetrical intermediates.



most probably cyclopentadienyl site exchange in the resonances attributed to (IV). accompanied by interconversion with the cis isomer (V) only, and

- (b). at higher temperature, a cis - trans interconversion of (V) and (VI), which eventually yields the high temperature limiting spectrum at + 60°C.

The behaviour in (a) may be explained by the process outlined above in which only symmetrically substituted intermediates are involved.

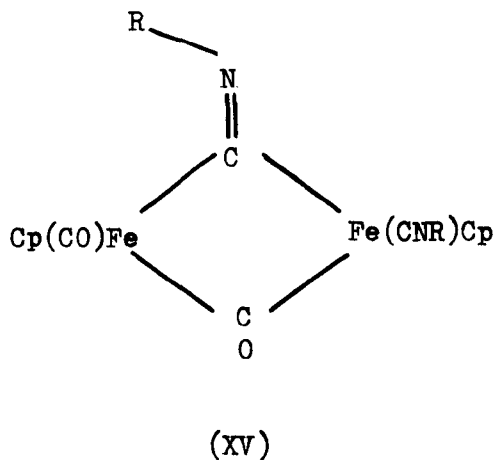
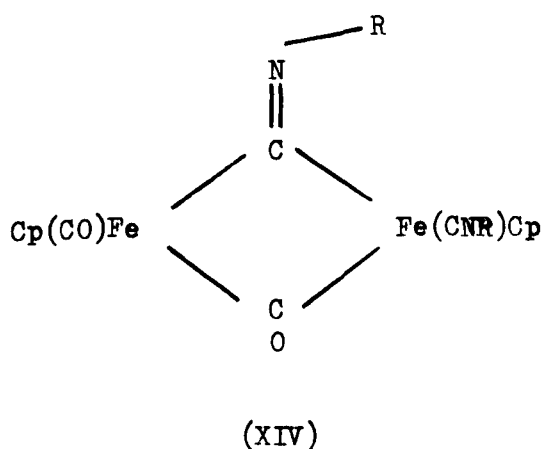
Scheme (1) cannot account for (V) \rightleftharpoons (VI) interconversion observed at higher temperature. This type of interconversion may be facilitated by an asymmetrically substituted intermediate of the type $\text{Cp}(\text{CO})_2 \text{Fe}-\text{Fe}(\text{CNBu}^t)_2 \text{Cp}$.

Scheme (2) illustrates that bridge-opening in this fashion results only in equilibration between (III) and (IV). However since (V) \rightleftharpoons (IV) and (VI) \rightleftharpoons (III) from consideration of scheme 1, it follows that interconversion of (V) and (VI) occurs, even though no concentration of (III) may actually be detected. Thus Scheme (2) provides a pathway for the linking of the two closed sets of Scheme 1.

The higher activation energy observed for (V) \rightleftharpoons (VI) interconversion may perhaps be a consequence of the greater strain introduced on bridge opening to yield an intermediate in which two sterically demanding CNBu^t ligands are bonded to one iron atom.

On cooling below -10°C, further changes consistent with the slowing down of nitrogen inversion occur. Figure (5) shows the effect of cooling on the spectrum of (1c) in the cyclopentadienyl region. At -90°C the resonances due to (III)/(IV) have now split into two unequal pairs in a ratio 2.5:1 assignable to the isomers (XIV) and (XV) having the two possible orientations of the alkyl group. an unambiguous assignment is not possible, although on steric grounds it seems likely that the most abundant isomer is (XV), the structure adopted in the solid state.¹² Within experimental error the same (XIV:XV) ratio is maintained for the complexes (1a), (1b) and (2). Figure (6) shows the temperature dependence of (2) between - 30°C and -90°C. At

- 60°C (2) exhibits a spectrum similar to (1c) at - 80°C. The broadness of resonance assigned to (I)/(II) at - 80°C for (1c) implies that nitrogen inversion is freezing out, and this resonance may actually be resolved into its components at - 80°C in the case of the ruthenium complex (Fig 6). While the resonances overlap somewhat, the results indicate a greater abundance of (XVI) over (XVII),



Both (1a)¹ and (1d)³ are known to adopt the structure (XVI) in the solid state. In common with the $\text{Cp}_2\text{M}_2(\text{CO})_3(\text{CNR})$ series ($\text{M}=\text{Fe}, \text{Ru}$), the ruthenium complexes exhibit a lower activation energy for isomer interconversion, but a higher activation energy for nitrogen inversion. The differences in activation energy for this process between the ruthenium and iron complexes has been described in Chapter 2. It would seem that either the $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNR})_2$ complexes are more energetically stable than the ruthenium complex, and/or the intermediate in which the nitrogen is sp^2 hybridised, is more stable in the $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNR})_2$ complexes than in the ruthenium complex.

The low temperature limiting ^{13}C spectra of the complexes (1a) - (1c), (2) are shown in figures (7) - (10). The ^{13}C spectrum of (1c) at - 80°C is shown in figure (11) and is consistent with the results obtained from the ^1H n.m.r. results. Assignments given in table (4) are based on chemical shifts and intensities. In particular the resolution of (μCN) and (Cot) resonances

associated with isomers (XIV) and (XV) may be noted in a ratio consistent with ^1H results. A similar splitting of the cp resonances into two unequal pairs is also found. On warming to -10°C the COt and μCN resonances coalesce to single peaks, while at room temperature, significant broadening of all resonances is observed, consistent with both CO and CNR bridge-terminal exchange.

^1H and ^{13}C spectral data for the complexes (3a) - (3c) are given in tables (3) and (4). Spectra at room temperature show the two cyclopentadienyl resonances expected for a (VII/VIII) mixture. For all complexes a small resonance at 4.44 δ is observed which may be assigned to a small amount of isomers (IX/X) in view of the behaviour at lower temperatures. On warming to 100°C in d^8 -toluene, only a slight broadening of resonances occurs. The activation energy for bridge-terminal exchange thus increases with increasing isonitrile substitution. The room temperature ^1H n.m.r. spectra of the complexes (3a) - (3c) are shown in figures (12) - (14), and figure (15) shows the temperature dependence of (3c) down to -80°C in the cyclopentadienyl region. On cooling to -80°C , the pair of cyclopentadienyl resonances broadens and reforms as three pairs of resonances of unequal intensity in the ratio 10:6:1.5 consistent with the three possible isomeric forms (XI) - (XIII). The complexes (3a) and (3b) behave similarly in this region. Previous results on (3a) found only two pairs of resonances, although the presence of the third was inferred from the difficulty in the fitting of simulated spectra to experimental spectra.

The ^1H n.m.r. temperature dependence of the methyl resonances of (3a) is shown in figure 16. At -90°C only three of the expected four bridging methyl resonances are observed. The fourth probably lies under these resonances, and will be due to the most minor isomer. Only one resonance of a possible three is observed in the terminal methyl region of the spectrum. At -90°C the peak is broad and assymetric and signals due to the three geometric isomers are probably coincident. The methyl resonances, due to bridging isonitrile, at 3.63 δ and 3.54 δ , together with one of the methyl resonances,

due to terminal isonitrile at 2.85 δ are due to the anti isomer (XII) (addition of polar solvent reduces the size of the bridging methyl peaks).⁷ The remaining methyl resonance, due to bridging isonitrile, at 3.57 δ and the remaining methyl resonance, due to terminal isonitrile, at 2.85 δ can be assigned to one of the two syn forms (XI) or (XIII). There is no basis to determine which one, although (XI) offers the least steric hindrance.

The resonance associated with (IX/X) also broadens on cooling to - 80°C and reforms as two resonances of approximately equal intensity. At room temperature rapid nitrogen inversion in the single possible isomer would result in equilibration of the cyclopentadienyl resonances.

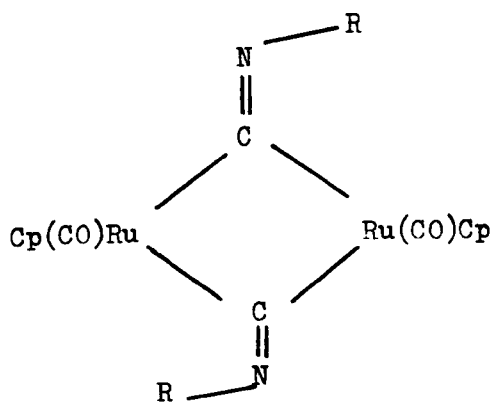
The ¹³C n.m.r spectra of the complexes (3a) - (3c) are shown in figures (17 - 19). The ¹³C spectrum of (3c) at - 80°C, shown in figure (20) is consistent with the ¹H n.m.r. results. Again the resolution of the μ CN resonance may be observed although only two of the four expected resonances are observed, probably due to coincidence of signals. At room temperature, a single resonance is found.

The adoption of the (VII/VIII) structure irrespective of the alkyl group (R) seems surprising in view of the results obtained on the mono and di-substituted derivatives. The trend usually seen is an increase of terminally co-ordinated isonitrile with increasing size of the alkyl group (R) attached to the isonitrile.

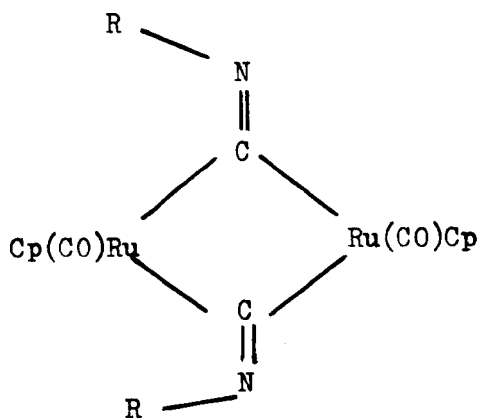
Table (5) shows the mass spectral data for the complexes (1a) - (1c) and (2). Again it can be seen, as with the $\text{Cp}_2\text{M}_2(\text{CO})_3(\text{CNR})$ complexes, that there is preferential loss of CO as compared to isonitrile. The presence of the $[\text{CpM}(\text{CNR})_2]^+$ ion indicates cleavage of a dimetal ion leaving the two isonitrile groups on one of the metal fragments. Besides CO and CNR losses the presence of the $[\text{M}(\text{CNR})_2]^+$ fragment indicates cyclopentadienyl loss.

The reaction between $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNR})$ (R = Me, Et, Prⁱ) and iodine yields almost quantitatively $\text{CpFe}(\text{CO})(\text{CNR})\text{I}$. This indicates preferential cleavage of a (III/IV) isomer to yield the observed product. It might be expected

that (1c) would yield the greatest proportion of the disubstituted iodide $\text{CpFe(CNR)}_2\text{I}$, but none was recovered from the reaction,



(XVI)



(XVII)

Experimental

The isonitriles ^{14,15} and $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ ¹⁶ were prepared by literature methods. Other chemicals were purchased. Reactions were carried out under nitrogen in purified solvents.

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer using 1.00mm NaCl cells. Proton and ¹³C n.m.r. spectra were obtained using a JEOL FX-100 spectrometer, ¹³C spectra in the presence of $\text{Cr}(\text{acac})_3$ (acac = acetylacetonate) as relaxation agent. Mass spectra were recorded on a AEI MS/12.

Preparation

- (a) $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNEt})_2$. The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (3.54g 10mmols) and ethyl isocyanide (2.0g, 30mmols) were stirred in refluxing benzene (100ml), and progress of the reaction was followed by infrared spectroscopy. When the reaction was complete solvent was removed under reduced pressure and the residue chromatographed on grade (1V) alumina using dichloromethane/petroleum ether (40/60) as eluent. The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNR})$ was eluted first followed by the product as a purple band. Recrystallisation from dichloromethane/petroleum ether (40/60) afforded (1.1g) of deep purple crystals. A third purple band was eluted by dichloromethane to give the trisubstituted complex $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNEt})_3$, which when recrystallised from dichloromethane/petroleum ether gave (400mg) of dark purple crystals. The complexes (1a) and (1c); (3a) and (3c) were prepared similarly. Complex (2) was prepared similarly using refluxing xylene in place of benzene.

TABLE 1
Analytical Data (%)

<u>Compound</u>	<u>Found</u>			<u>Calculated</u>		
	<u>C</u>	<u>H</u>	<u>N</u>	<u>C</u>	<u>H</u>	<u>N</u>
(1a)	50.5	4.21	7.37	50.5	4.13	7.20
(1b)	52.9	4.93	7.16	52.9	4.90	6.86
(1c)	54.4	5.45	6.50	55.0	5.50	6.42
(2)	45.8	4.53	5.51	45.6	4.56	5.32
(3a)	52.2	4.77	10.6	51.9	4.83	10.7
(3b)	55.1	5.46	10.2	55.2	5.75	9.66
(3c)	58.2	6.75	8.99	57.9	6.52	8.81

TABLE 2
Infrared Spectral Data^a

<u>Compound</u>	<u>Band</u>				
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
(1a)	1720 (7.1)	1784 (3.5)	1944 (5.1)	1990 (10.0)	2127 (1.2)
			1955 (4.4)		
(1b)	1697 (6.4)	1786 (7.9)	1944 (9.3)	1990 (10.0)	2128 (3.3)
			1954 (7.8)		2103 (3.2)
(1c)	1697 (9.4)	1784 (9.0)	1942 (10)	1986 (7.8)	2106 (4.5)
			1954 (6.9)		2046 (0.9)
(1d)*	1683 (9.0)	-	1945 (7.0)	1985 (10)	-
(1e) ⁺	1715 (2.6)	1750 (10)	1935 (5.0)	-	2050 (3.3)
		1779 (3.0)	1945 (4.3)		2099 (sh)
(2)	1694 (7.8)	1786 (1.8)	1955 (4.2)	1992 (10.0)	2166 (0.4)
(3a)	1702 (10.0)	-	1954 (3.5)	-	2120 (4.0)
(3b)	1678 (10.0)	-	1958 (4.6)	-	2115 (sh)
	1686 (sh)		1941 (9.6)		2095 (4.9)
			1930 (7.0)		
(3c)	1682 (10.0)	-	1950 (sh)	-	2145 (2.7)
	1686 (sh)		1940 (8.9)		2104 (sh)
			1930 (6.6)		2044 (sh)

^a in hexane solution; values in cm^{-1} with relative intensities in parentheses.

* (1d) = $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNPh})_2$, solvent CS_2 , ref (11)

⁺ (1e) = $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNBu}^t)_2$, ref (9)

TABLE 3

¹H n.m.r. Spectral Data^a

<u>Complex</u>	<u>Temperature</u>	<u>Isomer</u>	<u>Cp</u>	<u>μCH₃</u>	<u>tCH₃</u>	<u>CH₂</u>	<u>CH</u>	<u>Ratio</u> (<u>I + II/III + IV</u>)
(1a)	-10	(I/II)	4.84	3.61 (s)				
		(III/IV)	4.71	3.67 (s)	2.89 (s)			3.5 : 10
			4.50					
		(V/VI)	4.44		2.95 (s)			
(1b)	-10	(I/II)	4.82	1.36 (t,7.3)		3.92 (m) ^c		
		(III/IV)	4.71	1.38 (t,7.2)	0.99 (t,7.1)	3.92 (m) ^c		1.5 : 10
			4.56			3.18 (q) ^d		
		(V/VI)	4.45					
(1c)	-10	(I/II)	4.8	b			3.95 (sept)	
		(III/IV)	4.70	1.40	1.01	3.92 (sept) ^c		0.6 : 10
			4.53	1.34	0.99	3.50 (sept) ^d		
		(V/VI)	4.44					
(2)	-40	(I/II)	5.29	1.18 (d,6.3)		3.36 sept) ^c		
		(III/IV)	5.21	1.21 (d,6.4)	1.07	3.68 (sept) ^e		
			5.06		1.09			

Continued over.....

TABLE 3 Continued

<u>Complex</u>	<u>Temperature</u>	<u>Isomer</u>	<u>Cp</u>	<u>μCH₃</u>	<u>tCH₃</u>	<u>CH₂</u>	<u>CH</u>	<u>Ratio</u> (I + II/III + IV)
(3a)	0	(VII/VIII)	4.58 } 4.76 }	3.68	2.88			
		(IX/X)	4.53					
(3b)	0	(VII/VIII)	4.51 } 4.71 }	1.36 (t, 6.7)	0.97 (t, 7.4)	3.90 (m) ^c		
		(IX/X)	4.51			3.15 (q) ^d		
(3c)	0	(VII/VIII)	4.55	1.29 } 1.36 } (d, 6.5)	0.96 (d, 6.5)		3.94 (sept) ^c	
		(IX/X)	4.45				3.49 (sept) ^d	

^a Chemical shifts (δ) from tetramethylsilane in CD₂Cl₂ solvent; multiplicities and coupling constants in (Hz) given in parentheses. (s= singlet, d= doublet, t= triplet, q= quartet, sept= septet, μ = bridging, t= terminal).

^b Not detected.

^c Bridging.

^d Terminal.

^e Terminal CH not detected.

TABLE 4

 ^{13}C Spectral Data^a

Complex	Isomer	CO_t	CN_t	CO_μ	CN_μ	Cp	μCH_3	$t\text{CH}_3$	μCH_2	$t\text{CH}_2$	μCH	$t\text{CH}$
(1a) ^b	(I/II)	211.0	-	-	248.5	84.5	45.2					
	(III/IV)	212.4	161.4	280.1	257.5	84.5	45.2	29.7				
						85.2						
(1b)	(I/II)	211.0	-	-	245.4	85.3	15.7		d			
	(III/IV)	212.4	161.4	280.0	254.0	84.3	16.1		d	38.7		
						85.0						
(1c)	(III/IV)	212.8	161.1	280.5	250.6	84.7	23.9	22.6			62.1	47.5
(2)	(I/II)	198.0	-	-	227.4	87.3	23.0	-			63.1	
	(III/IV)	200.7	142.2	252.8	221.2	86.3	23.0	21.7			63.1	46.6
						86.8						
(3a) ^b	(VII/VIII)	213.0	163.8	-	258.8	84.1	45.0	29.2				
						83.7						
(3b)	(VII/VIII)	213.7	165.2	-	255.9	84.7	16.5	15.0	d			
						84.2						
(3c)	(VII/VIII)	213.8	163.8	-	252.3	84.3	23.8	22.6			61.5	47.1
						84.1						

Table 4 continued.....

Table 4 continued

^a Chemical Shifts in p.p.m. from TMS.

^b Disubstituted complexes at -10°C ($\text{M} = \text{Fe}$) or -40°C ($\text{M} = \text{Ru}$), trisubstituted complexes at 0°C ($\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$)

^d Not detected; may be under solvent resonance at 53.8 p.p.m.

TABLE 5
Mass Spectral Data^a

<u>Probable Ion</u>	<u>Complex</u>			
	<u>(1a)</u>	<u>(1b)</u>	<u>(1c)</u>	<u>(2)^b</u>
$[\text{Cp}_2\text{M}_2(\text{CO})_2(\text{CNR})_2]^+$	380 (14)	408 (8)	436 (7)	530 (26)
$[\text{Cp}_2\text{M}_2(\text{CO})_2(\text{CNR})_2]^+$	352 (5)	380 (4)	408 (2)	502 (1)
$[\text{Cp}_2\text{M}_2(\text{CNR})_2]^+$	324 (8)	352 (4)	380 (4)	474 (18)
$[\text{Cp}_2\text{M}(\text{CNR})]^+$	283 (97)	297 (45)	311 (30)	405 (11)
$[\text{Cp}_2\text{M}_2(\text{CN})]^+$	268 (11)	268 (26)	268 (26)	362 (10)
$[\text{Cp}_2\text{M}_2]^+$	242 (11)	242 (26)	242 (23)	336 (25)
$[\text{Cp}_2\text{M}(\text{CNR})_2]^+$	203 (84)	233 (81)	259 (58)	305 (100)
$[\text{M}(\text{CNR})_2]^+$	138 (81)	166 (54)	194 (61)	240 (29)
$[\text{CpM}(\text{CNR})]^+$	162 (89)	176 (92)	190(100)	236 (32)
$[\text{Cp}_2\text{M}]^+$	187 (89)	187 (70)	187 (52)	232 (14)
$[\text{CpM}(\text{CO})]^+$	149 (13)	149 (11)	149 (70)	195 (15)
$[\text{CpM}]^+$	121 (100)	121 (100)	121 (95)	167 (32)

^a Intensities given in parentheses.

^b ^{102}Ru isotope used in mass spectral data.

Figure 1

^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNMe})_2$ (1a)

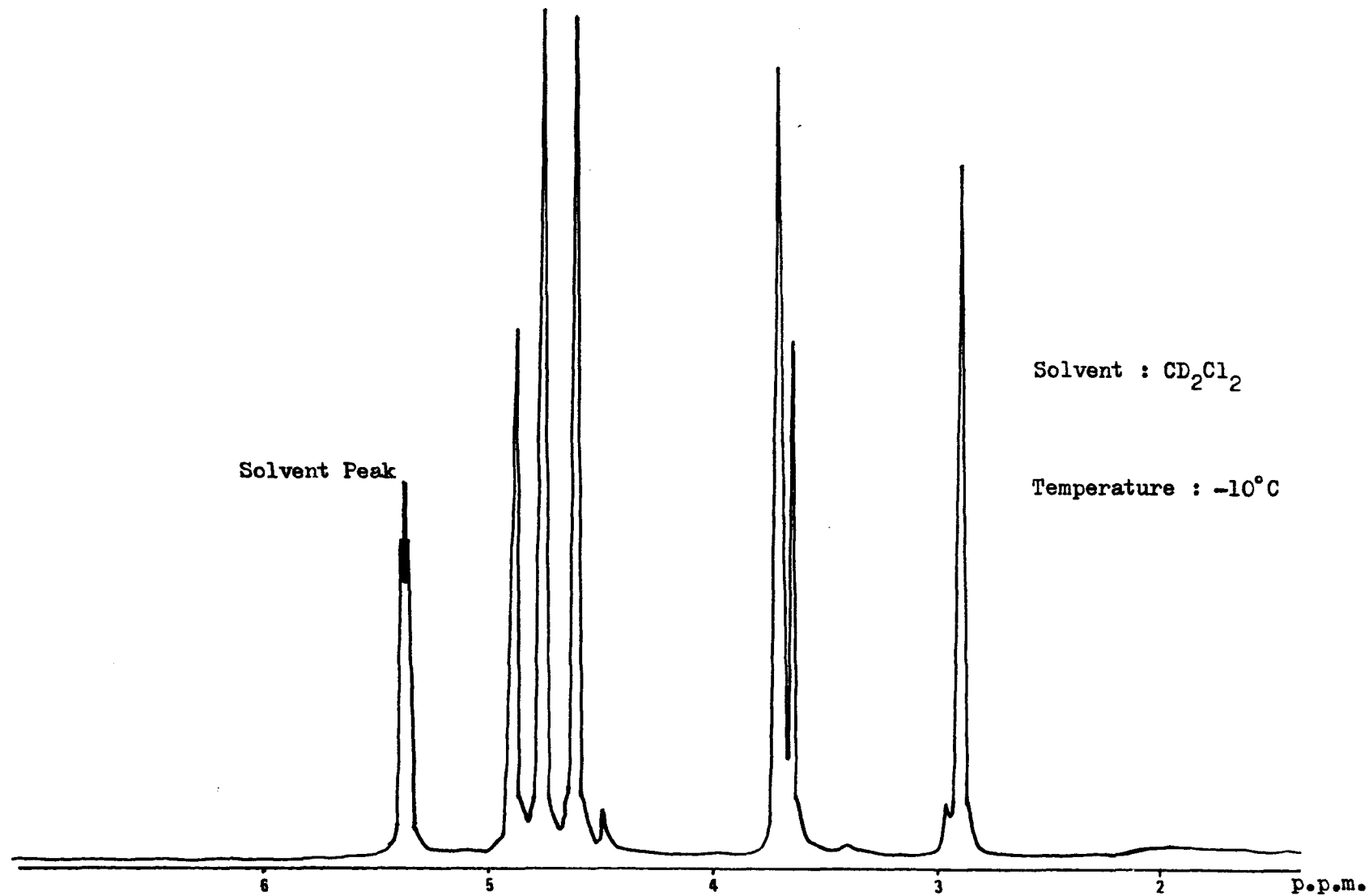
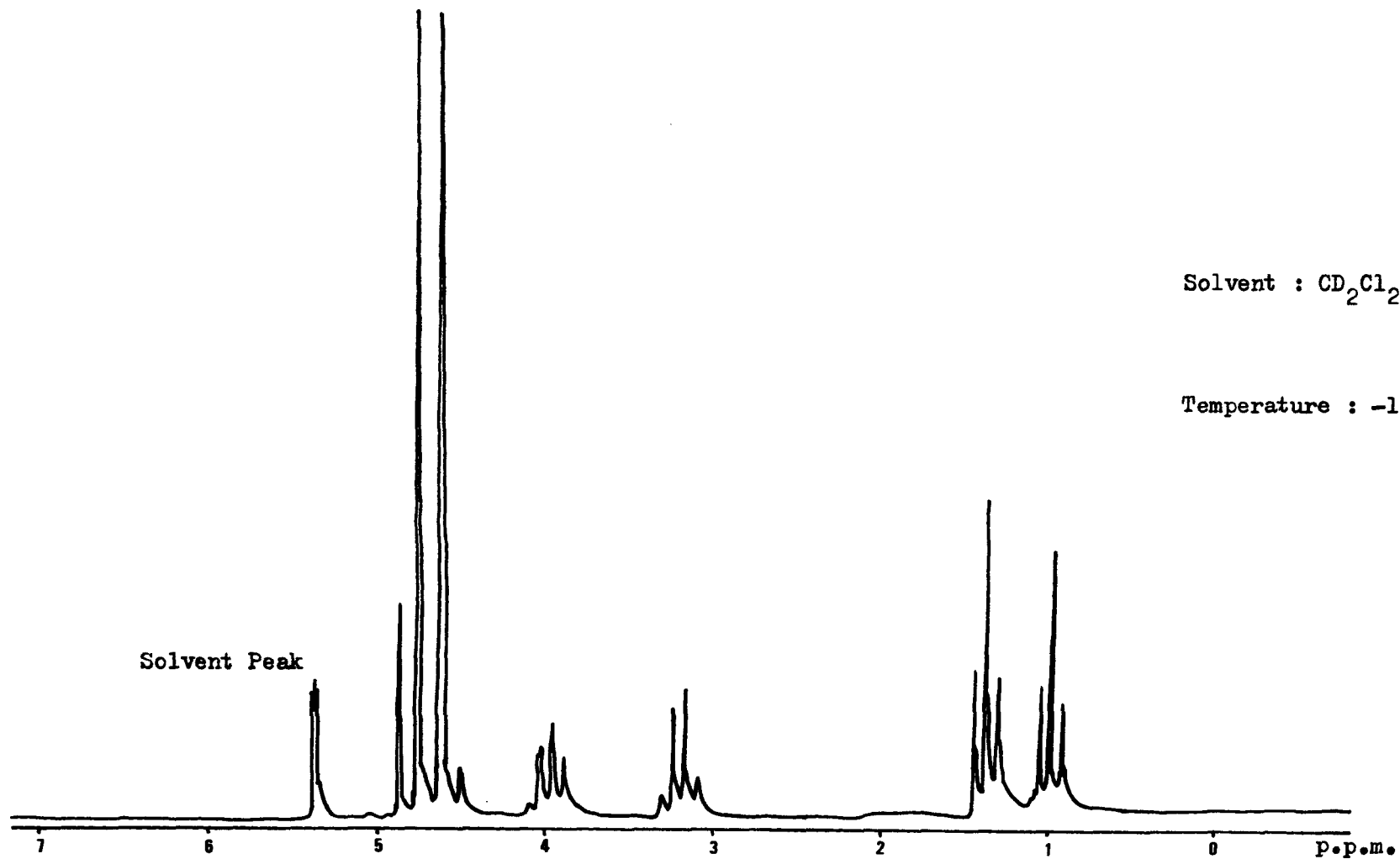


Figure 2

^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNEt})_2$ (1b)



Solvent : CD_2Cl_2

Temperature : -10°C

Solvent Peak

Figure 3

^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNPr}^i)_2$ (1c)

Solvent : CD_2Cl_2

Temperature : -10°C

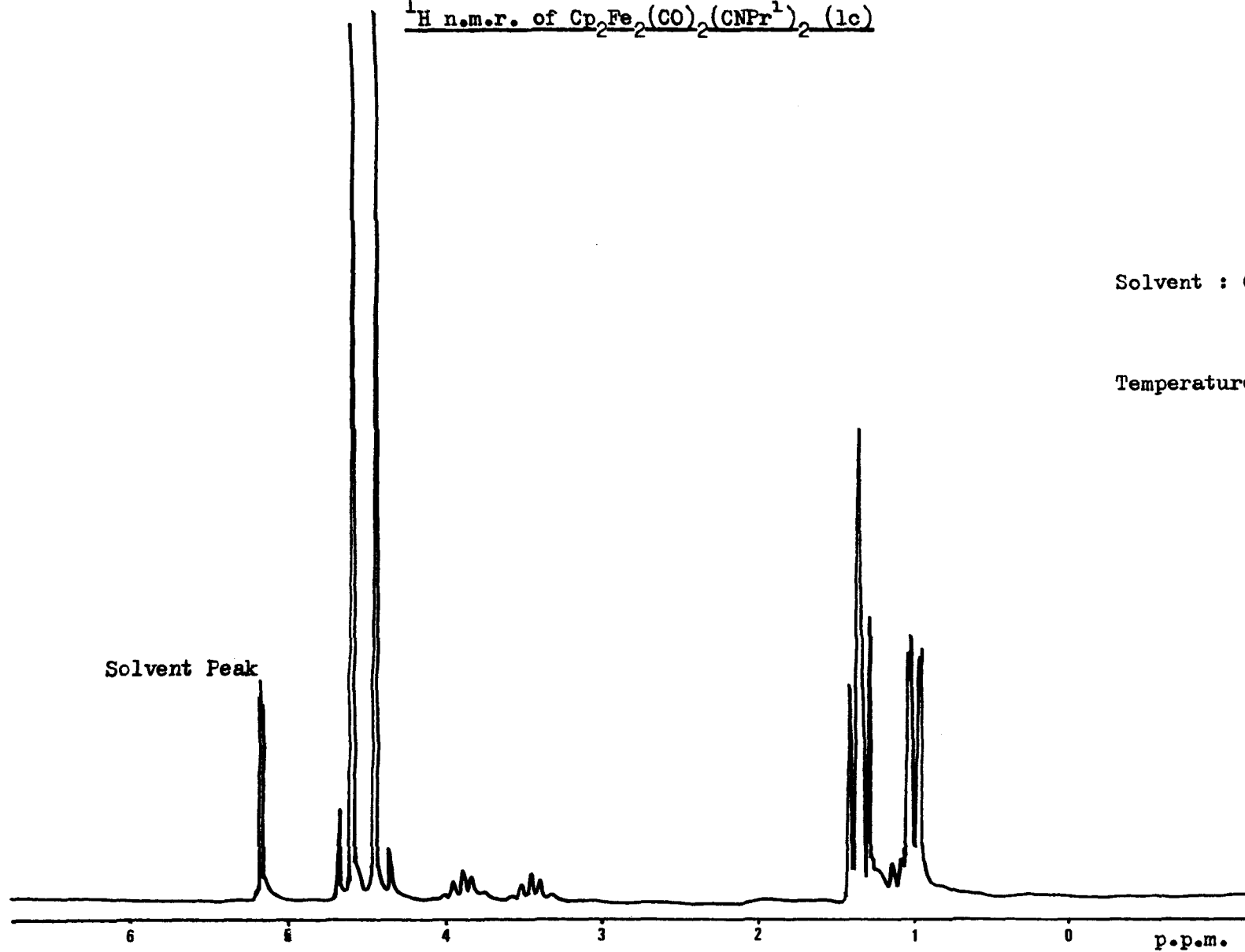


Figure 4

^1H n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{CNPr}^i)_2$ (2)

Solvent : CD_2Cl_2

Temperature : -40°C

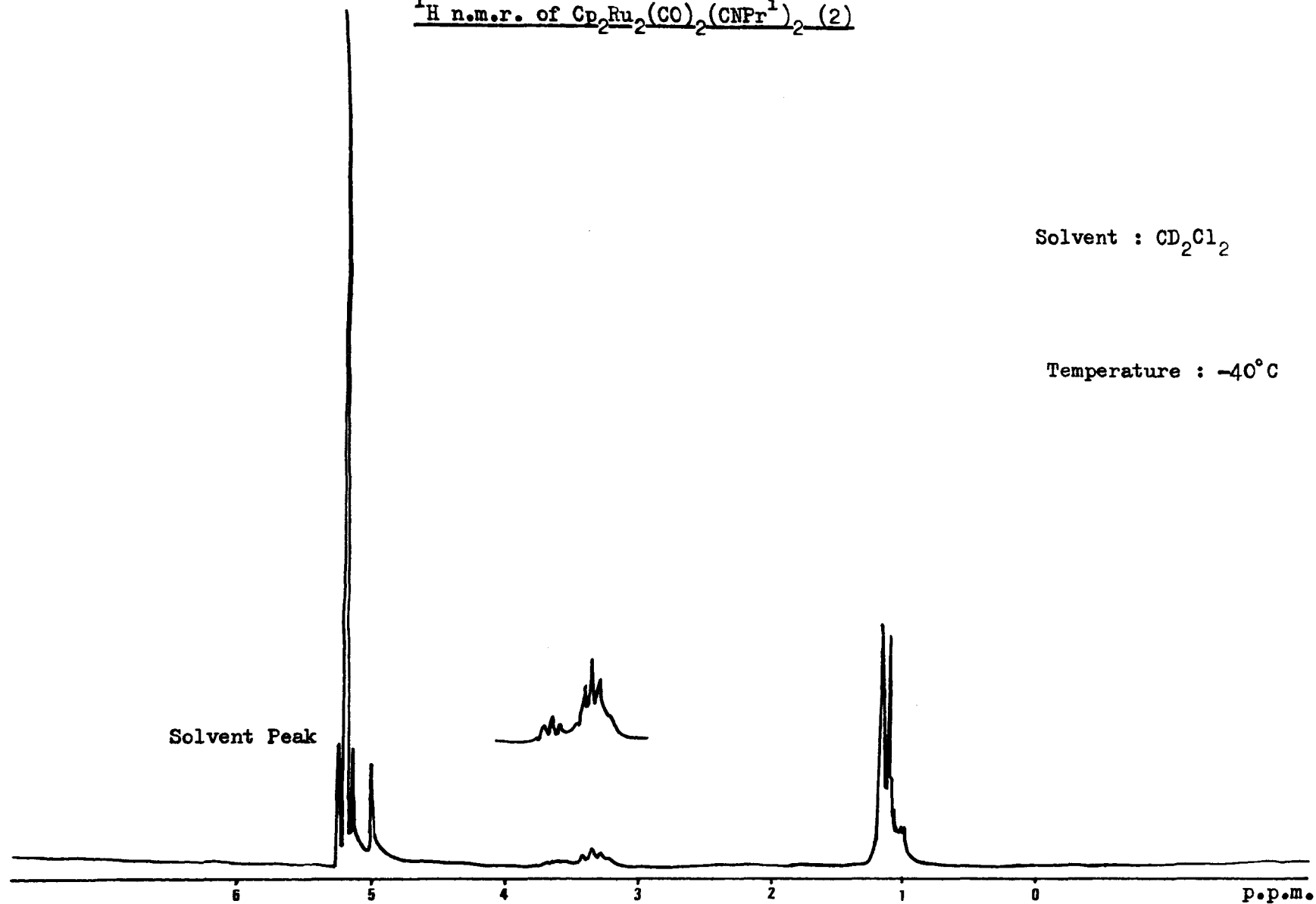


Figure 5

The V.T. ^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNPr}^i)_2$ (1c) in the cyclopentadienyl region

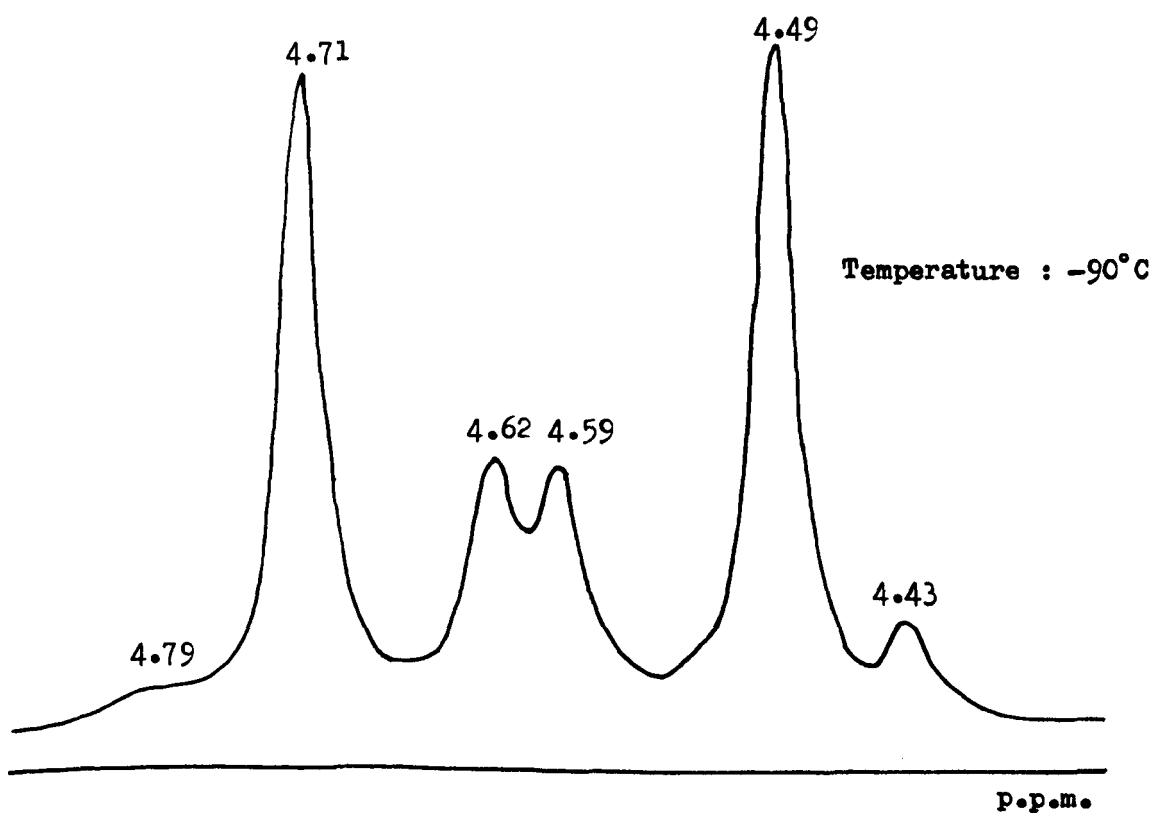
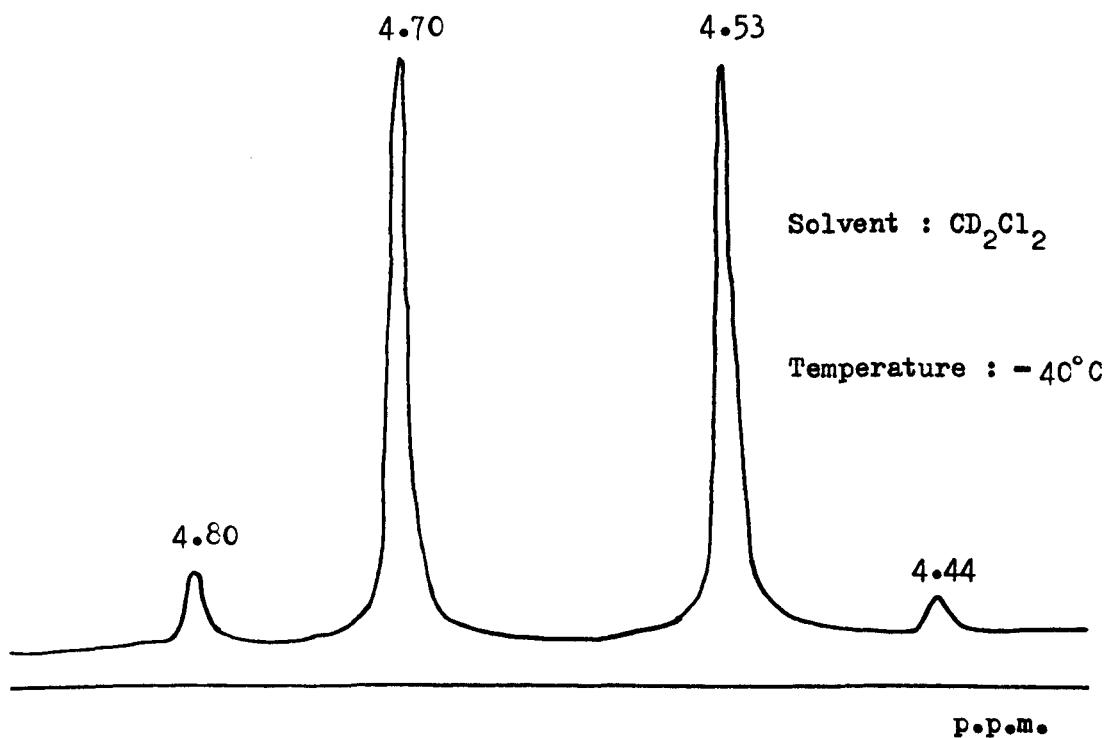


Figure 6

The V.T. ^1H n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{CNPr}^i)_2$ (2) in the cyclopentadienyl region

5.82

Solvent : CD_2Cl_2

Temperature : -30°C

x : Solvent Peak

x

5.22

5.04

p.p.m.

5.27

x

Temperature : -60°C

5.22

5.15

5.11

5.03

p.p.m.

5.26

x

5.21

Temperature : -80°C

5.02

5.15

5.10

p.p.m.

5.25

x

Temperature : -90°C

5.21

5.20

5.01

5.14

5.10

p.p.m.

Figure 7

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNMe})_2$ (1a)

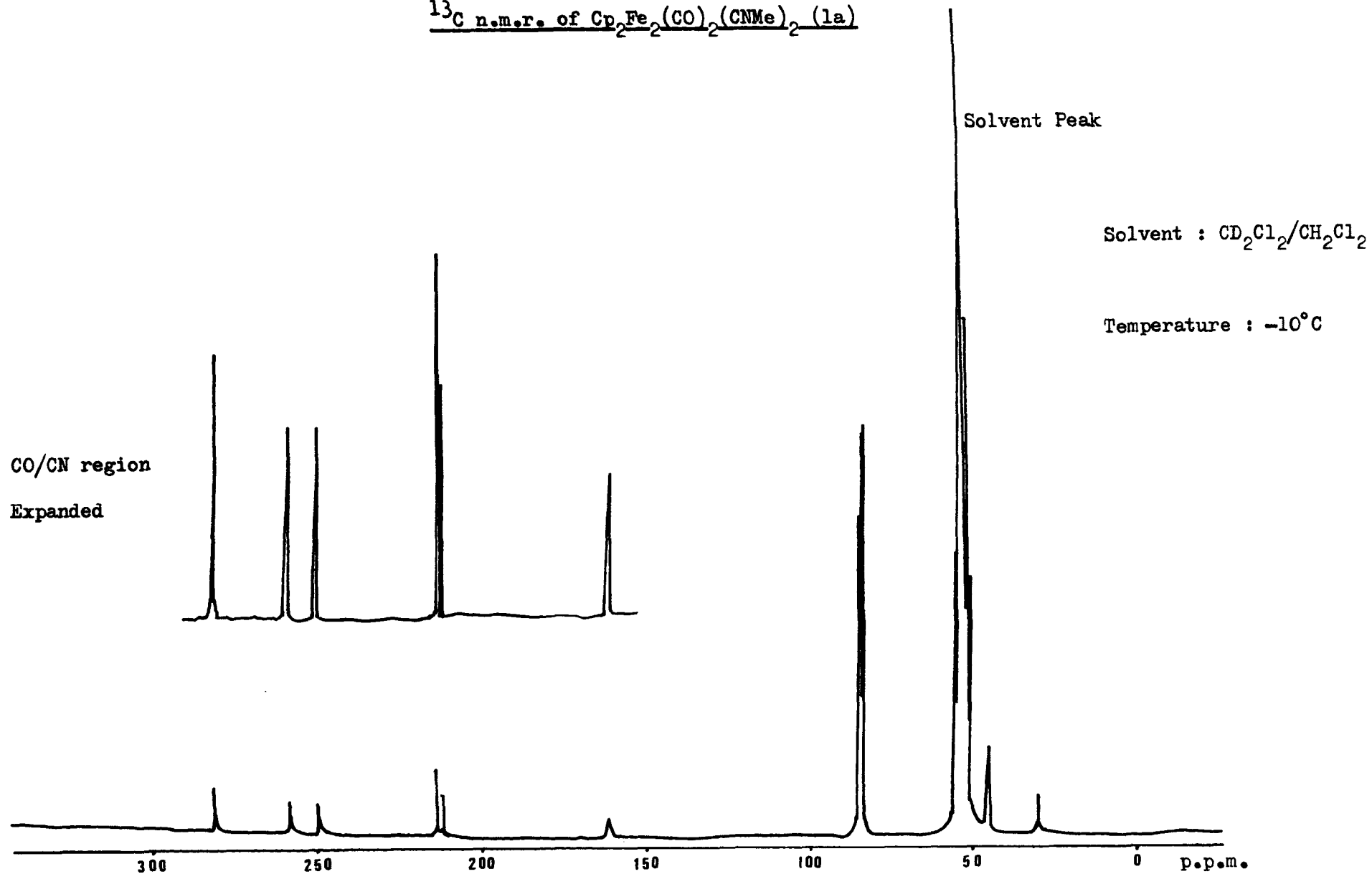


Figure 8

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNEt})_2$ (1b)

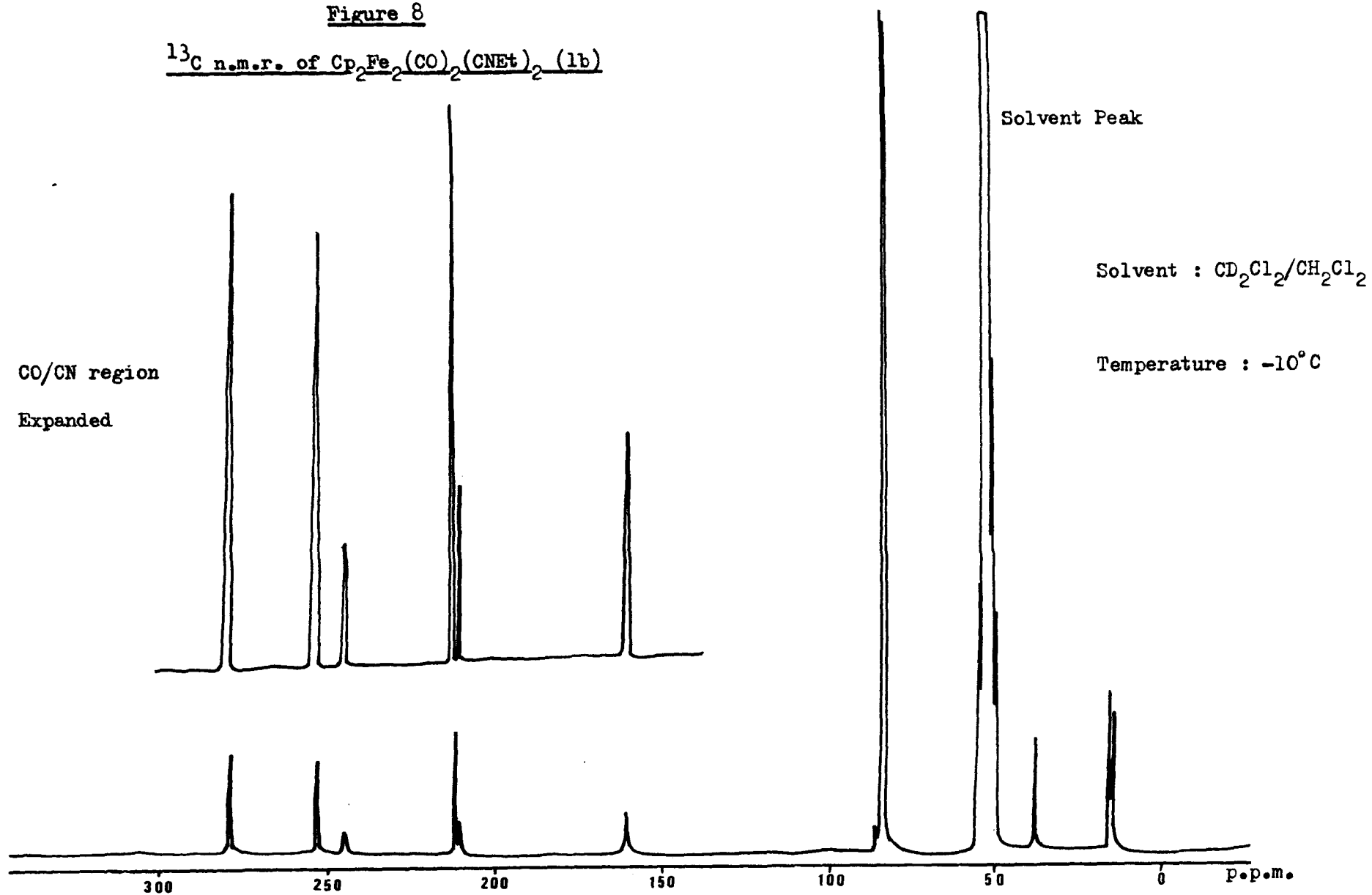


Figure 9

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNPr}^i)_2$ (1c)

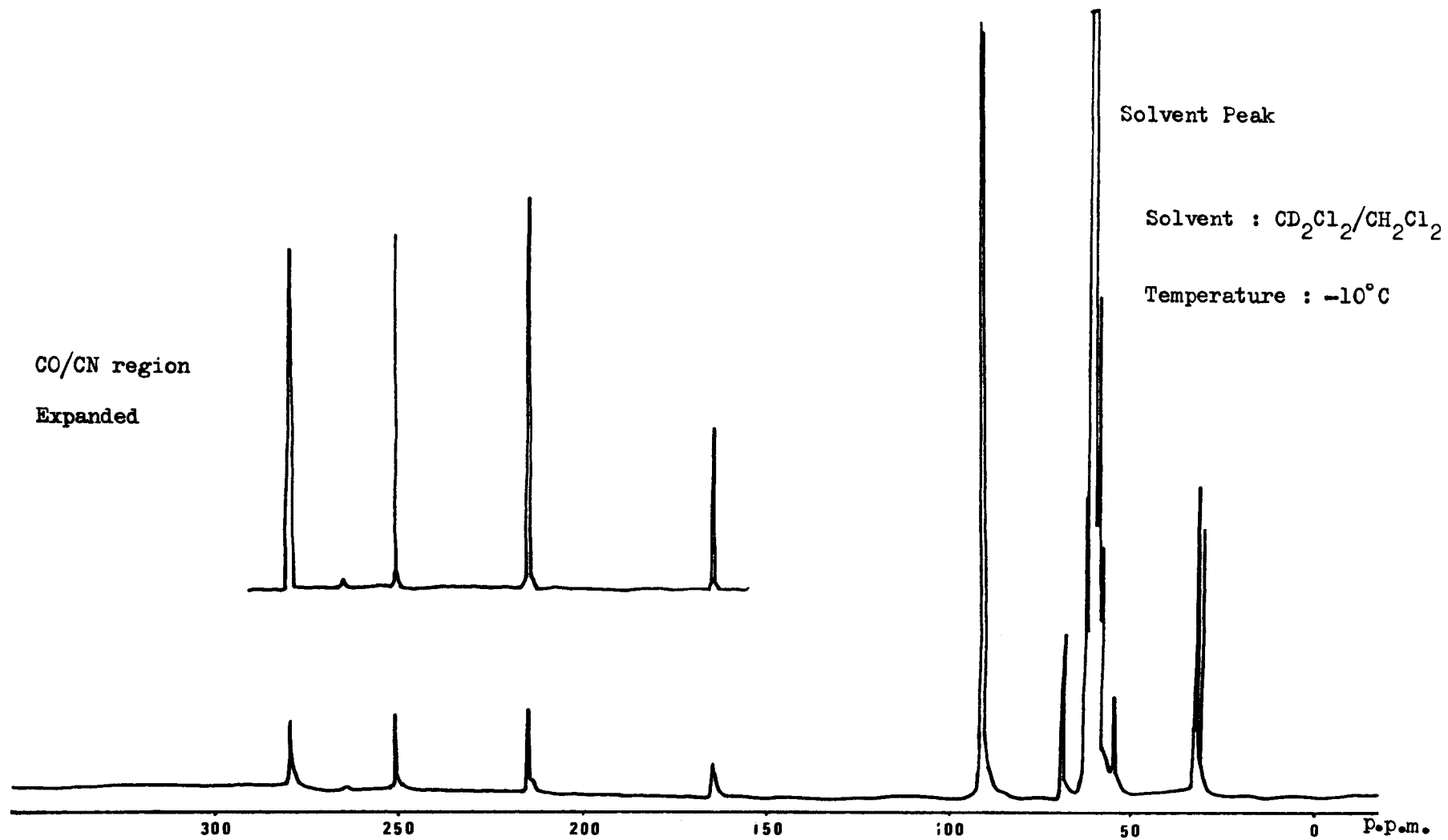


Figure 10

^{13}C n.m.r. of $\text{Cp}_2\text{Ru}(\text{CO})_2(\text{CNPr}^i)_2$ (2)

Solvent Peak

Solvent : $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$

Temperature : -40°C

CO/CN region

Expanded

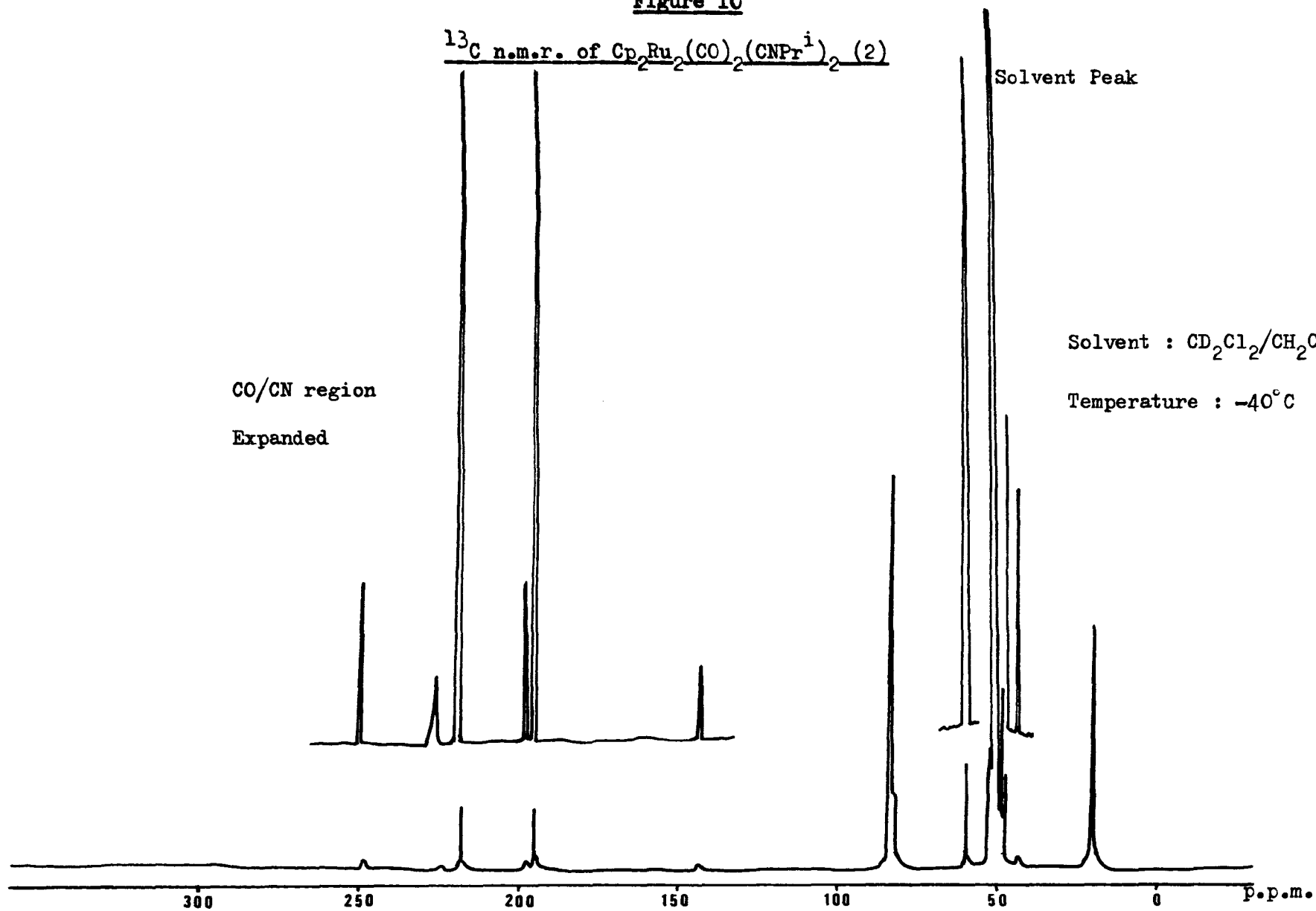


Figure 11

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CNPr}^i)_2$ (1c)

CO/CN region

Expanded

Solvent Peak

Solvent : $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$

Temperature : -90°C

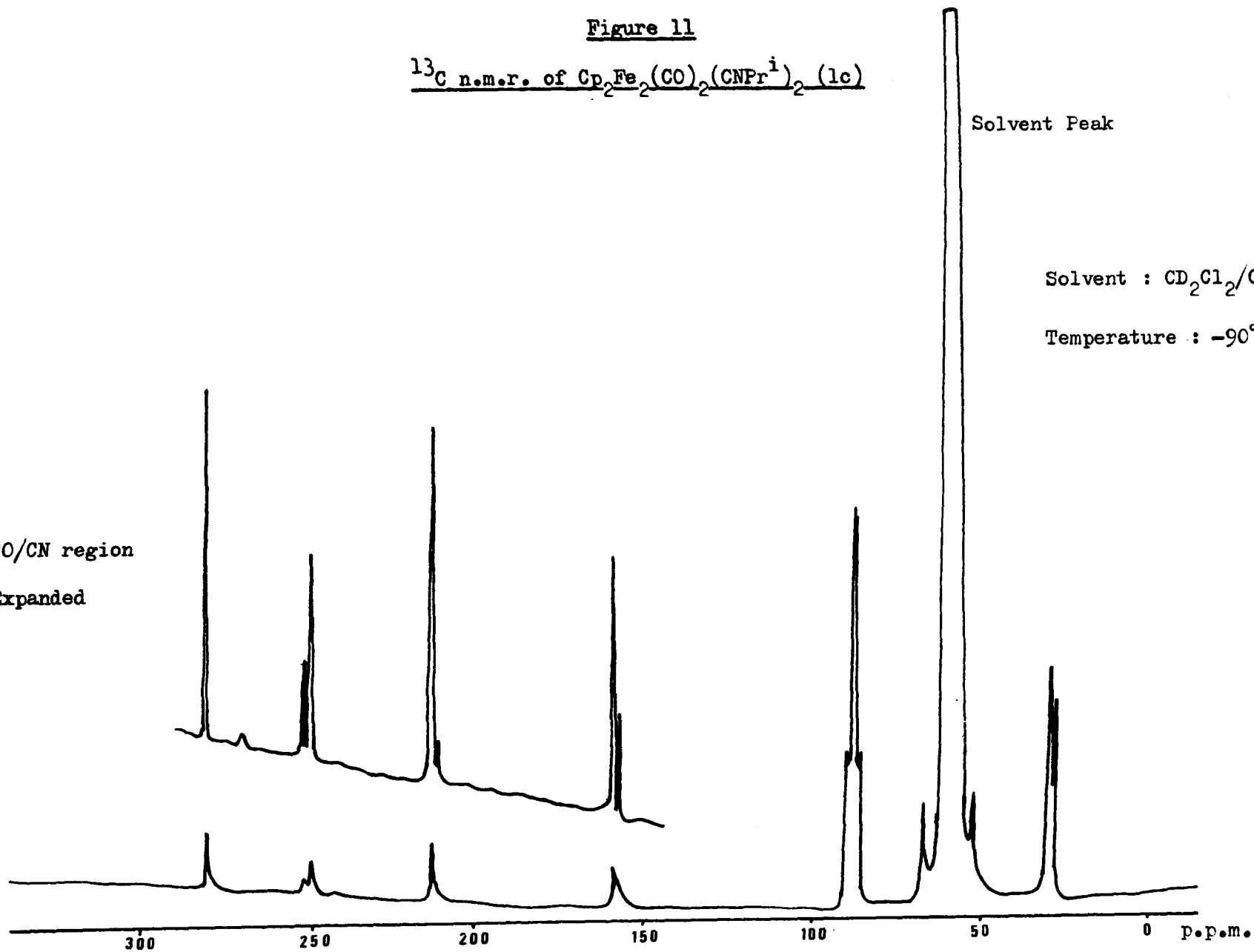


Figure 12

^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNMe})_3$ (3a)

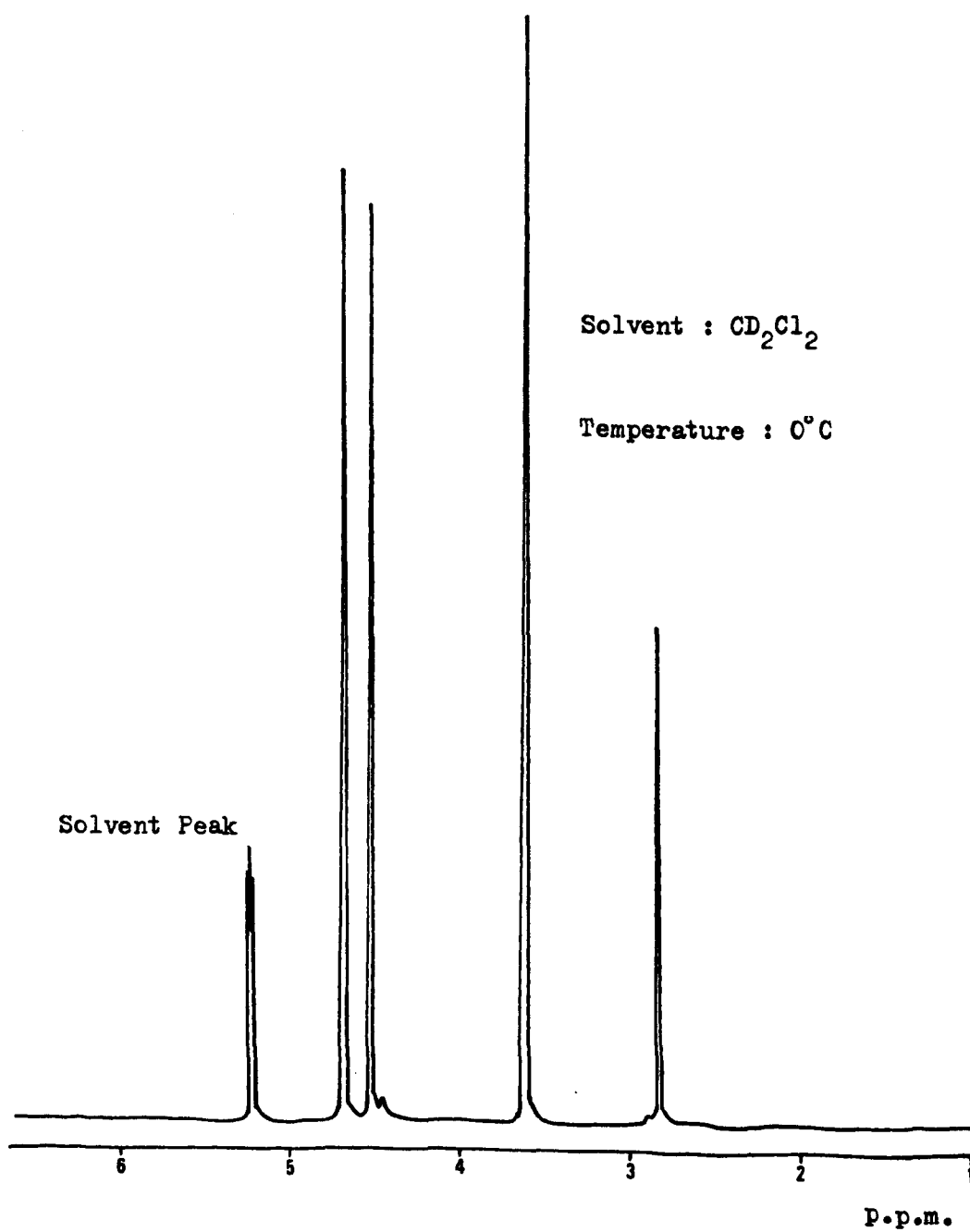


Figure 13

^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNEt})_3$ (3b)

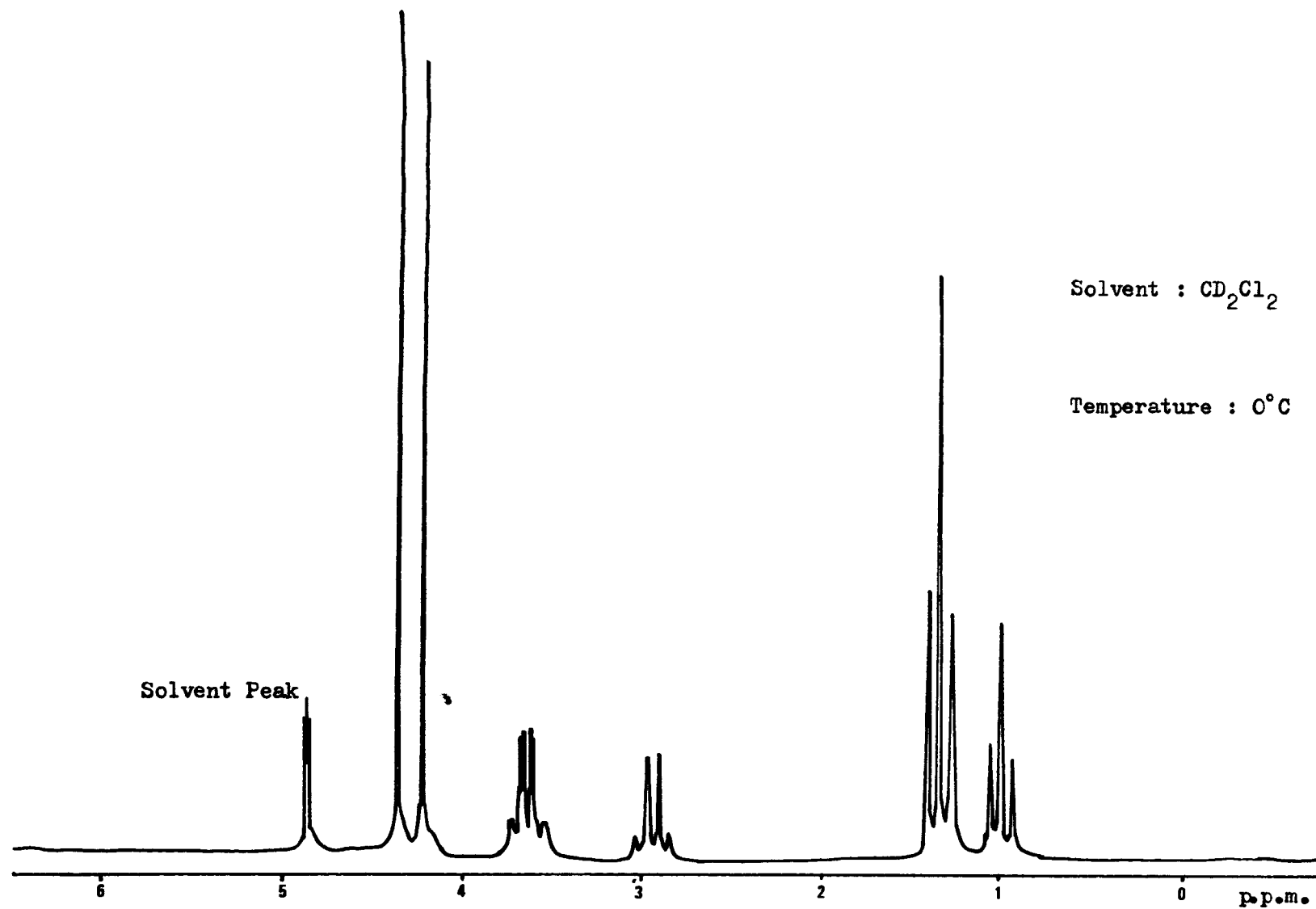


Figure 14

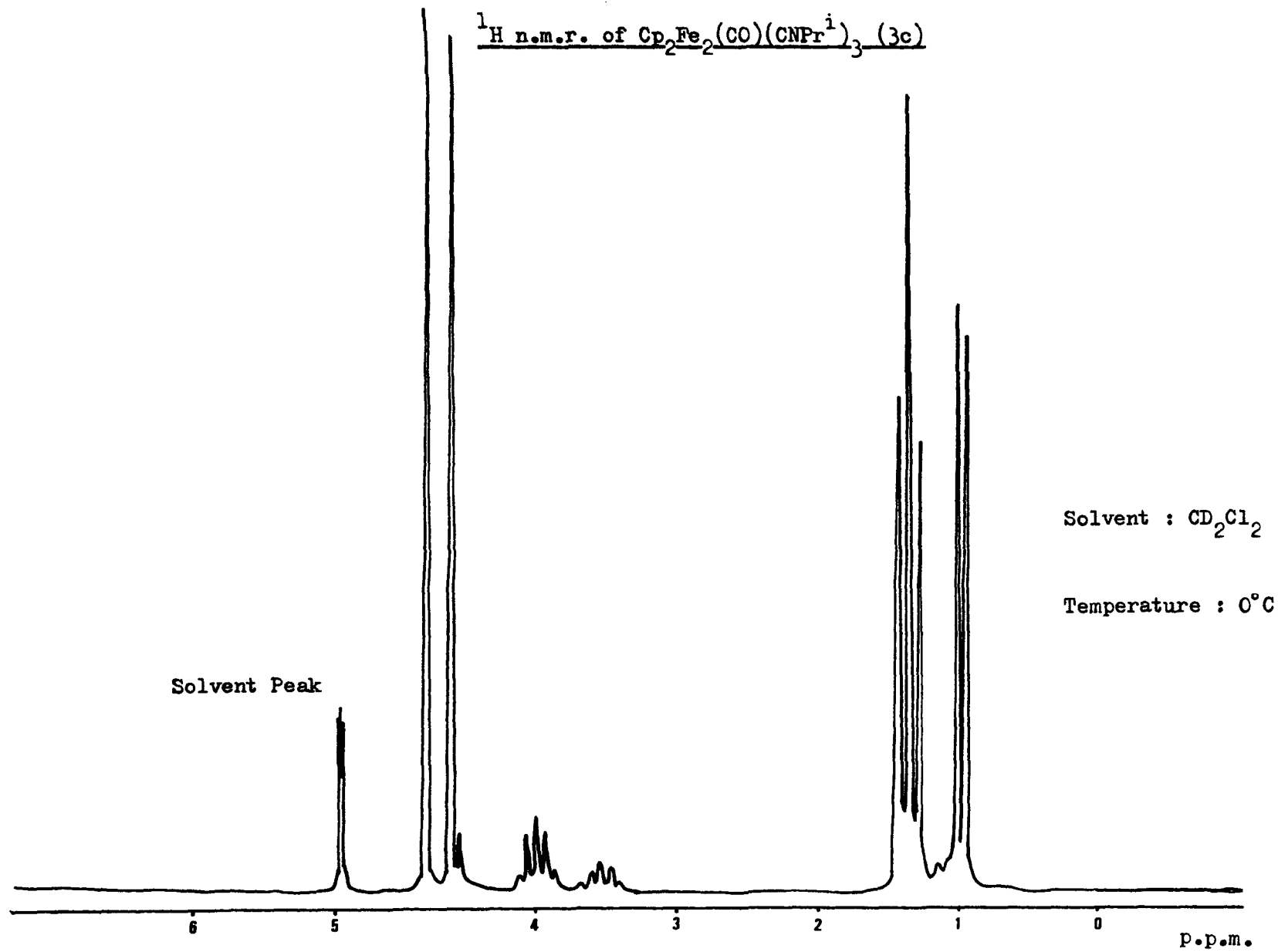


Figure 15

V.T. ^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNPr}^i)_3$ (3c) in the cyclopentadienyl region

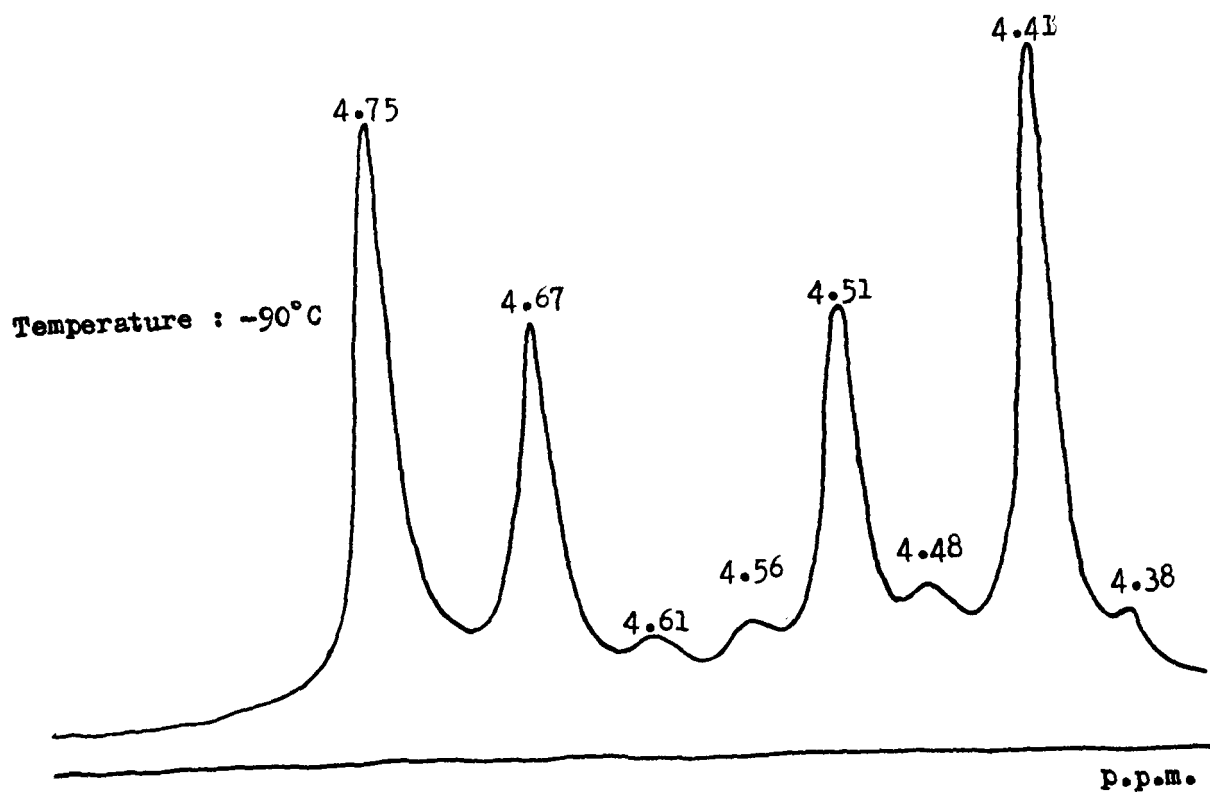
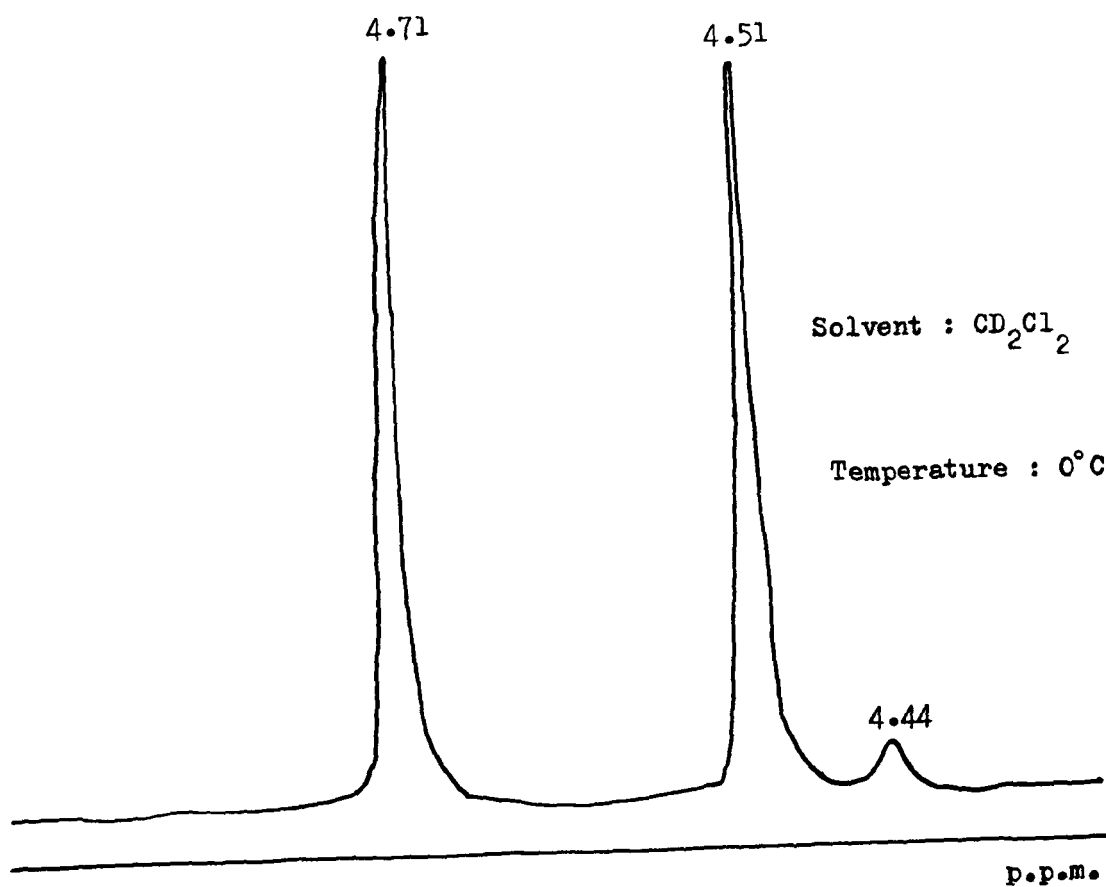


Figure 16

V.T. ^1H n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNMe})_3$ (3a) in the methyl region

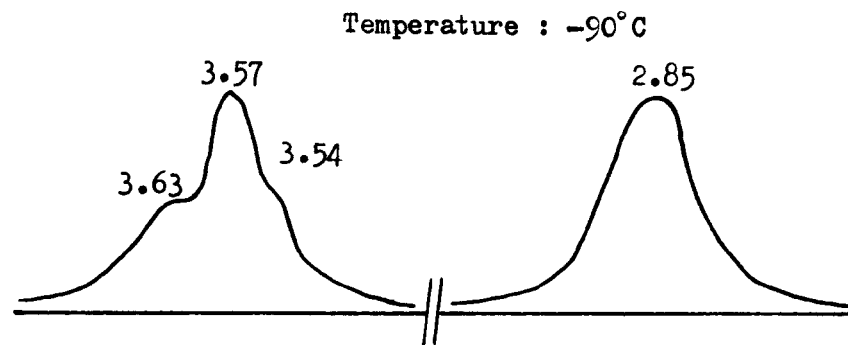
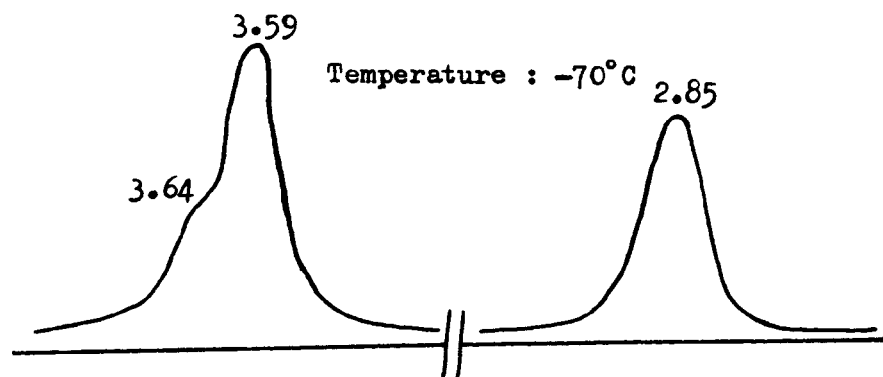
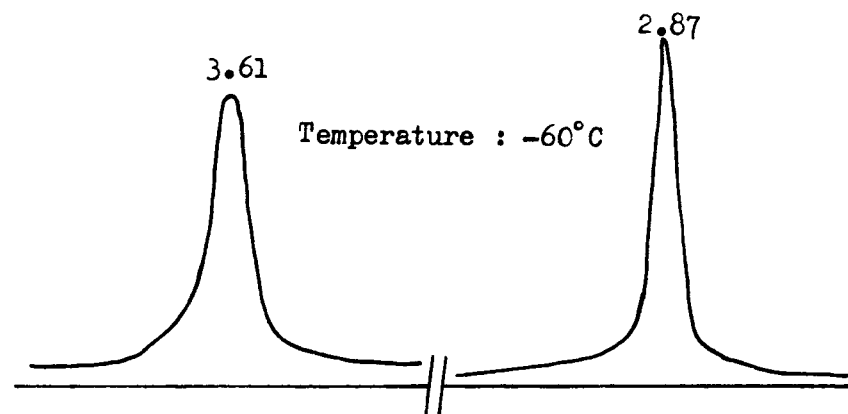
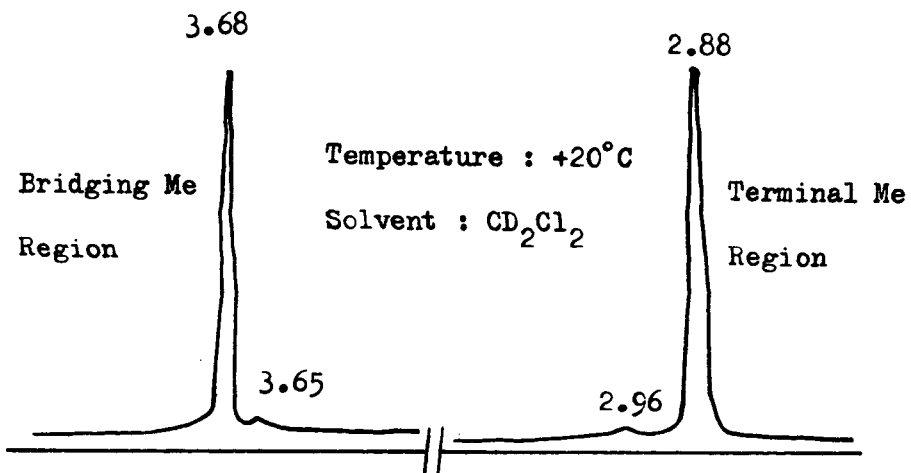
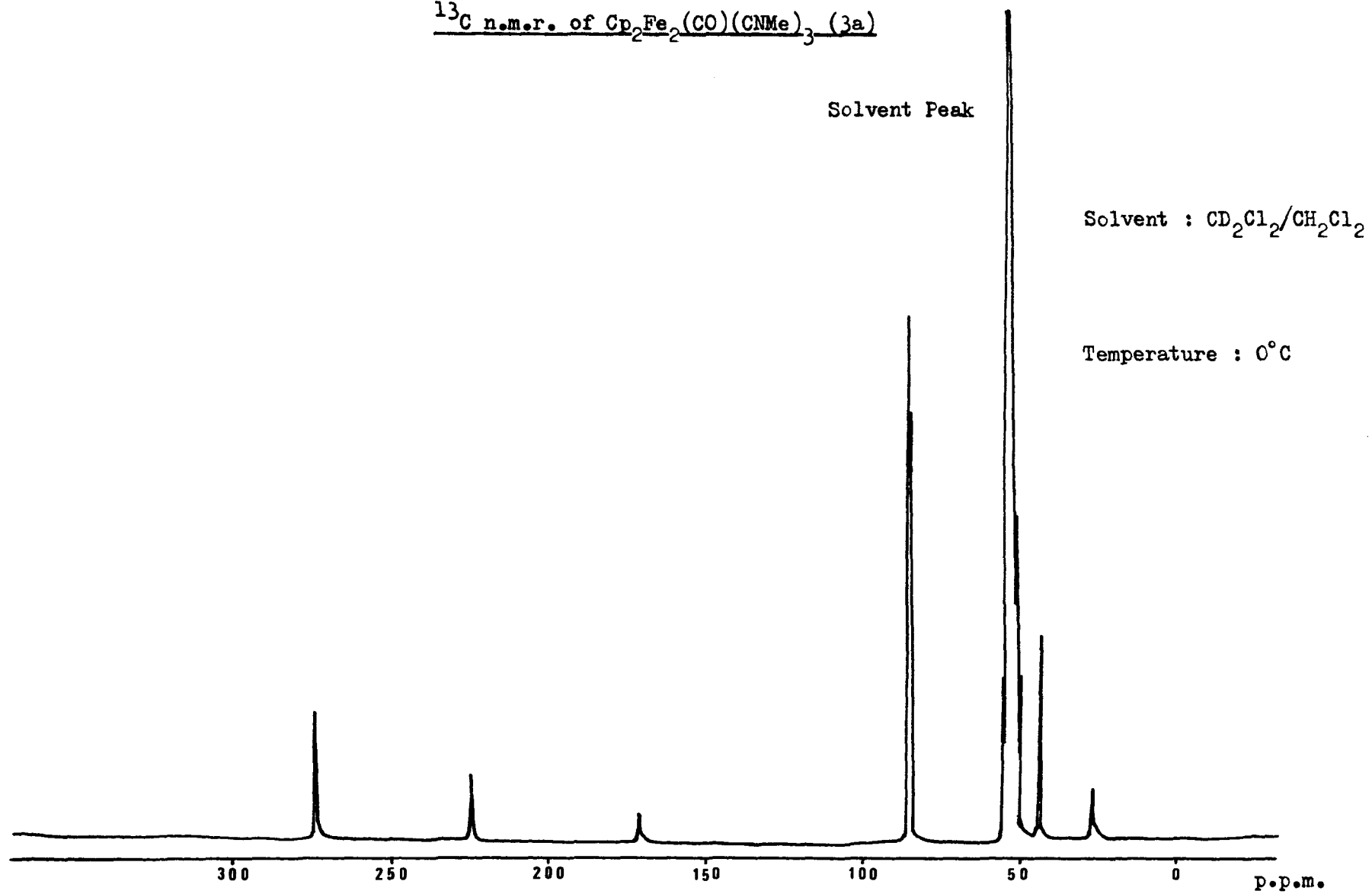


Figure 17

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNMe})_3$ (3a)



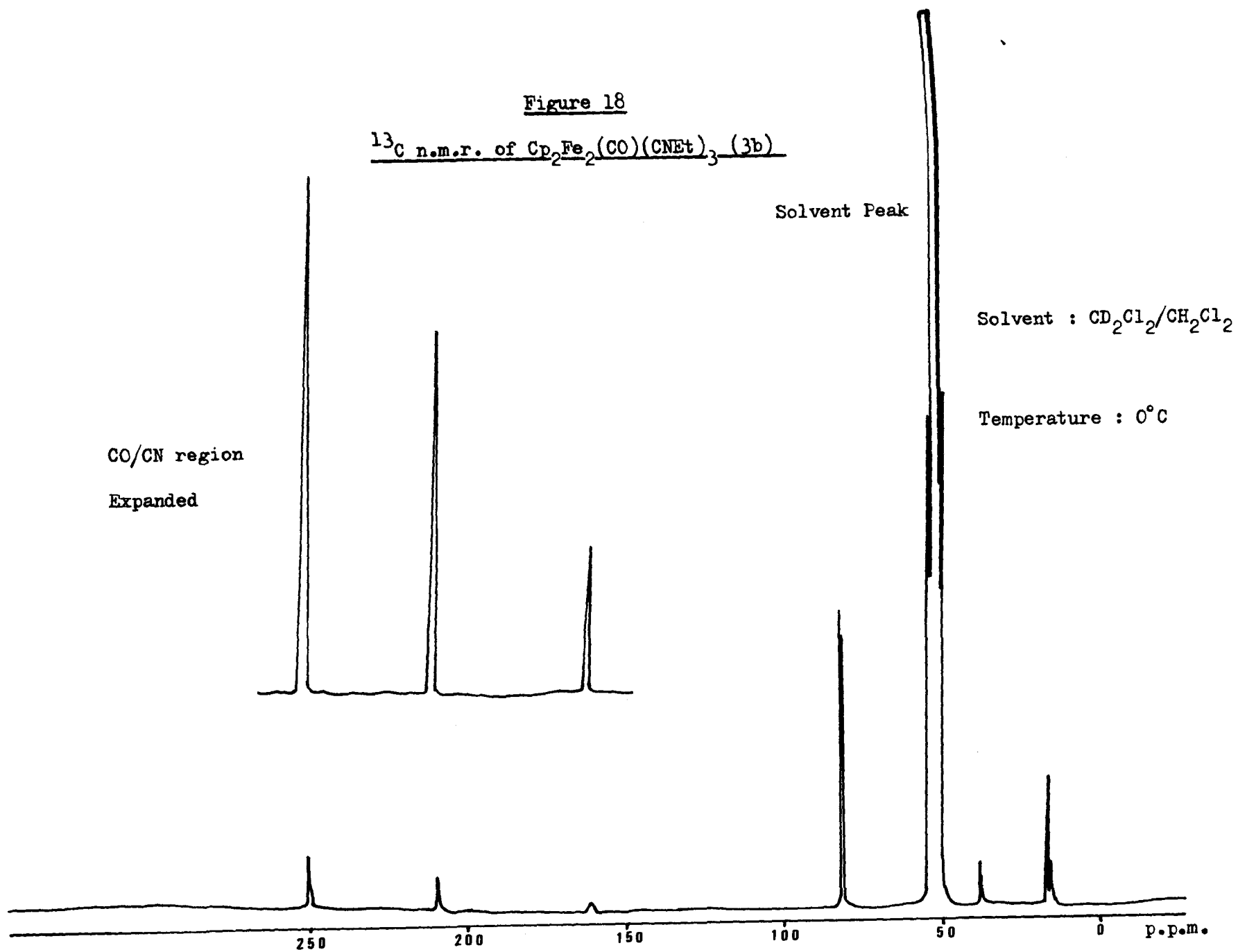


Figure 19

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNPr}^i)_3$ (3c)

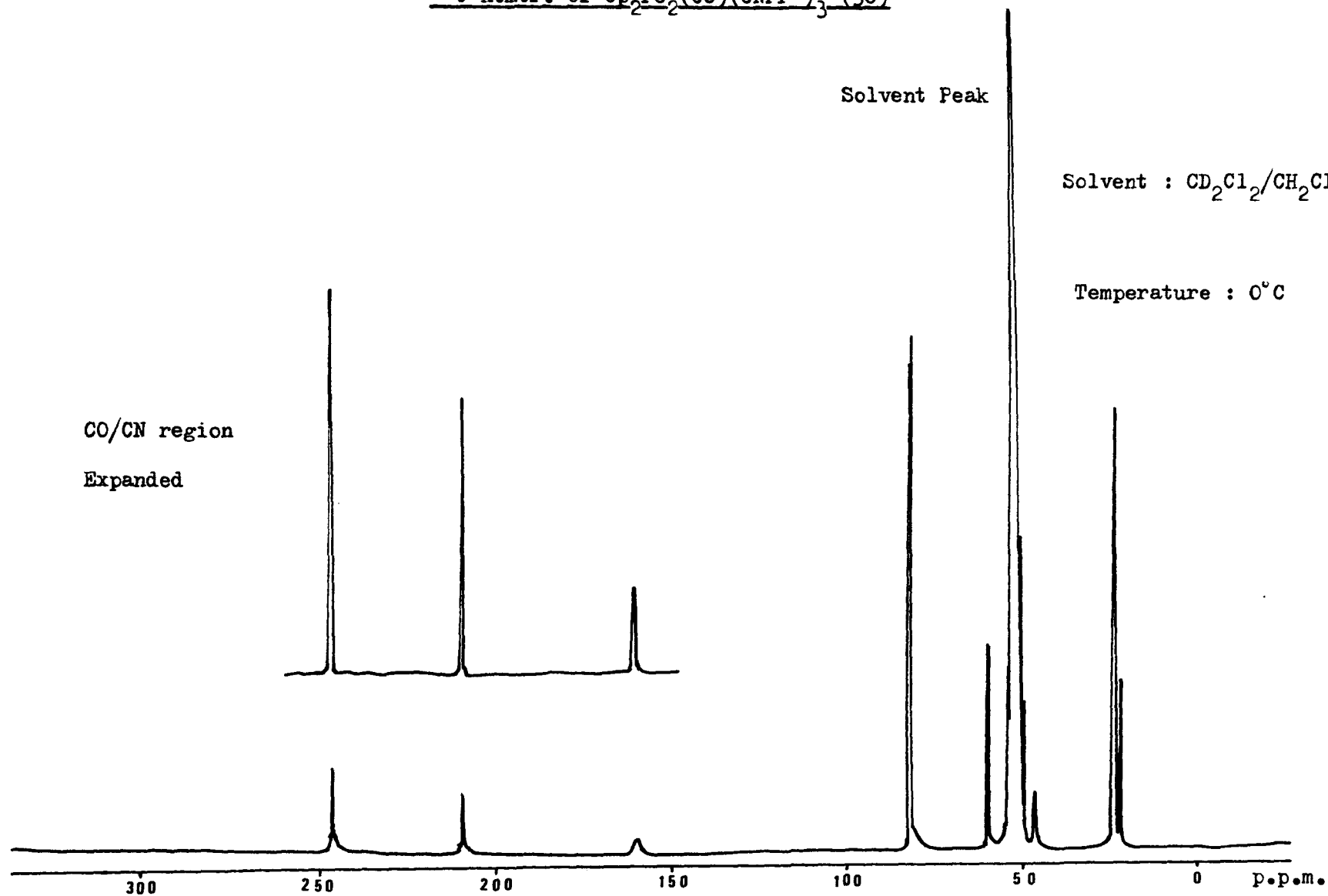


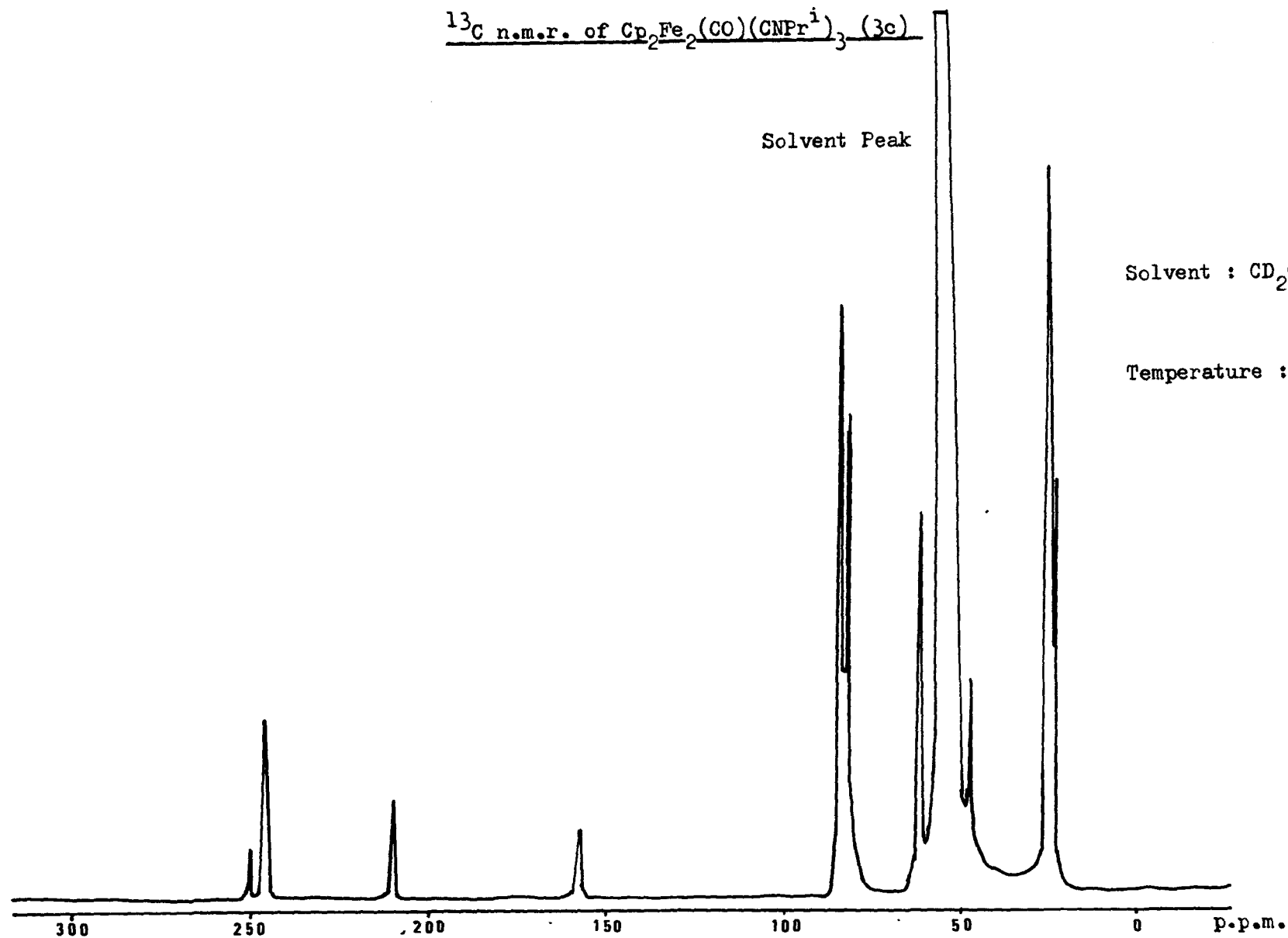
Figure 20

^{13}C n.m.r. of $\text{Cp}_2\text{Fe}_2(\text{CO})(\text{CNPr}^i)_3$ (3c)

Solvent Peak

Solvent : $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$

Temperature : -90°C



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17. Using equation from reference (13).

$$t[\cos^2(\theta - 90)] = (1 - t) (I_C / I_D) [\tan^2(\theta - 90)].$$

where C = Infrared absorption at ca. 1960 cm⁻¹.

D = Infrared absorption at ca. 2000 cm⁻¹.

θ = The angle Fe-Fe-CO in the complex.

(I_C/I_D) = assumed ratio of peaks in the infrared.

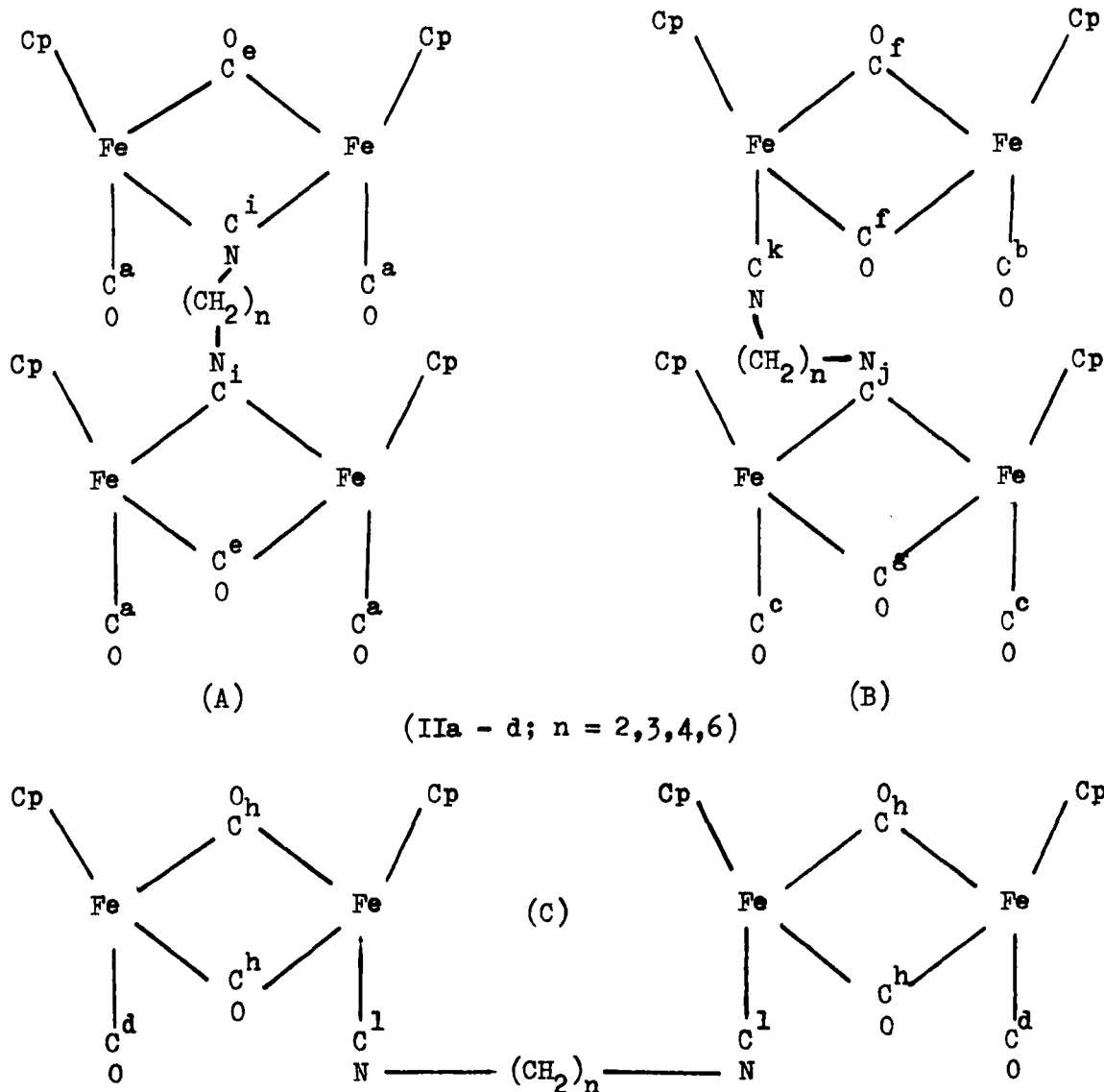
t = Trans isomer; (1 - t) = Cis isomer.

During the last decade it has become increasingly apparent that isonitriles may form one of the most versatile classes of ligand available to the transition metal chemist. Despite the large number of studies on complexes of bi and polydentate group (V) and group (VI) ligands, the chemistry of bi and polydentate isonitriles remains almost unexplored, although the recent work of Gray¹ and others² on the preparation and reactivity of $\text{Rh}_2[\text{CN}(\text{CH}_2)_n\text{NC}]_4^{2+}$ salts ($n = 3-8$) indicates the possibility of a rich and interesting chemistry. In chapters 2 and 3 the reactions of isonitriles with $\text{Cp}_2\text{M}_2(\text{CO})_4$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) were presented. In this chapter the study is extended to include the reactions of the bidentate isonitriles $\text{CN}(\text{CH}_2)_n\text{NC}$ ($n = 2, 3, 4, 6$) with the iron group carbonyls $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, $\text{Fe}_2(\text{CO})_9$, and $\text{Fe}_3(\text{CO})_{12}$.

It was found that the bidentate isonitriles $\text{CN}(\text{CH}_2)_n\text{NC}$ (1a-d; $n = 2, 3, 4, 6$) may best be prepared by the elimination of water from the diformamides $\text{OHCHN}(\text{CH}_2)_n\text{NHCHO}$ ($n = 2, 3, 4, 6$) using phosgene in the presence of triethylamine.³ The reaction of (1a) - (1d) with $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ in benzene at room temperature followed by chromatography yields exclusively red-purple crystalline complexes which analytical (Table 1) and other data show to have the composition $[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2\text{CN}(\text{CH}_2)_n\text{NC}$ (2a-d; $n = 2, 3, 4, 6$). Yields are not as satisfactory as those obtained in the preparations of the monodentate derivatives $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNR}$, and the formation of amounts of insoluble, polymeric material is thought to be responsible. No products were isolated involving chelation within a single Fe_2 moiety.

As isonitriles can function either as a bridging or terminal ligand, the three isomeric structures (A) to (C) are possible. In the diagram, cyclopentadienyl groups are represented in the cis configuration, although the possibility of cis/trans isomerism of the $\text{Cp}_2\text{Fe}_2(\text{CO})_3$ moieties raises the total number of isomers to ten [three each for (A) and (C) and four for (B)]. In common with work on the monosubstituted complexes $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNR}$

complexes, it does not appear possible to differentiate by n.m.r. between cis and trans isomers (if indeed, more than one isomer is present), and the discussion that follows is in terms of the structural isomers (A) to (C) only.



^{13}C and ^1H n.m.r. studies (Tables 2 and 3) show that all three isomers may be present, with the proportions depending on alkyl chain length, n , and that the molecules are fluxional in solution, undergoing isomer interchange accompanied by both CO and (CNCH_2-) bridge-terminal exchange, and cyclopentadienyl site exchange. Thus, the limiting low temperature proton spectrum of (IIa)(fig 1) shows the expected four cyclopentadienyl signals due to a mixture of isomers (A) and (B) in the ratio 1 : 4. On the basis of intensities and characteristic trends in chemical shifts,⁴ the resonance at 4.88 δ may be

assigned to the equivalent cyclopentadienyl ligands of (A) while the three other peaks at 4.86, 4.70 and 4.59 δ in the ratio of 2 : 1 : 1 may be assigned to (B). In the CH₂ region, a singlet is observed at 4.34 δ due to (A), while the multiplet at 3.71 δ may be assigned to (B), which may be regarded as an unsymmetrical 1,2-disubstituted ethane. Such compounds are known to exhibit AA'BB' spectra⁵ and the experimental spectrum may be simulated exactly using values of $\delta_A = 3.67$ and $\delta_B = 3.78$, with geminal and vicinal coupling constants of -14 and 6 Hz respectively. A rather large natural line width of ca. 3 Hz must be assumed in the simulated spectrum. Broadness of the alkyl resonances is a feature characteristic of the other complexes (IIb - d) and may be due to incompletely resolved resonances due to cis and trans isomers. Figures (2) and (3) show the temperature dependence of (IIa) in the cyclopentadienyl and CH₂ region respectively: figure 3 also shows the simulated spectrum for the AA'BB' system.

On warming to room temperature, both cyclopentadienyl and CH₂ resonances broaden, and in d⁸-toluene, a limiting high temperature spectrum consisting of single cyclopentadienyl and CH₂ resonances can be obtained at +80°C. This demonstrates the presence of both A \rightleftharpoons B interchange and cyclopentadienyl site exchange in isomer B. In terms of the Adams-Cotton mechanism, these processes are related. Thus, independent bridge-terminal isonitrile exchange at each Cp₂Fe₂(CO)₃ moiety results in A \rightleftharpoons B \rightleftharpoons C exchange [although (C) is depopulated below the limits of observation for n = 2] while it has been shown⁶ that cyclopentadienyl site exchange in the terminally bound isomer is an automatic consequence of bridge-terminal isonitrile exchange.

The ¹³C spectrum of IIa at -20°C (fig 4) in the CO and CN region shows the nine resonances expected for a mixture of isomers (A) and (B). The assignment shown is made on the basis of intensity and chemical shifts found for the related Cp₂Fe₂(CO)₃ (CNR) series⁴. Some of the assignments are not unambiguous: thus, the two resonances at 271.1 and 272.3 may be reversed. Some overlap of resonances is observed in the cyclopentadienyl region, but

the expected three CH_2 resonances can be seen clearly.

The ^{13}C and ^1H n.m.r. spectra of complexes (IIb - d), are shown in figures (5 - 10). The spectra of (IIb) (Fig 5,6) indicates a mixture of isomers (B) and (C). Only four of the expected five cyclopentadienyl absorptions can be seen, although a clear shoulder is observable on the resonance at 4.71 δ . Thus the resonance at 4.86 δ is assigned to the equivalent cyclopentadienyl groups of the $\text{Cp}_2\text{Fe}_2(\text{CO})_3$ residue of (B) containing the bridging isonitrile, with the remaining four resonances assignable to the terminal $\text{Cp}_2\text{Fe}_2(\text{CO})_3$ residue of (B) and isomer (C). In the $\alpha - \text{CH}_2$ region, the expected three triplets can be seen clearly. The ^{13}C spectrum at -40°C in the CO and CN region shows only eight of the nine resonances expected. The most probable assignments shown are based on intensity and chemical shift; in particular the intensity of the resonance at 209.5 p.p.m. indicates a coincidence of carbonyls (b) and (c). On warming to room temperature, both CO and CN resonances broaden, indicating both CO and CN bridge-terminal exchange. A high temperature limiting spectrum could not be obtained because of limited solubility in other solvents and slow decomposition at elevated temperatures.

Spectra of (IIc) and (IIId) may be interpreted on the same basis as (IIb) and show clearly a decrease in the amount of isomer (B) relative to (C). Inspection of molecular models shows that for $n = 2$, the structural form (A) provides the least amount of steric hindrance between $\text{Cp}_2\text{Fe}_2(\text{CO})_3$ moieties and allows free $\text{CH}_2 - \text{CH}_2$ bond rotation. As the length of the alkyl chain increases and the interaction between $\text{Cp}_2\text{Fe}_2(\text{CO})_3$ moieties becomes less relevant, isomers (B) and particularly (C) become progressively more abundant. The table below shows the effective ratios of bridged to terminally bound isonitrile calculated from isomer population in the ^1H n.m.r. spectra of the complexes.

The complex (IIa) can be thought as being equivalent to $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNEt}$ with one proton on the methyl group being replaced with a $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CN}-)$ moiety. The effect of doing this results in a dramatic shift in the bridge

to terminal ratio.

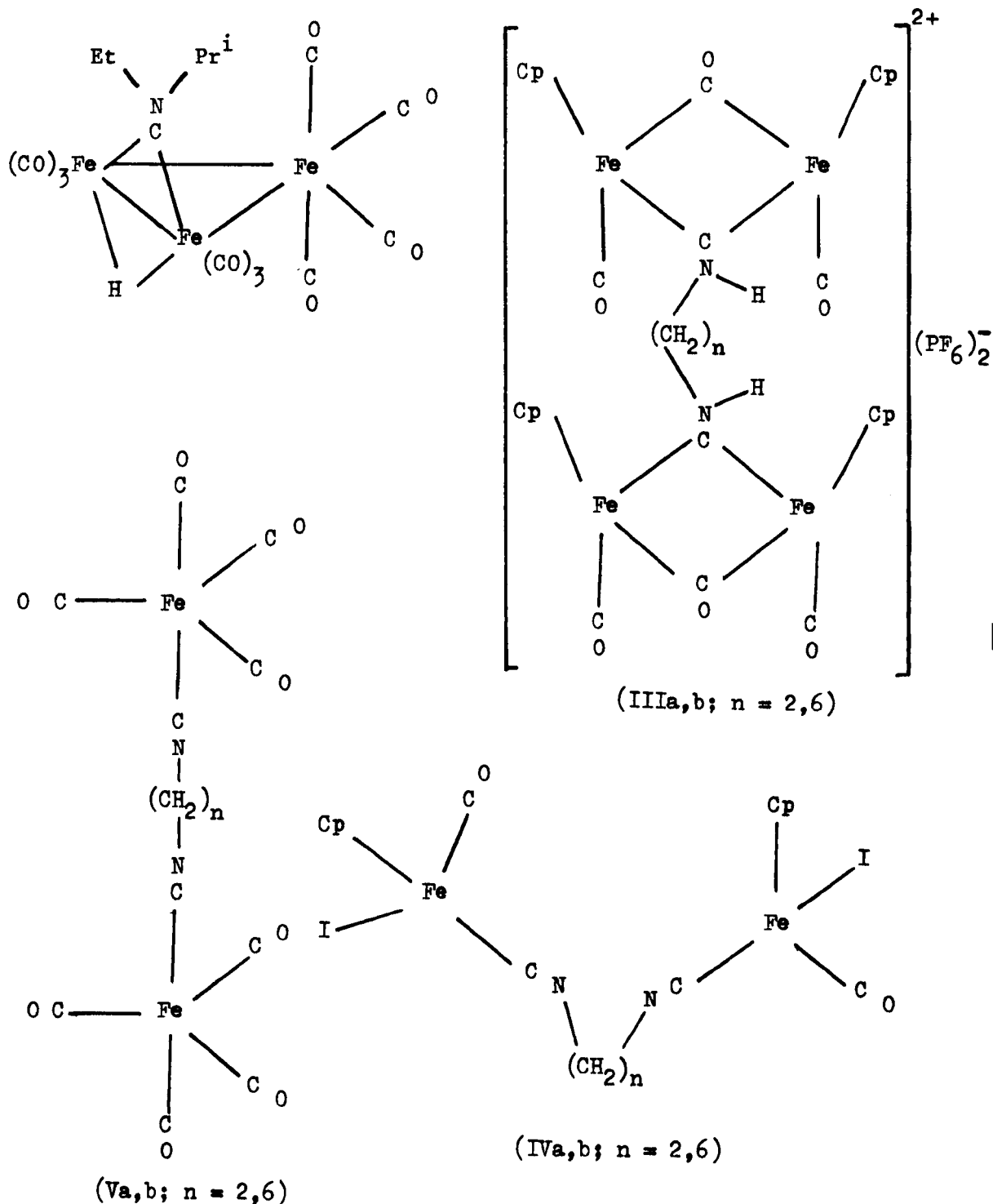
<u>Compound</u>	<u>(Bridged : terminal) ratio</u>		<u>n</u>
(IIa)	1	: 0.6	2
(IIb)	1	: 1.5	3
(IIc)	1	: 5.0	4
(IIId)	1	: 15.0	6
$\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CNET}$	1	: 17.0	-

Infrared spectra (Table 4) are in accord with the n.m.r. results. Band (Z) may be assigned to the symmetric terminal CO vibrations of (A) and the $\text{Cp}_2\text{Fe}_2(\text{CO})_3$ residue of (B) containing a bridging isonitrile. Band (Y) may be assigned to the asymmetric terminal CO vibrations of (A) and the $\text{Cp}_2\text{Fe}_2(\text{CO})_3$ residue of (B) containing a bridging isonitrile, with the terminal CO vibrations of (C) and the $\text{Cp}_2\text{Fe}_2(\text{CO})_3$ residue of (B) containing a terminal isonitrile ligand. Band (X) in the bridging CO region may be attributed to (A) and the $\text{Cp}_2\text{Fe}_2(\text{CO})_3$ residue of (B) containing a bridging isonitrile, while band (W) is due to (C) and the $\text{Cp}_2\text{Fe}_2(\text{CO})_3$ residue of (B) containing a terminal isonitrile. The presence of two components of band (V) for (IIa) confirms the presence of isomers (A) and (B).

These complexes exhibit a reactivity similar to that of the $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{-CNR}$ derivatives. Protonation of (IIa, d) with 75% aqueous HPF_6 yields the non-fluxional, at room temperature, bridged iminium derivatives (IIIa,b). At elevated temperatures, it is conceivable that CN bond rotation may occur. Recent work has shown that the complex $\text{Fe}_3(\text{CO})_{10}(\text{H})[\text{CNET}(\text{Pr}^i)]$ (shown over) undergoes CN bond rotation, which is fast on the n.m.r. time scale at room temperature, although it can be 'frozen out' at ca. -50°C .⁸

Characteristic of these iminium salts are the bridging CN vibration at $1520 - 1570\text{ cm}^{-1}$ and the considerably deshielded CN resonance at ca. 315p.p.m. in the ^{13}C spectrum.⁴ The spectra of (IIIa,b) are illustrated in figures (11 - 14). Reaction of (IIa,d) with iodine results in cleavage to yield

$\text{CpFe}(\text{CO})_2\text{I}$ and $[\text{CpFe}(\text{CO})\text{I}]_2 \text{CN}(\text{CH}_2)_n\text{NC}$ (IVa,b; $n = 2,6$). This is a reaction characteristic of $\text{Cp}_2\text{Fe}_2(\text{CO})_n(\text{CNR})_{4-n}$ ($n = 1 - 4$) derivatives,⁹ but interestingly only poor yields of the $\text{CpFe}(\text{L})(\text{CO})\text{I}$ complexes are obtained when $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{L})$ complexes are cleaved, where $\text{L} = \text{P}(\text{OR})_3$, PR_3 , or CS .^{10, 11} The ^1H n.m.r. spectrum of (IVa) (Figure 15) shows two cyclopentadienyl resonances of equal intensity consistent with the presence of two diastereoisomers (one meso, the other one dl).



Reaction of bidentate isonitrile (Ia,d) with either $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$ yields exclusively the $[\text{Fe}(\text{CO})_4]_2[\text{CN}(\text{CH}_2)_n\text{NC}]$ complexes (Va,b; $n = 2,6$), isolated as pale yellow solids, but decomposing slowly to give $\text{Fe}_3(\text{CO})_{12}$ in the solid state. The infrared spectrum is typical in terms of intensities of the bands of an axially substituted trigonal bipyramidal $\text{Fe}(\text{CO})_4\text{L}$ complex,¹² and the singlet ^{13}C CO resonance observed down to -90°C is consistent with the low activation energy for the intramolecular exchange commonly found in similar five co-ordinate species. It is interesting to compare these results with the reaction of $\text{Fe}_2(\text{CO})_9$ with $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ which yields both the related $[\text{Fe}(\text{CO})_4]_2\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ and the chelated $\text{Fe}(\text{CO})_3\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ in the ratio 1 : 1.¹³ No chelate complexes have been found in this work, and other workers have shown that the alkyl chain length must be at least eight carbons before chelate behaviour is observed due to the particular requirements of the linear CNR linkage.^{14, 15}

Experimental

$\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$ were prepared from $\text{Fe}(\text{CO})_5$; ¹⁶ all other starting materials were obtained commercially. Reactions involving metal carbonyls were carried out under nitrogen in purified solvents. N.m.r. spectra were recorded on a JEOL FX-100 instrument, while infrared spectra were recorded on a Perkin - Elmer 257 instrument. ¹³C n.m.r. spectra were run in the presence of $\text{Cr}(\text{acac})_3$ (acac = acetylacetonate) under nitrogen.

Preparations

- (a) 1,6-diisocyanohexane. Triethylamine (320 cm³) and di-N-formyl-1,6-diaminohexane (prepared from 1,6-diaminohexane and ethyl formate)¹⁷ were dissolved in dichloromethane (450 cm³). With magnetic stirring, phosgene (99g) is bubbled in through a wide bore tube sufficiently rapidly to cause the solution to reflux. The reaction was allowed to cool to room temperature and ammonia (40g) is bubbled into the solution over a period of one hour. After filtration and removal of the solvent, the residue is distilled to yield 1,6-diisocyanohexane (40g, 59%; bp 100 - 110°C/0.01mm Hg; ¹H n.m.r.: $\text{CH}_2(\alpha)$, 3.19δ(m, $J_{\text{NH}} = 6.4$ Hz); $\text{CH}_2(\beta, \gamma)$, 1.26δ(m); ¹³C n.m.r.: CN, 155.2 p.p.m. ($J_{\text{CN}} = 6.1$ Hz), $\text{CH}_2(\alpha)$, 41.3 p.p.m. ($J_{\text{CN}} = 6.1$ Hz), $\text{CH}_2(\beta)$, 28.7 p.p.m., $\text{CH}_2(\gamma)$, 25.4 p.p.m.] other diisonitriles were prepared similarly.
- 1,2-diisocyanoethane. [bp 60 - 65°C/0.01mm Hg; ¹H n.m.r.: CH_2 , 3.71δ(s, br); ¹³C n.m.r.: CN, 158.6 p.p.m. ($J_{\text{CN}} = 3.0$ Hz), CH_2 , 36.3 p.p.m. ($J_{\text{CN}} = 5.6$ Hz)].
- 1,3-diisocyanopropane. [bp 70 - 80°C/0.01mm Hg; ¹H n.m.r.: $\text{CH}_2(\alpha)$, 3.55δ(m, $J_{\text{NH}} = 1.9$ Hz, $J_{\text{HH}} = 6.2$ Hz), $\text{CH}_2(\beta)$, 1.96δ(m, $J_{\text{NH}} = 1.8$ Hz); ¹³C n.m.r.: CN, 157.0 p.p.m. ($J_{\text{NC}} = 7.3$ Hz), $\text{CH}_2(\alpha)$, 37.9 p.p.m. ($J_{\text{NC}} = 7.3$ Hz), $\text{CH}_2(\beta)$ 27.7 p.p.m.].
- 1,4-diisocyanobutane. [bp 80 - 90°C/0.01mm Hg; ¹H n.m.r.: $\text{CH}_2(\alpha)$, 3.41δ($J_{\text{NH}} = 2.0$ Hz), $\text{CH}_2(\beta)$, 1.78δ(m); ¹³C n.m.r.: CN,

156.0 p.p.m. ($J_{\text{CN}} = 5.7 \text{ Hz}$), $\text{CH}_2(\alpha)$, 40.4 p.p.m. ($J_{\text{CN}} = 5.9 \text{ Hz}$), $\text{CH}_2(\beta)$ 25.4 p.p.m. .

Safety note. Explosions have been reported previously on the distillation of isonitriles. During phosgene addition, exit gases were passed through a sodium hydroxide solution and monitored for phosgene using filter paper soaked in an alcoholic solution containing 10% of a 1:1 mixture of p-dimethylaminobenzaldehyde and colourless diphenylamine.

- (b) Preparation of $[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2 \text{CN}(\text{CH}_2)_6\text{NC}$. 1,6-diisocyanohexane (0.68g) was added to a solution of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (3.54g) in benzene (80 cm^{-3}) and stirred overnight at room temperature. Solvent was removed under reduced pressure and the residue was chromatographed on alumina grade (IV) using dichloromethane as eluent. After elution of starting material, a second purple band gave the product (IIId) as purple crystals after recrystallisation from dichloromethane/petroleum-ether (40:60) (1.5g, 36%). Complexes (IIa - c) were prepared similarly.
- (c) Preparation of $[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2 \text{CN}(\text{H})(\text{CH}_2)_6(\text{H})\text{NC} (\text{PF}_6)_2$. $[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2 \text{CN}(\text{CH}_2)_6\text{NC}$ (400mg) was suspended in diethylether and enough dichloromethane added to bring it into solution. HPF_6 (75% aq) was added dropwise until precipitation ceased. The brick red precipitate was collected and purified by reprecipitation using dichloromethane/petroleum-ether to yield (IIIb) (480mg, 85%), (IIIa) was prepared in the same way.
- (d) Preparation of $[\text{CpFe}(\text{CO})\text{I}]_2 \text{CN}(\text{CH}_2)_6\text{NC}$. Iodine (500mg) was added to a solution of (IIId) (500mg) in chloroform (15 cm^{-3}) and refluxed for 30 minutes. The excess iodine was removed by extraction with sodium thiosulphate solution and the solvent was removed. The residue was chromatographed on alumina grade (IV). Dichloromethane eluted first a brown band which yielded $\text{CpFe}(\text{CO})_2\text{I}$ (300mg,

42%) and secondly a black green band which gave the product (IVb) (230mg, 19%) which was recrystallised from dichloromethane/petroleum-ether. (IVa) was prepared similarly.

(e) Preparation of $[\text{Fe}(\text{CO})_4]_2 \text{CN}(\text{CH}_2)_6\text{NC}$. 1,6-diisocyanohexane (136mg) was added to an excess of $\text{Fe}_2(\text{CO})_9$ (1.0g) in diethylether (50 cm^3) and the mixture was refluxed for 30 minutes. The solvent was removed and the residue chromatographed on alumina grade (IV). A light yellow band was eluted by a 1:1 mixture of dichloromethane/petroleum-ether (40:60). The solvent was removed at ice temperature under reduced pressure (0.1mm Hg) to yield a light yellow solid (Vb) (400mg, 85%). (Va) was prepared similarly. The same products are obtained on reaction of (Ia,d) with $\text{Fe}_3(\text{CO})_{12}$ in refluxing benzene.

TABLE 1
Analytical Data

<u>Complex</u>	<u>Calculated</u>			<u>Found</u>		
	<u>C</u>	<u>H</u>	<u>N</u>	<u>C</u>	<u>H</u>	<u>N</u>
(IIa)	49.2	3.28	3.83	48.9	3.29	4.10
(IIb)	49.9	3.49	3.75	49.8	3.45	4.31
(IIc)	50.5	3.69	3.69	50.3	3.60	3.91
(IId)	51.8	4.06	3.55	52.1	4.27	3.76
(IIIa)	35.2	2.54	2.73	35.6	2.57	3.52
(IIIb)	37.8	3.15	2.59	37.3	3.15	2.80
(IVa)	30.4	2.22	4.43	30.6	2.09	4.73
(IVb)	34.9	3.20	4.07	34.8	3.13	3.59
(Va)	34.6	0.96	6.73	34.9	1.02	7.64
(Vb)	40.7	2.54	5.93	41.3	2.60	6.53

TABLE 2

 ^1H N.m.r. Spectra Data^a

<u>Complex</u>	<u>Cp</u>	<u>CH₂(α)</u>	<u>CH₂(β)</u>	<u>CH₂(γ)</u>	<u>ratio A:B:C</u>
(IIa) ^c	4.88 (A) ^b	4.34 (s)	-	-	1 : 4 : 0
	4.86 } 4.70 } (B) 4.59 }	3.71 (m)	-	-	
(IIb) ^c	4.86 (B)	3.81 (B, b; t, J = 5.7)	(0.83 - 1.80)(B+C,m)		0 : 4 : 1
	4.70 } 4.59 } (B + C) 4.57 }	3.42 (B,te; t, J = 5.8)			
(IIc) ^c	4.83 (B)	3.84 (B, b; t, br)	(1.16 - 1.80) (B+C,m)	-	0 : 1 : 2
	4.69 } (B + C) 4.58 }	3.48 (B,te, t, br) 3.18 (C; t, br)			
(IIId) ^c	4.83 (B)	3.87 (B, b; t, J = 7.4)	(0.53 - 1.74) (B + C; m)		0 : 1 : 7
	4.69 } (B + C) 4.58 }	3.35 (B, te; t, br) 3.19 (C; t, J = 5.9)			
(IVa) ^d	4.83 } 4.81 }	4.10 (s)			

Cont over.....

Table 2 continued.....

<u>Complex</u>	<u>Cp</u>	<u>CH₂(α)</u>	<u>CH₂(β)</u>	<u>CH₂(γ)</u>	<u>ratio A:B:C</u>
(IVb)	4.73	3.77 (t, J = 6.2)	(1.41 - 1.99) (m)		

^a Chemical shifts in p.p.m. from tetramethylsilane; s = singlet, t = triplet, m = multiplet.

^b A,B,C, = isomers A,B,C; te = terminal, b = bridging.

^c d² - dichloromethane solution.

^d d - chloroform solution.

TABLE 3

 ^{13}C N.m.r. Spectral Data^a

Complex	CO(te)				CO(b)				CN(b)		CN(te)		Cp	Other ^f	
	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>	<u>f</u>	<u>g</u>	<u>h</u>	<u>i</u>	<u>j</u>	<u>k</u>	<u>l</u>			
(IIa) ^b	209.9	212.1	210.4	-	271.1	278.6	272.3	-	253.6	246.7	160.8	-	86.6	CH ₂ (A)	60.9
													86.3	CH ₂ (B,b)	57.5
													85.5	CH ₂ (B,t)	45.0
(IIb) ^b	-	209.5	207.5	211.7	-	277.6	271.6	278.3	-	247.7	161.0	158.4	86.2	CH ₂ (α ,B,b)	g
													85.9	CH ₂ (α ,B,t)	41.2
													85.1	CH ₂ (α ,C)	39.7
														CH ₂ (β ,B)	29.2
														CH ₂ (β ,C)	27.7
(IIc) ^{b,c}	-	-	-	211.0	-	-	-	278.5	-	-	-	-	86.3	CH ₂ (α ,C)	42.9
													86.1	CH ₂ (β ,C)	22.9
													85.3		
(IId) ^{b,d}	-	-	-	211.6	-	-	-	278.7	-	-	-	158.4	85.0	CH ₂ (α ,C)	43.2
													85.8	CH ₂ (β ,C)	27.6
														CH ₂ (γ ,C)	23.6

Cont over.....

TABLE 3 Cont.

Complex	CO(te)					CO(b)			CN(b)		CN(te)		Cp	Other ^f	
	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>	<u>f</u>	<u>g</u>	<u>h</u>	<u>i</u>	<u>j</u>	<u>k</u>	<u>l</u>			
(IIIa) ^e		207.5				254.9			320.1		-		89.6	CH ₂	58.2
(IIIb) ^e		207.9	}			254.9			319.6		-		89.7	CH ₂ -α	59.9
		208.2											90.3		CH ₂ -β
														CH ₂ -γ	26.4
(Va) ^b		210.9				-			-		160.8			CH ₂	45.6
(Vb) ^b		212.3				-			-		154.4			CH ₂ -α	45.6
														CH ₂ -β	28.4
														CH ₂ -γ	25.2

^a Chemical shifts in p.p.m from tetramethylsilane.

^b (CH₂Cl₂/CD₂Cl₂) solution; spectra of (IIa - d) at -30°C.

^c Limited solubility; only carbonyl resonances of isomer (B) detectable.

^d Resonances of minor isomer (B) not detected.

^e CH₃CN/CD₃CN solution.

^f A,B,C, = A,B,C isomers; b = bridging, t or te = terminal.

^g Resonance under solvent peak at 53.9 p.p.m.

TABLE 4
Infrared Spectral Data (cm⁻¹)

<u>Complex</u>	<u>CNt</u>	<u>COt</u>		<u>COb</u>		<u>CNb</u>
		<u>Z</u>	<u>Y</u>	<u>X</u>	<u>W</u>	<u>V</u>
(IIa) ^a		1990(10) ^b	1946(6.5)	1790(4.3)	1750(5.9)	1722(3.1) 1706(3.5)
(IIb) ^a		1987(10)	1967(sh) 1943(9.7)	1797(3.7)	1759(10)	1711(5.2)
(IIc) ^a		1987(6.2)	1943(8.0)	1783(2.4)	1755(10)	1711(2.2)
(IId) ^a		1984(3.8)	1947(8.2)	1779(2.0)	1755(10)	1715(sh)
(IIIa) ^c		2015 1990		1825		1525
(IIIb) ^c		2010 1980		1820		1570
(IVa) ^d	2149	1980				
(IVb) ^d	2163	1975				
(Va) ^d	2171	2060 2003 1979				
(Vb) ^d	2175	2057 1995 1969				

^a (10% CH₂Cl₂/CS₂) solution; CNt obscured by solvent absorption but can be seen at ca. 2130 cm⁻¹ in CH₂Cl₂ solution.

^b Relative intensities given in parentheses.

^c Nujol mull.

^d Hexane solution.

Figure 1

$^1\text{H.n.m.r. of } [\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2[\text{CN}(\text{CH}_2)_2\text{NC}] \text{ (IIa)}$

Solvent : CD_2Cl_2

Temperature : -40°C

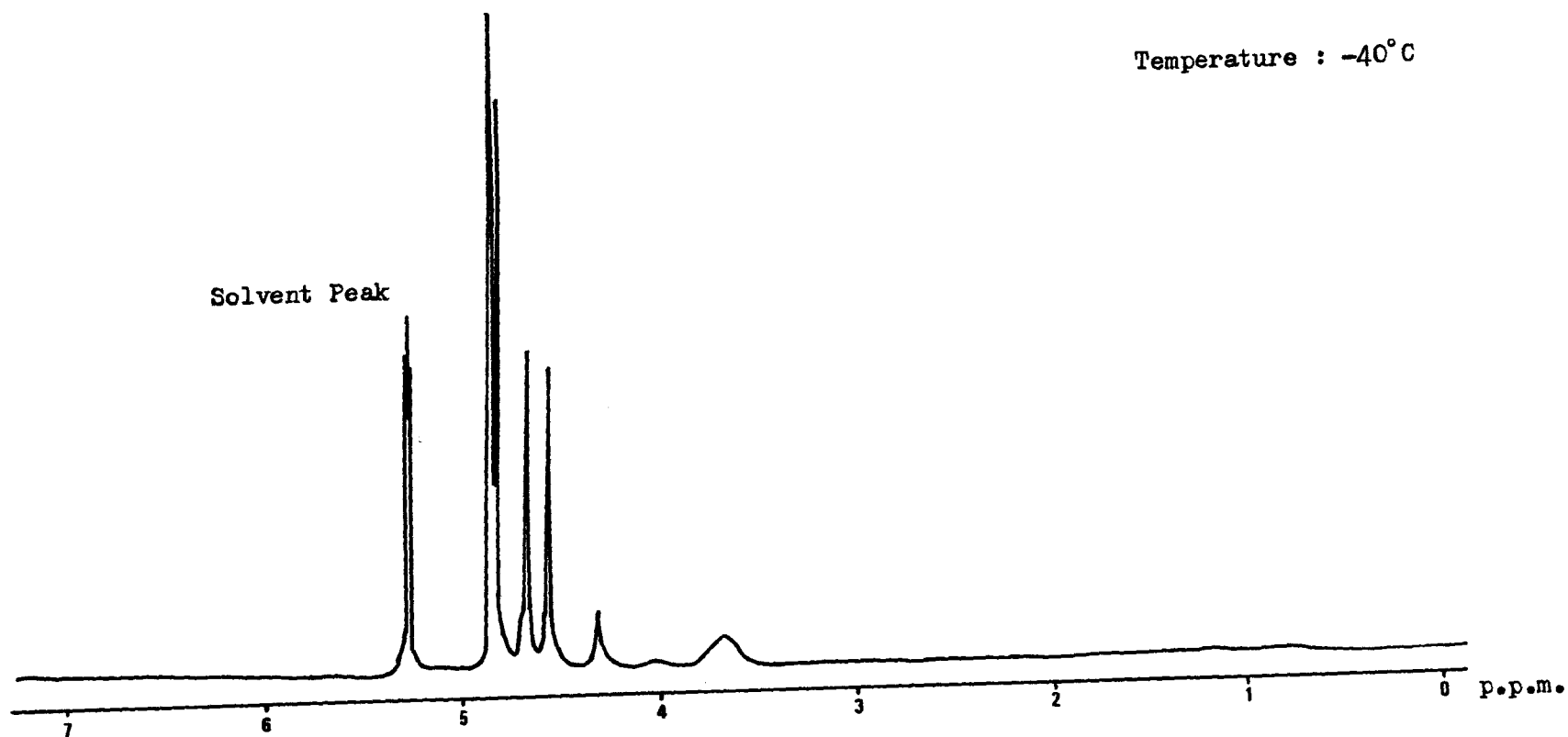


Figure 2

V.T. ^1H n.m.r. of $[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2[\text{CN}(\text{CH}_2)_2\text{NC}]$ (IIa) in the cyclopentadienyl region

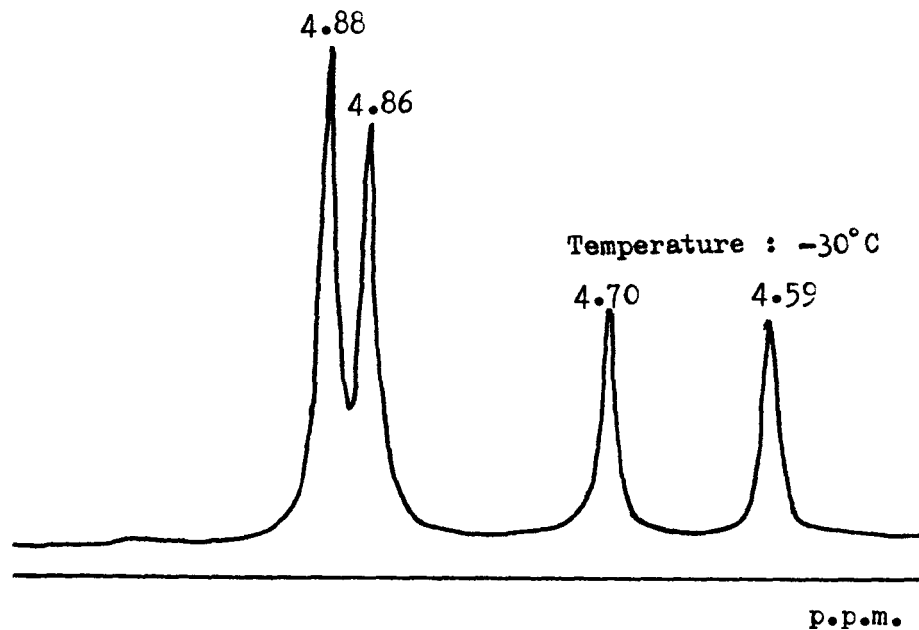
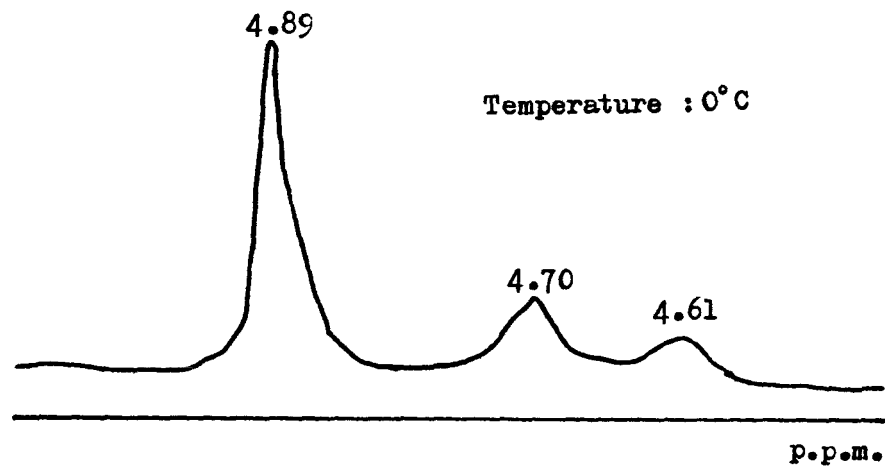
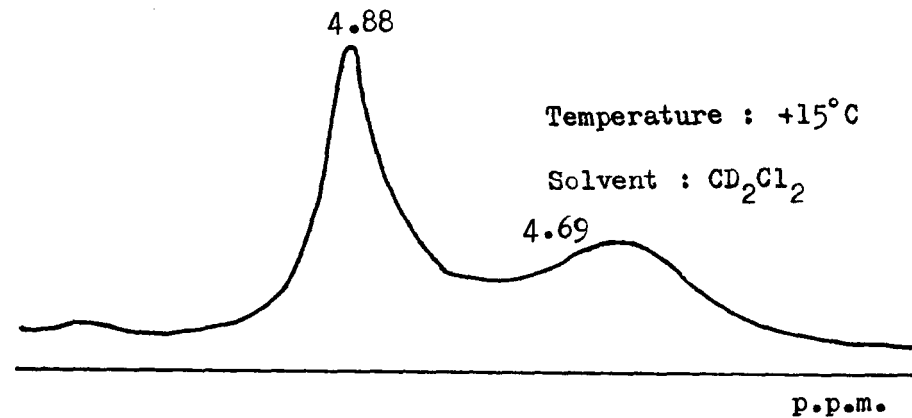
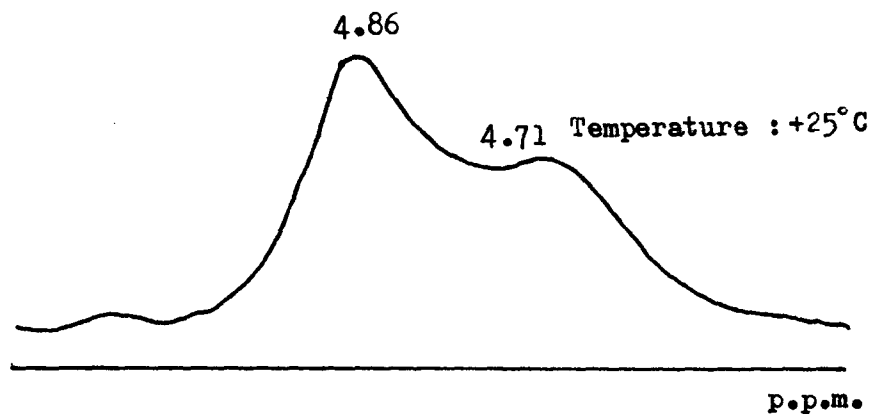


Figure 3

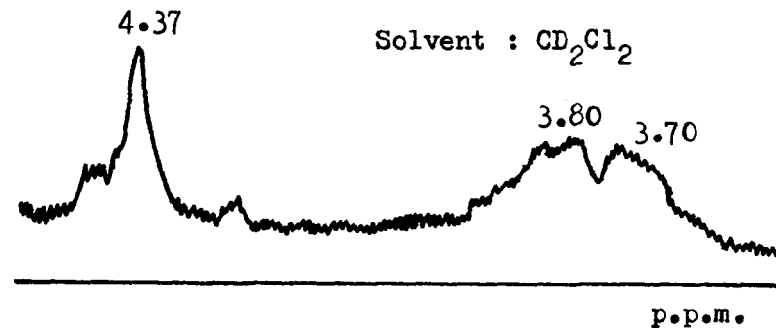
V.T. ^1H n.m.r. of $[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2[\text{CN}(\text{CH}_2)_2\text{NC}]$ (IIa) in the alkyl region

Temperature : $+25^\circ\text{C}$



Temperature : 0°C

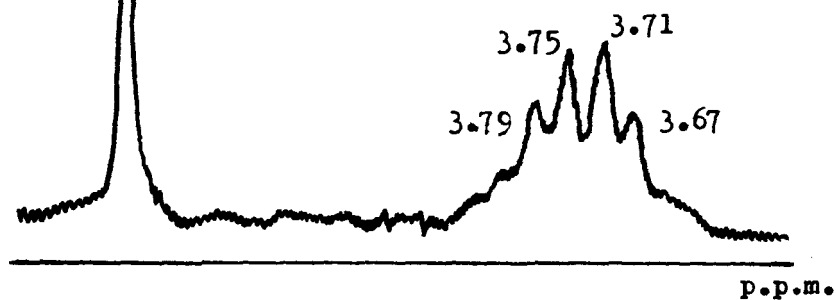
Solvent : CD_2Cl_2



Computer Simulation of an AA'BB' System

4.35

Temperature : -15°C



$\delta_A = 3.67$

$\delta_B = 3.78$

Geminal Coupling = -14 Hz

Vicinal Coupling = 6 Hz

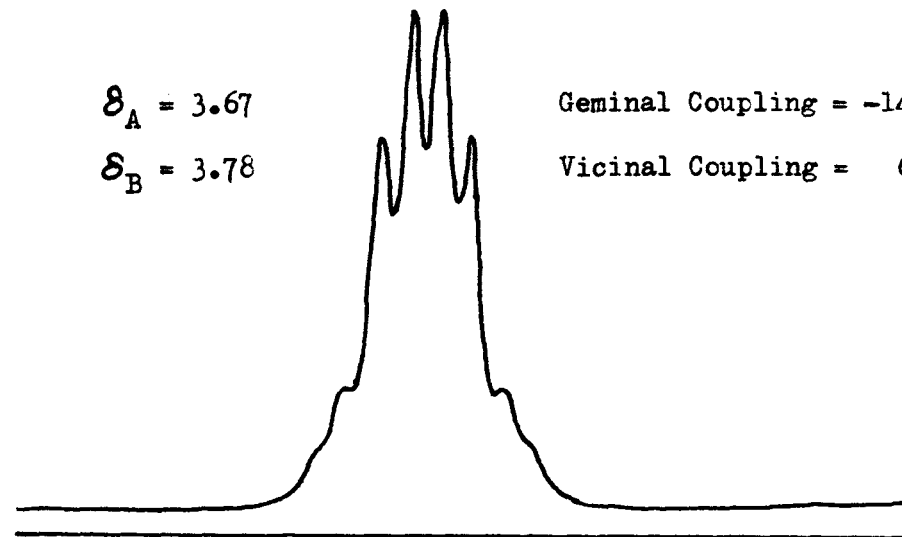


Figure 4

^{13}C n.m.r. of $[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2[\text{CN}(\text{CH}_2)_2\text{NC}]$ (IIa)

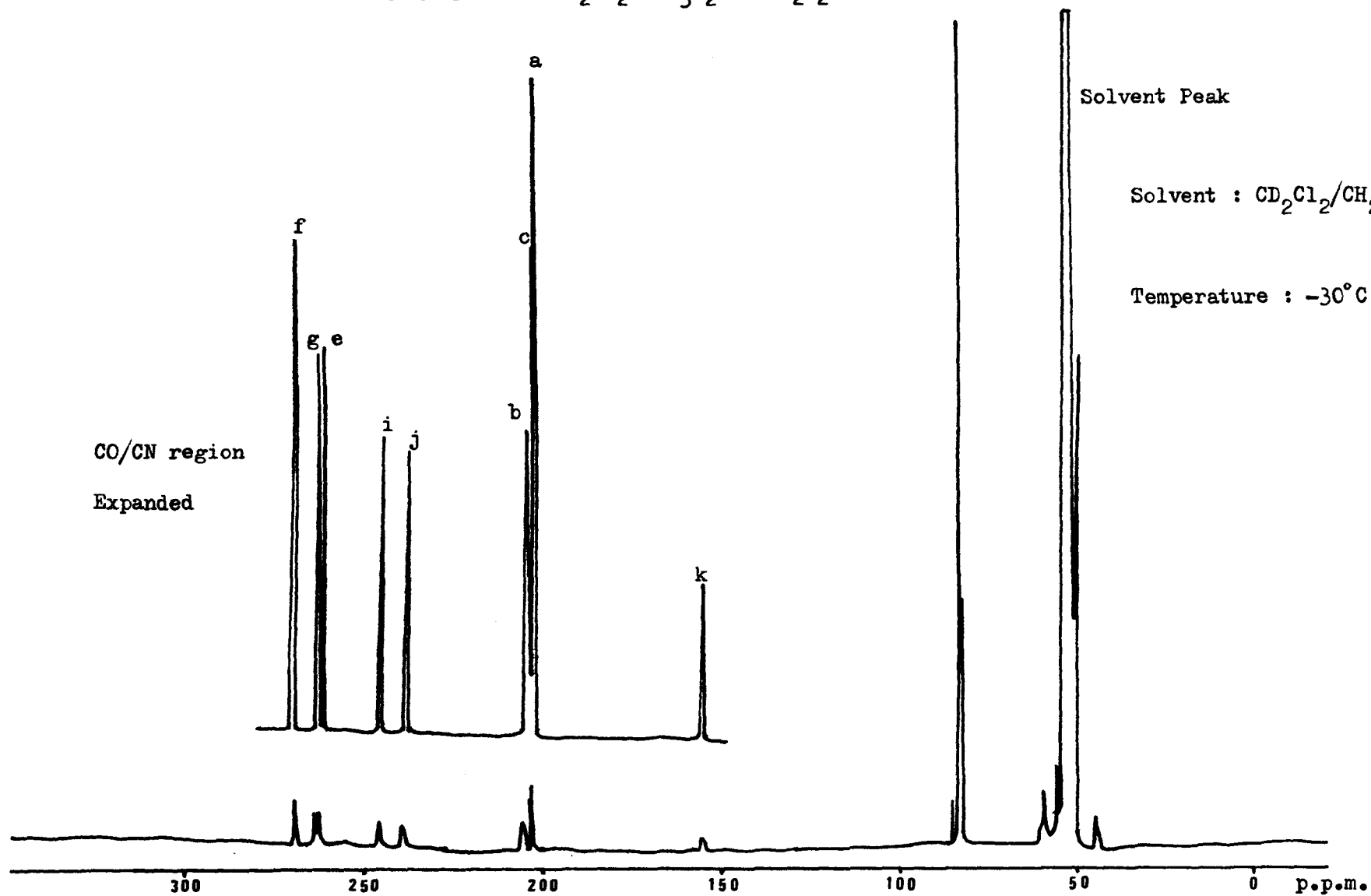


Figure 5

^1H n.m.r. of $[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2[\text{CN}(\text{CH}_2)_3\text{NC}](\text{Iib})$

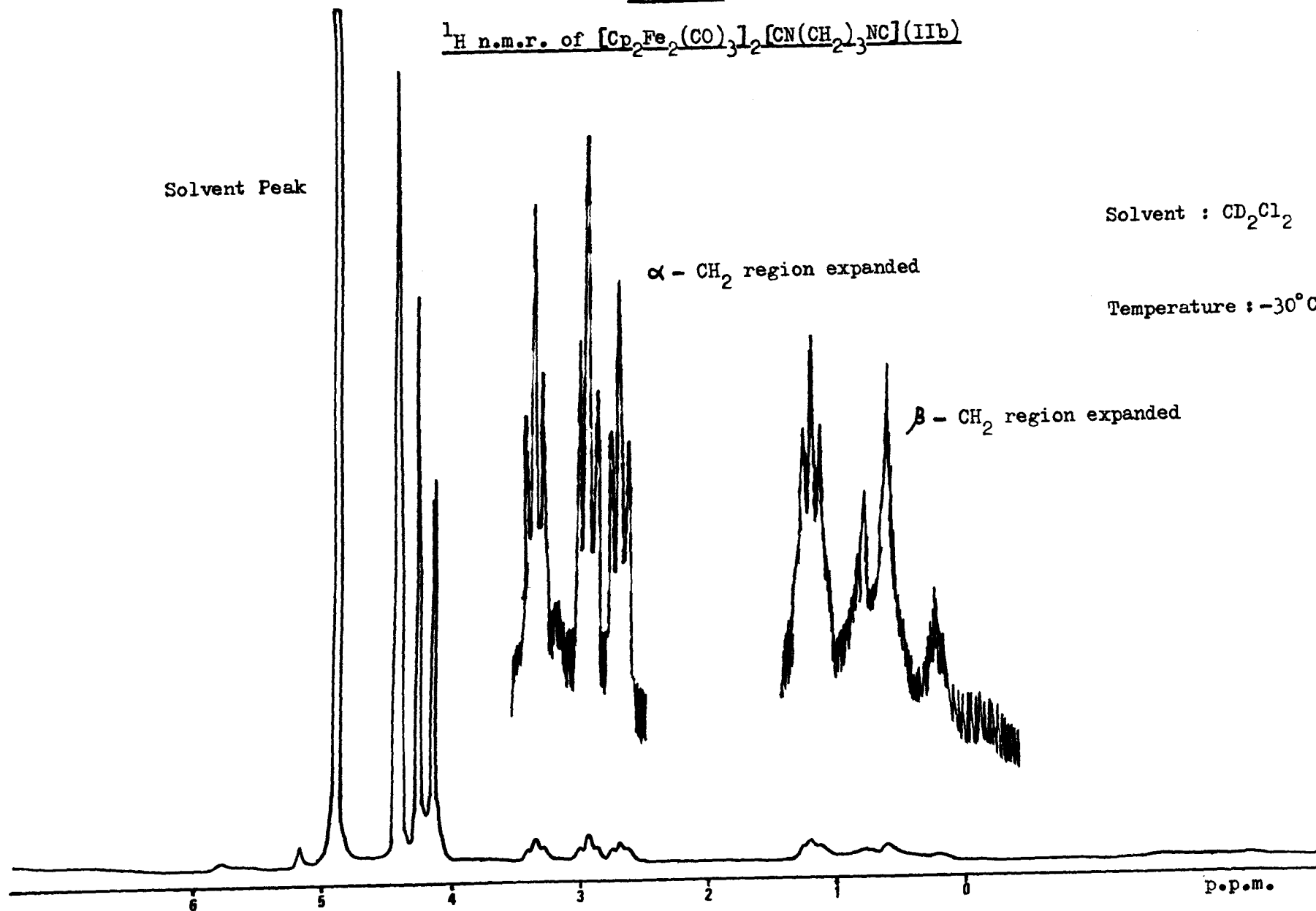
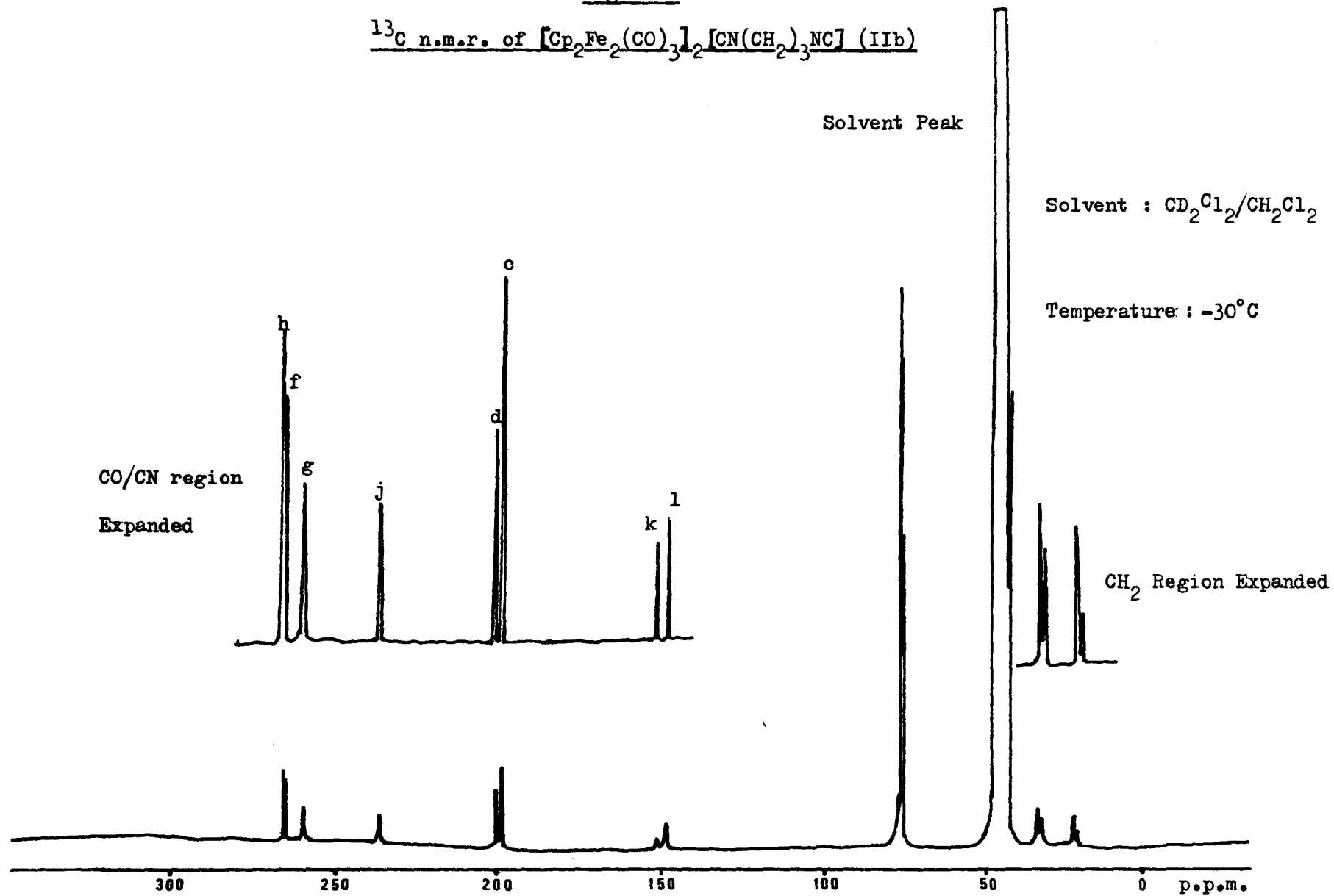


Figure 6

^{13}C n.m.r. of $[\text{Cp}_2\text{Fe}(\text{CO})_3]_2[\text{CN}(\text{CH}_2)_3\text{NC}]$ (Iib)



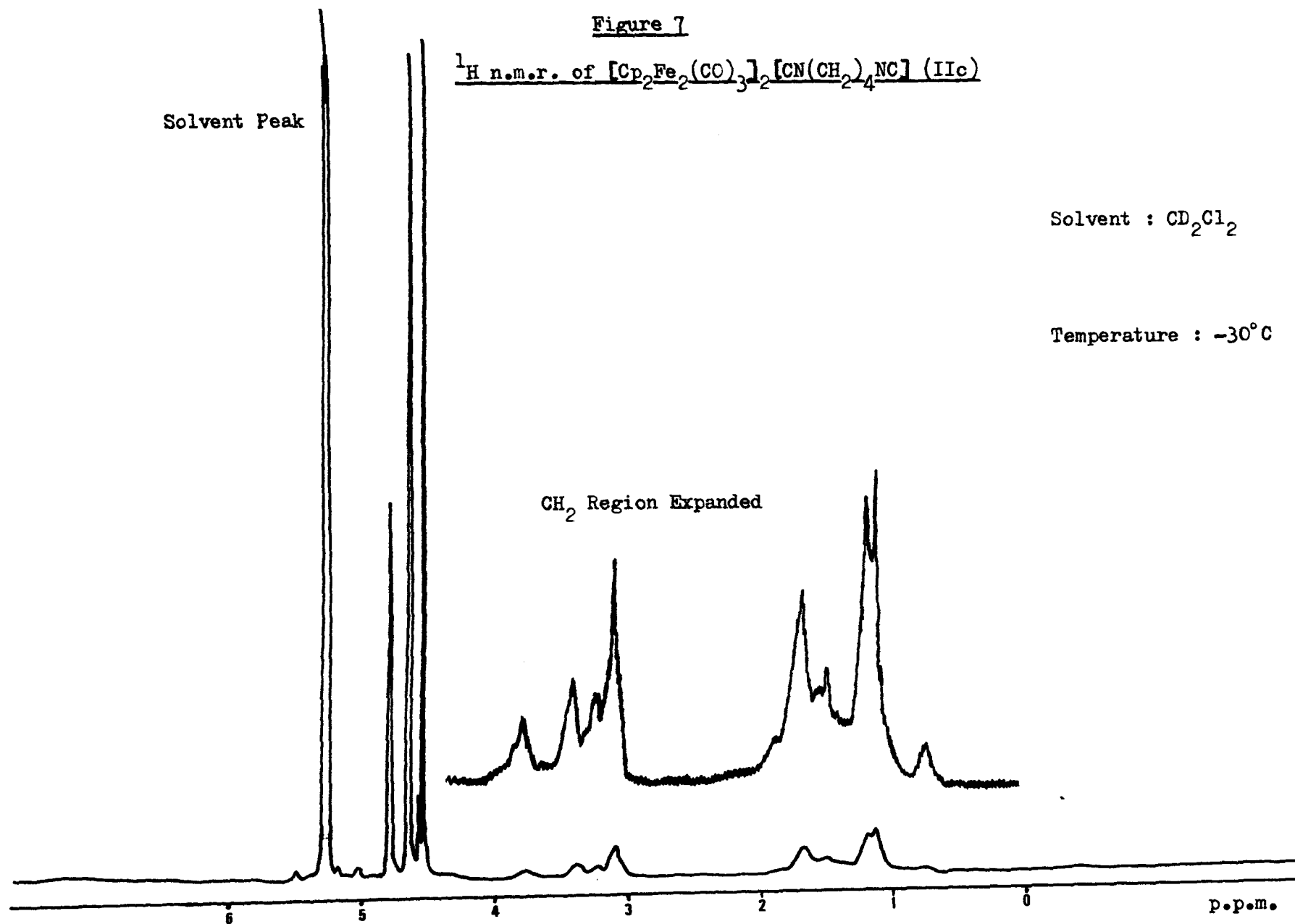
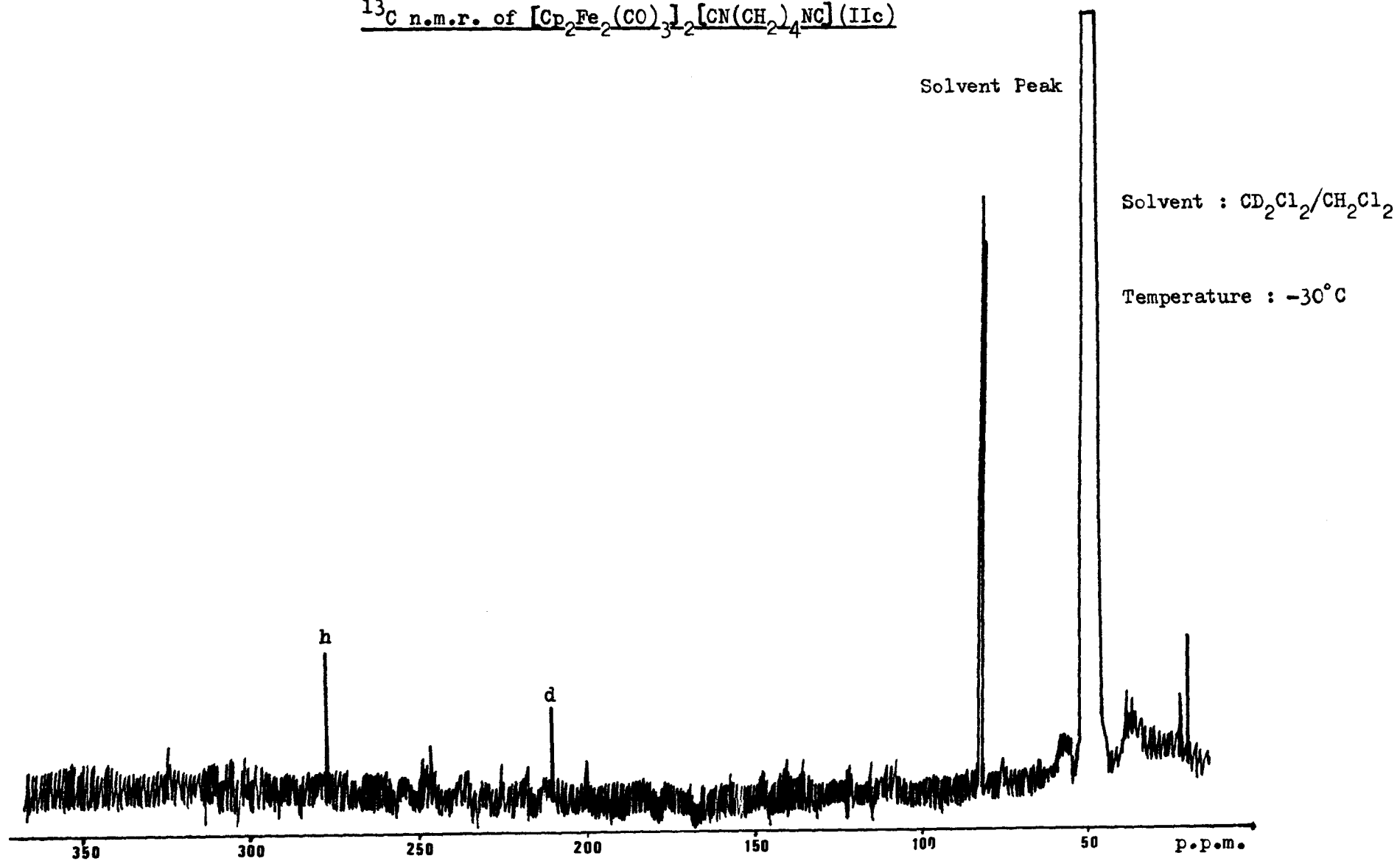


Figure 8

^{13}C n.m.r. of $[\text{Cp}_2\text{Fe}(\text{CO})]_3[\text{CN}(\text{CH}_2)_4\text{NC}]$ (IIc)



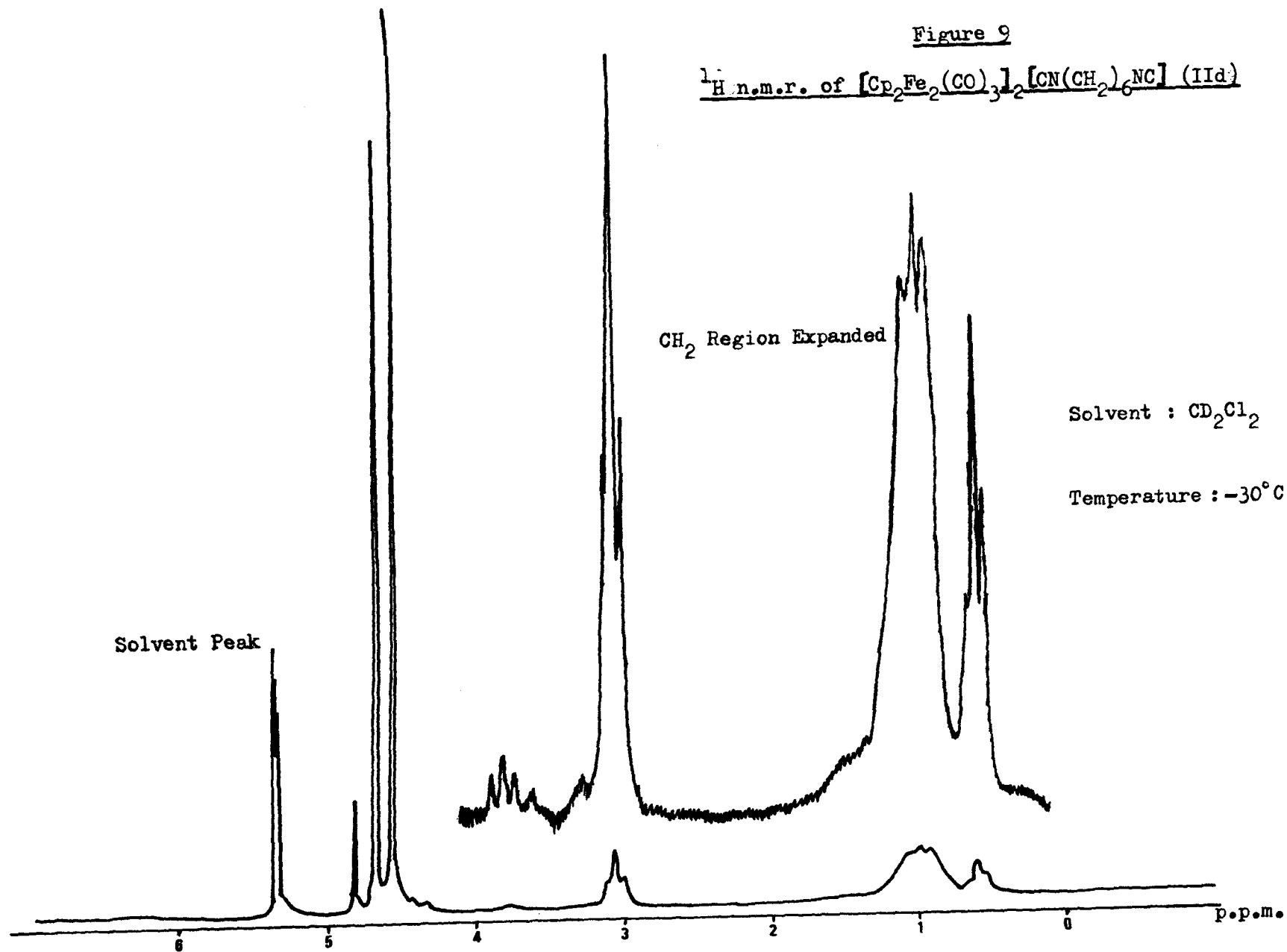


Figure 10

^{13}C n.m.r. of $[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2[\text{CN}(\text{CH}_2)_6\text{NC}]$ (IIa)

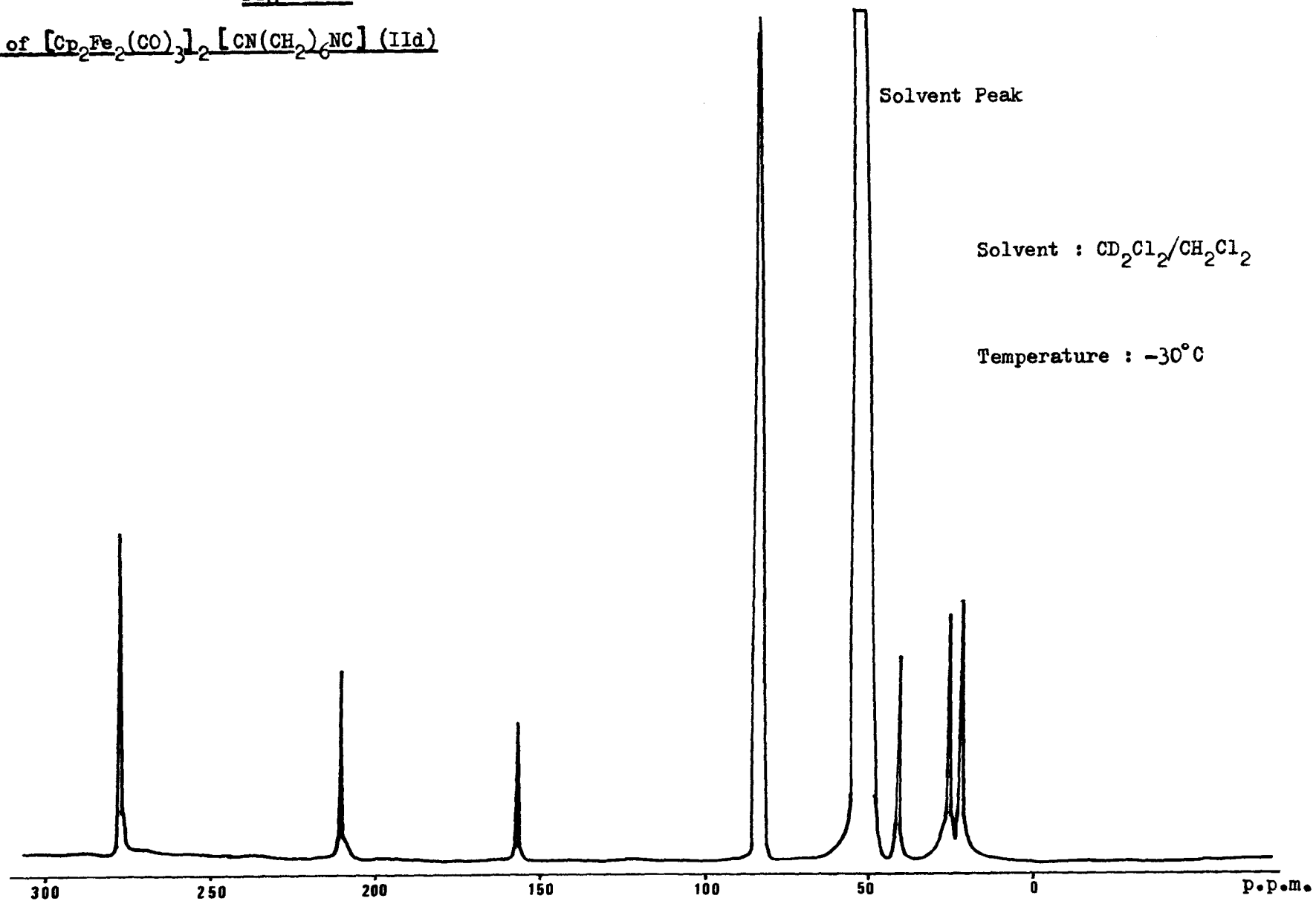


Figure 11

^1H n.m.r. of $\{[\text{Cp}_2\text{Fe}(\text{CO})_3]_2[\text{CN}(\text{H})(\text{CH}_2)_2(\text{H})\text{NCl}]\}^{2+}(\text{PF}_6)^- \text{ (IIIa)}$

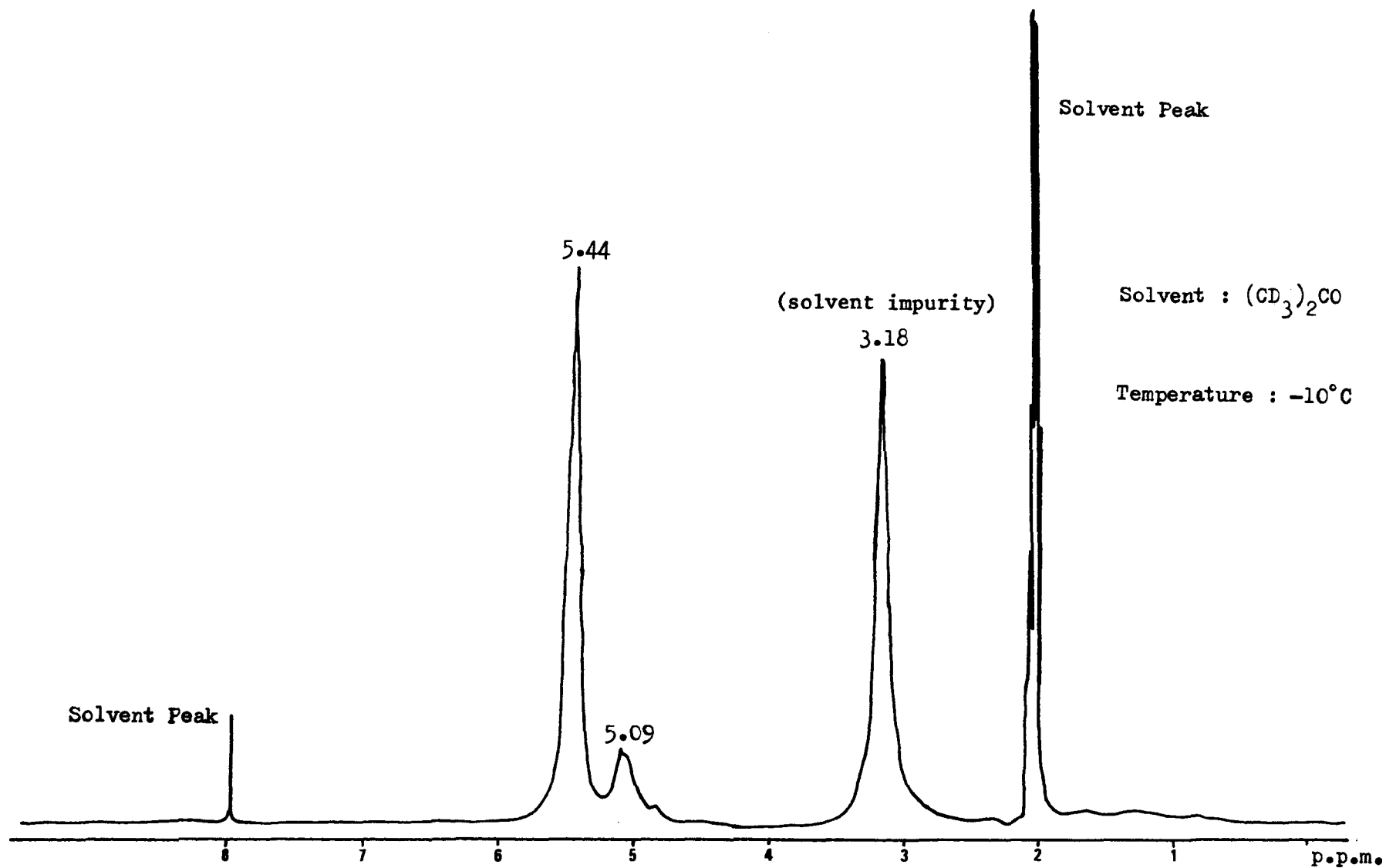
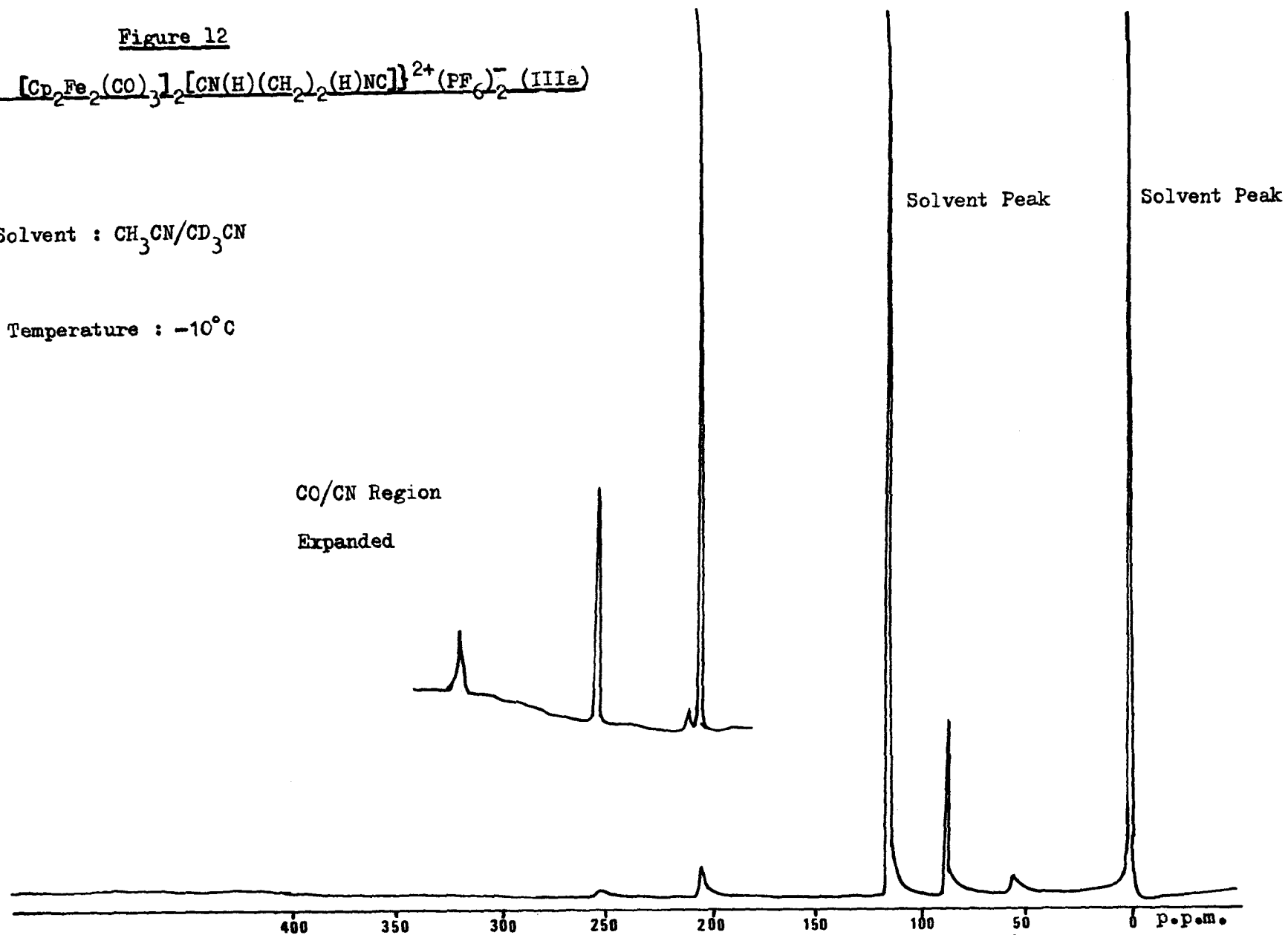


Figure 12

^{13}C n.m.r. of $[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2[\text{CN}(\text{H})(\text{CH}_2)_2(\text{H})\text{NC}]^{2+}(\text{PF}_6)_2^-$ (IIIa)

Solvent : $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$

Temperature : -10°C



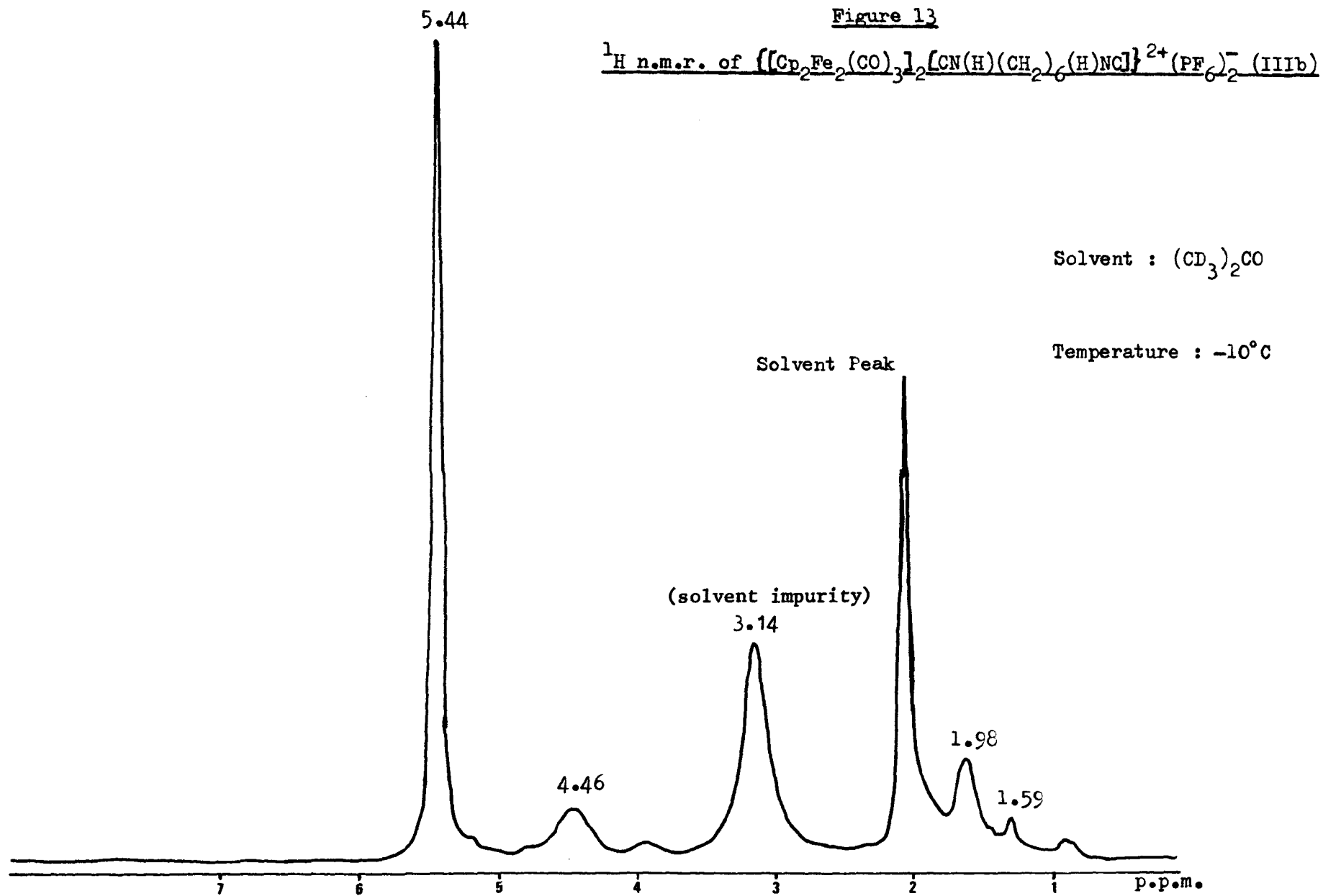


Figure 14

^{13}C n.m.r. of $\{[\text{Cp}_2\text{Fe}_2(\text{CO})_3]_2[\text{CN}(\text{H})(\text{CH}_2)_6(\text{H})\text{NC}]\}^{2+}(\text{PF}_6)_2$ (IIIb)

Solvent Peak

Solvent Peak

Solvent : $\text{CD}_3\text{CN}/\text{CH}_3\text{CN}$

Temperature : -10°C

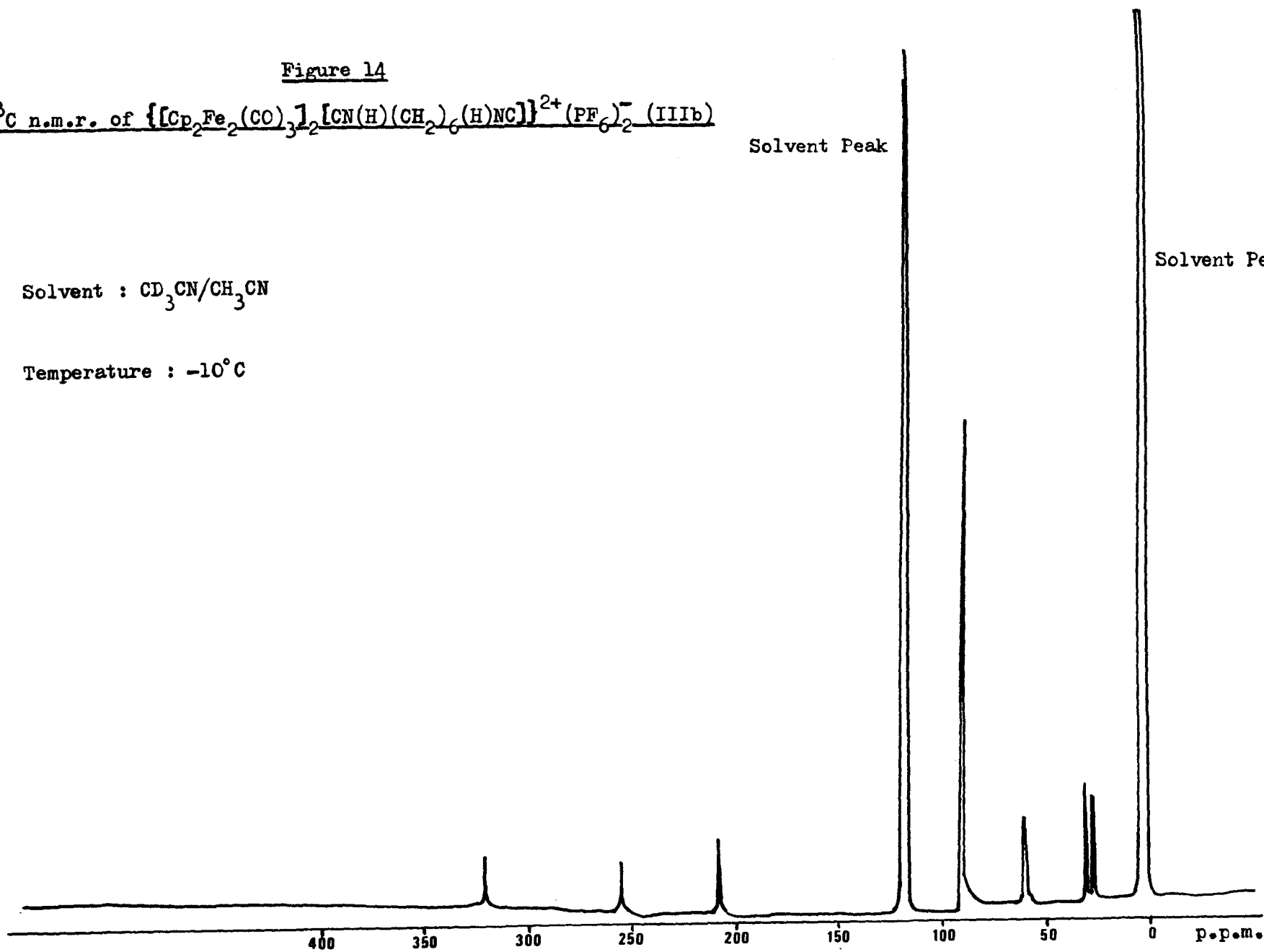
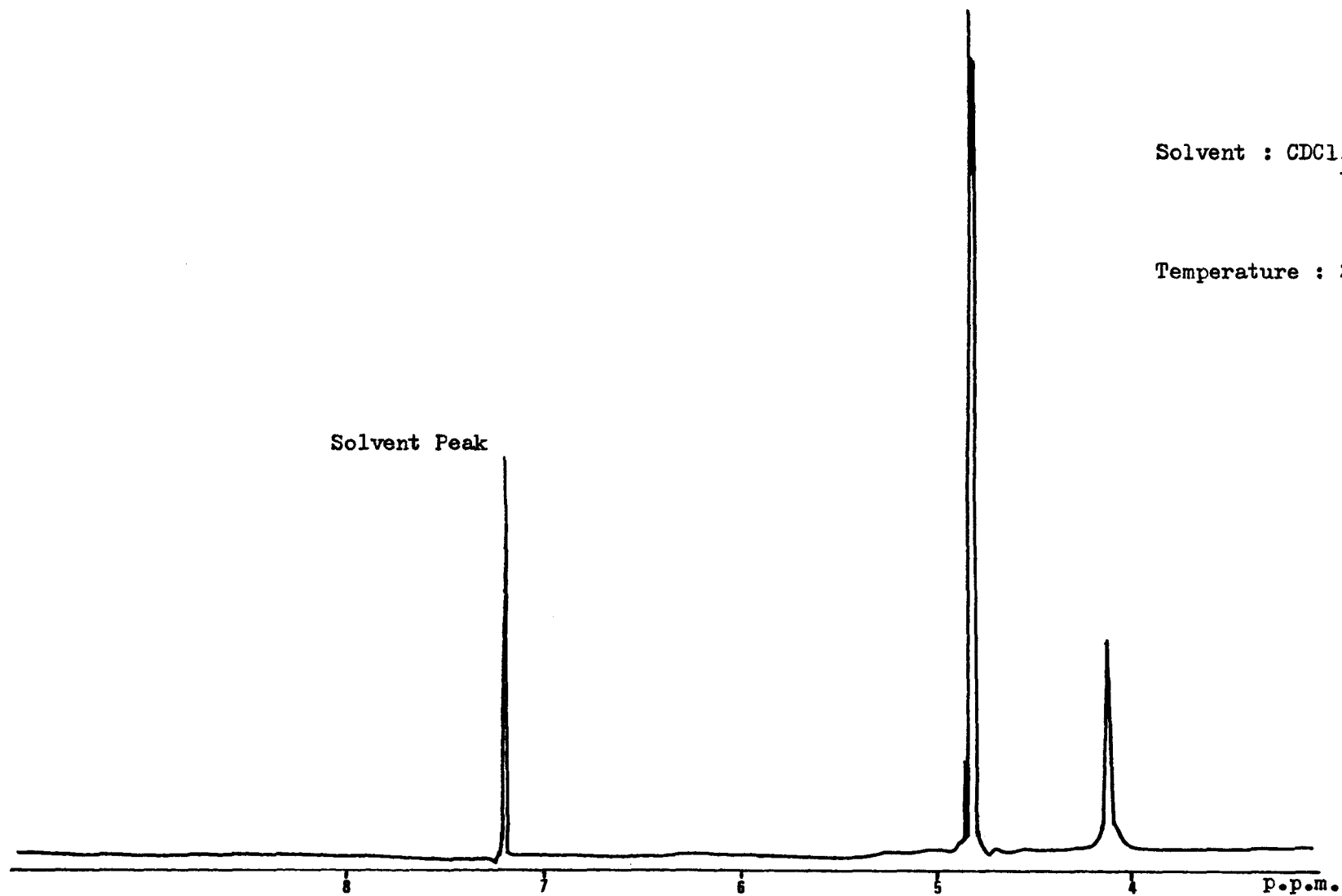


Figure 15

^1H n.m.r. of $[\text{CpFe}(\text{CO})\text{I}]_2[\text{CN}(\text{CH}_2)_2\text{NC}]$ (IVa)

Solvent : CDCl_3

Temperature : 20°C

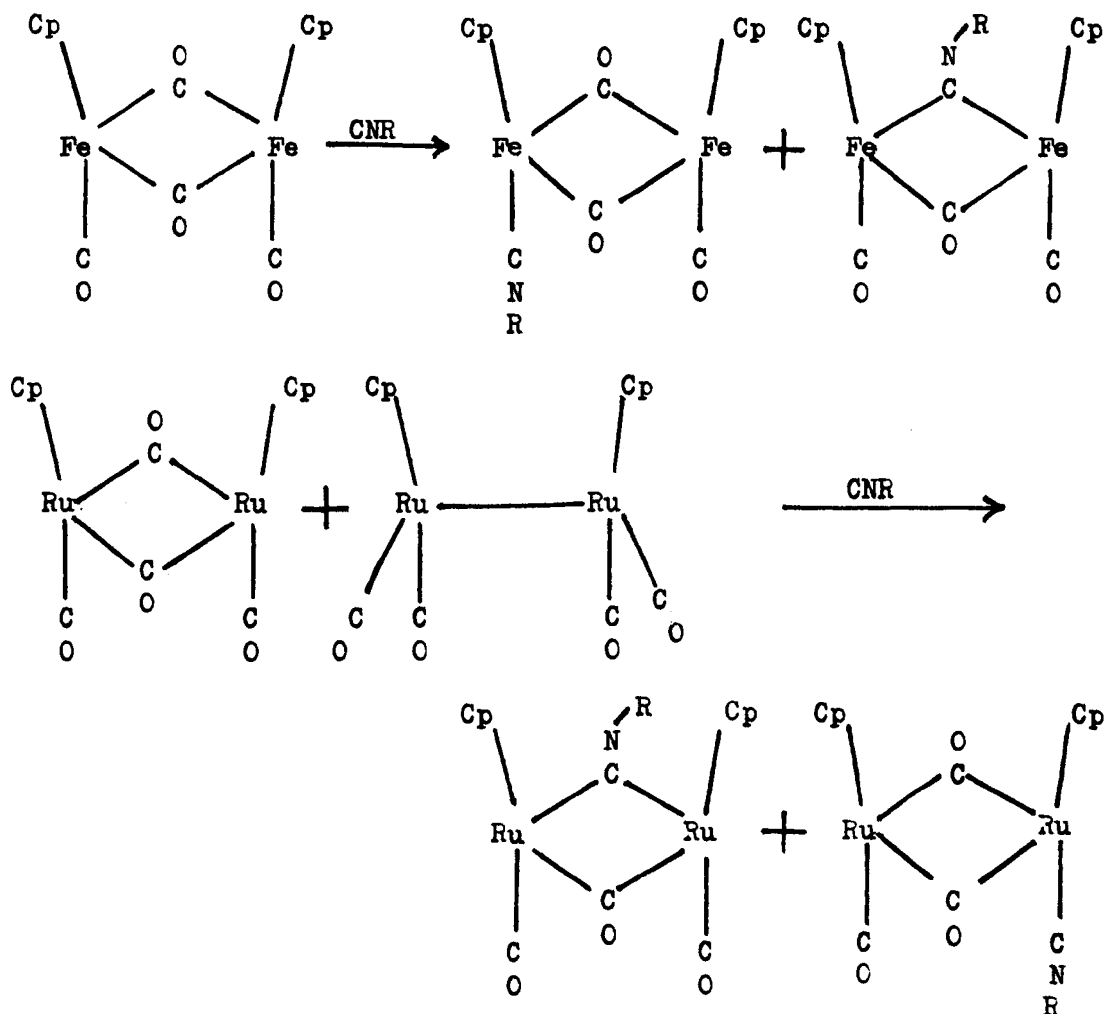


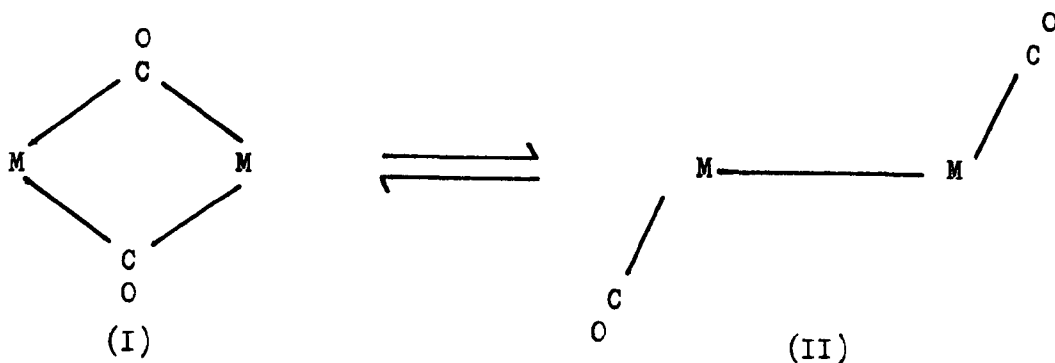
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CHAPTER 5

The complex $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ reacts with isonitriles under mild conditions to yield primarily mono-substituted carbonyl complexes $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CNR})$.¹ Although isonitrile ligands may occupy a bridging or terminal position within the complex, there is no evidence of non-bridged isomers upon substitution. Thus doubly bridged $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ remains doubly bridged upon isonitrile substitution. In solution $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ exists as an approximate 1:1 mixture of doubly bridged : non-bridged isomers.² Reaction of isonitriles with $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ results in the mono-substituted isonitrile complexes $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CNR})$ which exist in solution as the doubly bridged species.³ In this case a structural conversion of the type (I) \rightarrow (II) has occurred. To further investigate these types of structural conversions, the iron group carbonyl complexes $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ and $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ were reacted with various phosphorus (III) ligands.





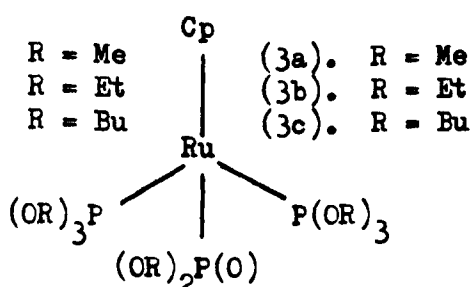
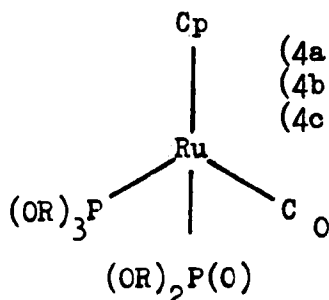
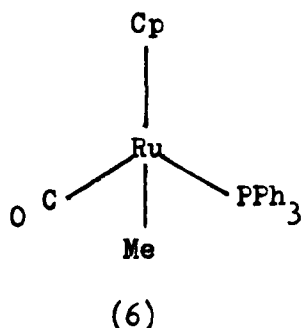
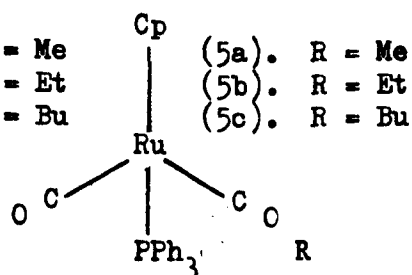
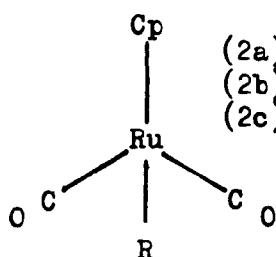
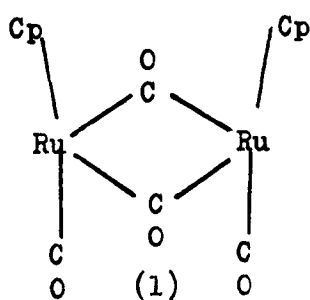
Reactions of tertiary phosphines and phosphites with polynuclear transition metal carbonyl complexes under mild conditions usually results only in carbonyl substitution, although in some cases, disproportionation may be observed.⁴ Previously unique were the reactions of the dimers $\text{Cp}_2\text{M}_2(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}$) with alkyl phosphites which yield as two of the products the alkyl $\text{CpM}(\text{CO})_{3-x}[\text{P}(\text{OR})_3]_x\text{R}$ ($x = 0, 1$) and phosphonate $\text{CpM}(\text{CO})_2[\text{P}(\text{OR})_3]\text{P}(\text{O})(\text{OR})_2$ complexes.^{5,6} Discussed below are the reactions between tertiary phosphites and phosphines with the iron group carbonyls $\text{Cp}_2\text{M}_2(\text{CO})_4$ ($\text{M} = \text{Fe}, \text{Ru}$).

(a). Reaction of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (1) with tertiary alkyl phosphites.

Reaction of (1) with a five fold excess of $\text{P}(\text{OR})_3$ proceeds smoothly in refluxing xylene to yield as products the alkyl $\text{CpRu}(\text{CO})_2\text{R}$ (2a-c; $\text{R} = \text{Me}, \text{Et}, \text{Bu}^n$) and phosphonate $\text{CpRu}[\text{P}(\text{OR})_3]_2\text{P}(\text{O})(\text{OR})_2$ (3a-c; $\text{R} = \text{Me}, \text{Et}, \text{Bu}^n$) complexes. The reactions may be followed conveniently by infrared monitoring of the disappearance of (1). Analysis of the crude reaction mixture (vide infra) at this point indicates a 1:1 mixture of (3a-c) and the mono-substituted derivatives $\text{CpRu}(\text{CO})[\text{P}(\text{OR})_3]\text{P}(\text{O})(\text{OR})_2$ (4a-c; $\text{R} = \text{Me}, \text{Et}, \text{Bu}^n$). Although (4b) has been isolated by careful chromatography the general difficulty in separation was overcome by continuing to reflux until complete substitution had been achieved to yield only (3a, c) as isolated products.

The alkyl complexes have been prepared previously by reaction of $\text{Na}[\text{CpRu}(\text{CO})_2]$ with the appropriate alkyl iodide,⁷ and infrared and spectroscopic data are in agreement with published results. Because difficulty was experienced in separation of these volatile substances from reaction

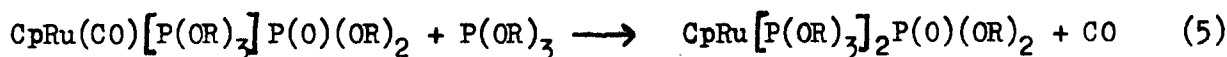
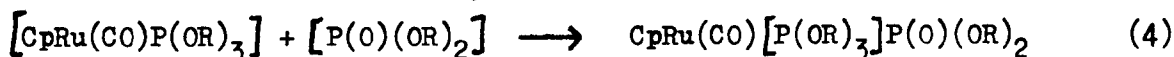
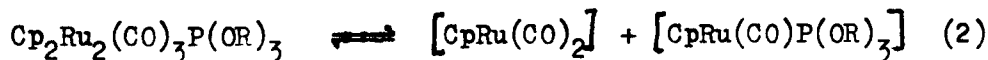
impurities, they were further characterised by reaction with PPh_3 , which results in insertion of carbon monoxide into the Ru - R bond to yield the crystalline $\text{CpRu}(\text{CO})(\text{PPh}_3)\text{COR}$ complexes (5a-c; $\text{R} = \text{Me}, \text{Et}, \text{Bu}^n$). These complexes are identical with specimens prepared by the reaction of PPh_3 with authentic $\text{CpRu}(\text{CO})_2\text{R}$ (2a-c). The complexes were characterised by analysis, infrared and nmr spectroscopy. Particularly characteristic are the $\nu(\text{CO})$ acyl stretching frequencies at ca. 1600cm^{-1} and the acyl ^{13}C carbonyl resonance at ca. 255ppm. It is of interest to note that in (5b, c) the $\alpha\text{-CH}_2$ protons form an AB system in the nmr spectrum (confirmed by decoupling) due to the proximity to the chiral ruthenium centre. The ^1H nmr spectra of (5a-c) are shown in figures (1)-(3), and the computer simulated spectrum for (5b) confirms the ABX_3P nature of the spectrum (figure 4). Especially in the case of (2a), prolonged reaction with PPh_3 also yields the alkyl complex $\text{CpRu}(\text{CO})(\text{PPh}_3)\text{Me}$ (6) resulting from decarbonylation of $\text{CpRu}(\text{CO})(\text{PPh}_3)\text{COMe}$ (5a); characteristic of (6) and the parent derivative $\text{CpRu}(\text{CO})_2\text{Me}$ (2a) are the high field ^1H and ^{13}C resonances of the methyl group. The ^1H nmr spectrum of (6) is shown in figure (5). Both the carbonyl insertion and decarbonylation reactions are well established for the analogous iron complexes. ^{8a,b}



The new complexes $\text{CpRu}[\text{P}(\text{OR})_3]_2\text{P}(\text{O})(\text{OR})_2$ (3a-c) form part of a small but growing number of covalent transition metal phosphonate derivatives. They are isolated as slightly hygroscopic white solids (3a) or oils (3b,c) which are unstable in air. All the complexes exhibit molecular ions in the mass spectrum and fragmentation occurs mainly by loss of R or OR, but fragments due to $\text{CpRu}[\text{P}(\text{OR})_3]_2^+$, $\text{CpRu}[\text{P}(\text{OR})_3]^+$ and $\text{CpRu}[\text{P}(\text{OR})_3]\text{P}(\text{O})(\text{OR})_2^+$ may be identified. A band at ca. 1150cm^{-1} in the thin film infrared spectra of (3a-c) may be assigned to $\nu_{\text{P=O}}$ although some overlap with C - O vibrations may be present; a corresponding assignment has been made to the bands at 1165cm^{-1} in the spectrum of $\text{CpMo}(\text{CO})_2[\text{P}(\text{OMe})_3]\text{P}(\text{O})(\text{OMe})_2$,⁵ and at $(1100-1180\text{cm}^{-1})$ in the spectra of $\text{CpFe}(\text{CO})_x[\text{P}(\text{OR})_3]_{2-x}\text{P}(\text{O})(\text{OR})_2$ ($x = 1, 2$) complexes.⁹ The ^{31}P nmr spectra show a doublet at ca. 160 ppm and a triplet at ca. 110 ppm ($J \approx 80$ Hz) assignable to co-ordinated phosphite and phosphonate respectively. Resonances in the region ca. 80 - 120 ppm may thus be characteristic of phosphonate covalently bound to transition metals,¹⁰ and represent a considerable downfield shift from values found for alkyl phosphonates (ca. 30 ppm).¹¹ The ^1H nmr spectrum of (3a) is also in agreement with this formulation, showing overlapping resonances at 3.49 δ (doublet; $J_{\text{PH}} = 10.5$ Hz) and 3.61 δ (broad inner peak flanked by two sharp singlets). The former may be assigned to phosphonate, while the latter may be assigned to co-ordinated $\text{P}(\text{OMe})_3$ and is characteristic of the $\text{X}_9\text{AA}'\text{X}_9$ pattern previously observed for $\text{CpRu}[\text{P}(\text{OMe})_3]_2\text{Cl}$.¹² The cyclopentadienyl resonance consists of a slightly broadened quartet consistent with an AXY_2 system in which $J_{\text{AX}} \approx J_{\text{AY}}$. The ^1H nmr spectra of the complexes (3a-c) are illustrated in figures (6)-(8). The cyclopentadienyl resonance of $\text{CpRu}(\text{CO})\text{P}(\text{OEt})_3 - \text{P}(\text{O})(\text{OEt})_2$ (4b) is the triplet expected for an AXY system in which $J_{\text{AX}} \approx J_{\text{AY}}$; non-equivalence of the ethyl substituents of the phosphonate ligand may also be detected. The ^1H nmr spectrum of (4b) is illustrated in figure (9).

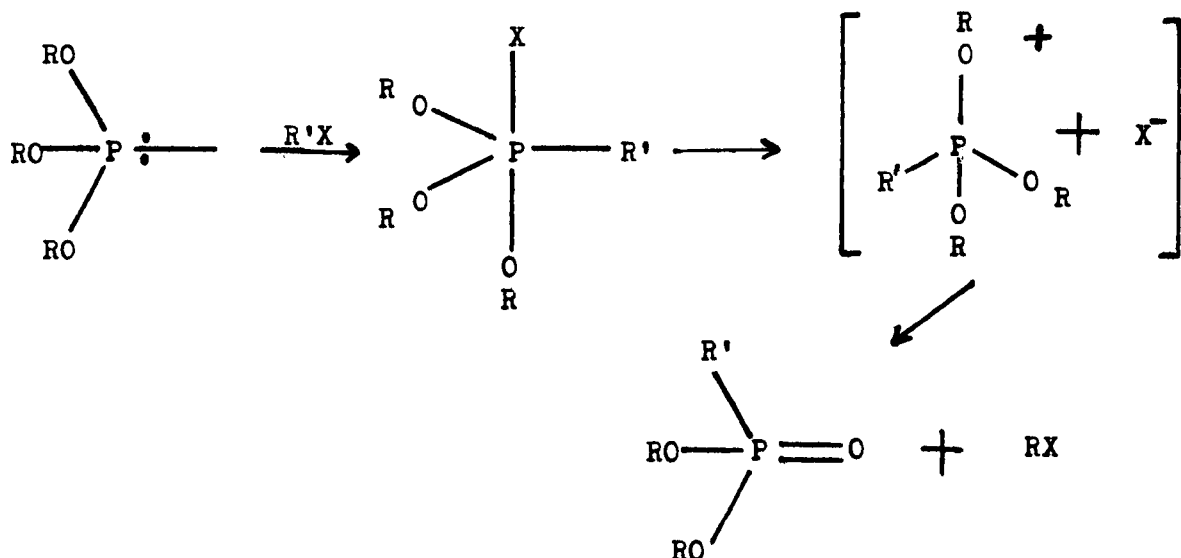
A scheme accounting for these results is shown by the following equations:





If the reaction is stopped immediately after the disappearance of (1), ^{31}P analysis of an aliquot reveals doublets at ca. 96 ppm and 149 ppm ($J_{\text{PP}} \approx 60$ Hz) assignable to phosphonate and co-ordinated phosphite respectively of the mono-substituted $\text{CpRu}(\text{CO})[\text{P}(\text{OR})_3]\text{P}(\text{O})(\text{OR})_2$ (4a-c) derivatives, in addition to signals due to the $\text{CpRu}[\text{P}(\text{OR})_3]_2\text{P}(\text{O})(\text{OR})_2$ (3a-c) complexes; intensities indicate an approximate 1:1 ratio of the two complexes. On this basis, the intermediacy of the mono-substituted dimer of equation (1) seems likely although we have neither isolated or detected this complex during the reaction. One cannot however dismiss as the reaction pathway an intramolecular decomposition of a di-substituted derivative.

Studies on the reactions of the $\text{Cp}_2\text{M}_2(\text{CO})_6$ dimers ($\text{M} = \text{Cr}, \text{Mo}$) show that C - O bond cleavage probably takes place by two competing pathways, one analogous to the scheme above (although involving a di-substituted dimer as the immediate precursor) and the other involving an Arbusov rearrangement of the initially formed disproportionation product $\{\text{CpM}(\text{CO})_2[\text{P}(\text{OR})_3]_2\} \text{CpM}(\text{CO})_3$. Classically the Arbusov rearrangement concerns the reaction of alkyl phosphites with alkyl halides. Presumably the first step in this reaction is addition of $\text{R}'\text{Cl}$ followed by the loss of Cl^- , followed by Cl^- attack upon R.



In the case where $M = Cr$ the radical pathway is preferred and it is known that di-substitution of $Cp_2Cr_2(CO)_6$ to yield $Cp_2Cr_2(CO)_4[P(OMe)_3]_2$ results in significant lengthening of the Cr - Cr bond and an increase in the concentration of monomeric paramagnetic $CpCr(CO)_2P(OMe)_3$ in solution compared to $CpCr(CO)_3$.⁶ Although an Arbusov type rearrangement involving a disproportionated intermediate of the type $\{CpRu(CO)[P(OR)_3]_2\} CpRu(CO)_2$ cannot be dismissed here, the preferred pathway is that which is outlined above in view of the reactions described in (c), which seem more characteristic of radical intermediates. $CpM(CO)_2$ radicals ($M = Fe, Ru$) have been cited as primary photo-products of the irradiation of the $Cp_2M_2(CO)_4$ dimer ($M = Fe, Ru$),¹³ although recent work on the photo-substitution of $Cp_2Fe_2(CO)_4$ by $P(OR)_3$ ligands indicates that this may not be the case.¹⁴

(b). Reaction of $Cp_2Fe_2(CO)_4$ (1a) with tertiary alkyl phosphites.

Thermal reaction of $Cp_2Fe_2(CO)_4$ (1a) with $P(OR)_3$ ligands in refluxing benzene has been reported to yield only mono-substituted dimers of the type $Cp_2Fe_2(CO)_3P(OR)_3$.¹⁵ We have found that reaction of the mono-substituted dimers $Cp_2Fe_2(CO)_3P(OR)_3$ (7a,b; $R = Me, Et$) with a three fold excess of phosphite in refluxing xylene yields as isolated products the acyl $CpFe(CO)-[P(OR)_3]COR$ (8a,b; $R = Me, Et$) and phosphonate $CpFe(CO)[P(OR)_3]P(O)(OR)_2$ (9a,b; $R = Me, Et$) complexes. Reactions may be conveniently followed by infrared monitoring of the disappearance of (7a,b).

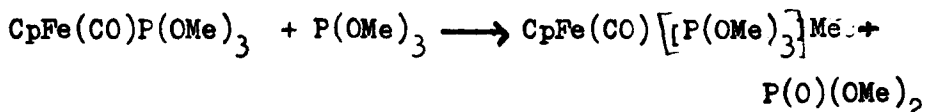
The acyl complexes (8a,b) are undoubtedly the products of the facile insertion of carbon monoxide into the Fe - R bond of the initially formed $CpFe(CO)_2R$ (10a,b; $R = Me, Et$) complexes in the presence of excess phosphite. Amounts of $CpFe(CO)_2R$ (10a,b) can be detected by infrared spectroscopy during the course of the reaction.

The alkyls (10a,b) have been prepared previously,¹⁶ and their reaction with various phosphines and phosphites studied under a variety of reaction conditions.^{17,18} We have found that reaction of authentic $CpFe(CO)_2Et$ (10b) with $P(OEt)_3$ in refluxing xylene results in the formation of $CpFe(CO)P(OEt)_3-$

COEt (8b), identical to samples from the reaction between (7b) and $P(OEt)_3$. Reaction of authentic $CpFe(CO)_2Me$ (10a) with $P(OMe)_3$ in refluxing xylene results in the formation of $CpFe(CO)[P(OMe)_3]COMe$ (8a) and the alkyl $CpFe(CO)[P(OMe)_3]Me$ (11) in the ratio 4:1. Analysis of reaction aliquots by nmr spectroscopy during early stages of the reaction of $CpFe(CO)_2Me$ with $P(OMe)_3$ shows that a significant proportion of the complex (11) produced arises probably from a direct carbonyl substitution. A similar observation has been made for the reaction of $CpFe(CO)_2Me$ with PPh_3 in ether solvents.¹⁸ No $CpFe(CO)[P(OEt)_3]Et$ was isolated in the reaction of $CpFe(CO)_2Et$ with $P(OEt)_3$; it is known, however, that the analogous $CpFe(CO)(PPh_3)Et$ is unstable to heat, undergoing elimination of ethylene.¹⁸

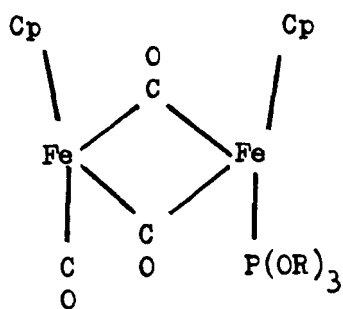
The products (8a) and (11) are recovered in a 1:1 ratio in the reaction of (7a) with $P(OMe)_3$. The presence of (11) could be accounted for in a number of ways as follows;

- (i). Thermal decarbonylation of the acyl compound, similar to the thermal decarbonylation of $CpRu(CO)(PPh_3)COMe$ (5a), to the alkyl compound may occur.
- (ii). Simple substitution of (10a) by $P(OMe)_3$ to produce (11).
- (iii). In the postulated reaction scheme outlined below, instead of the radical recombination of equation (9) the following could occur.



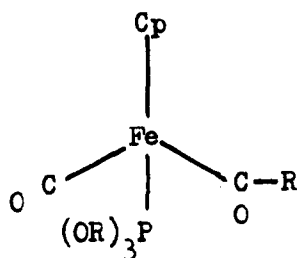
Radicals of the type $CpFe(CO)P(OMe)_3$ are generated in equation (6), but they could also be generated from di-substituted phosphite dimers of the type $Cp_2Fe_2(CO)_2[P(OMe)_3]_2$. This species was not isolated or detected during the course of the reaction.

$CpFe(CO)[P(OMe)_3]Me$ has been synthesised previously by the substitution



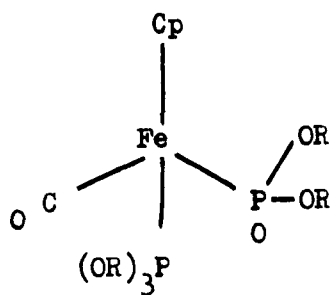
(7a). R = Me

(7b). R = Et



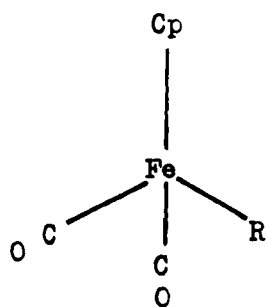
(8a). R = Me

(8b). R = Et



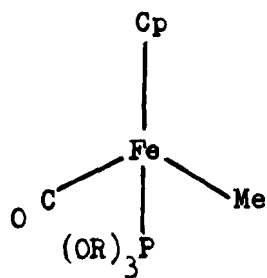
(9a). R = Me

(9b). R = Et



(10a). R = Me

(10b). R = Et



(11).

of PPh_3 in $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Me}$ by $\text{P}(\text{OMe})_3$,¹⁷ and by the uv decarbonylation of $\text{CpFe}(\text{CO})[\text{P}(\text{OMe})_3]\text{COMe}$.¹⁸

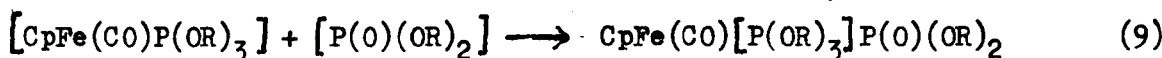
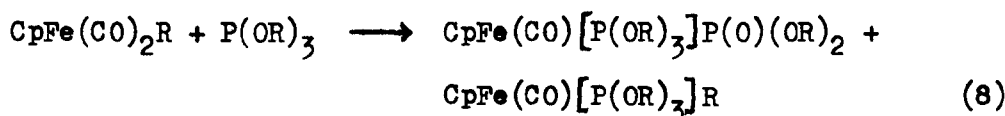
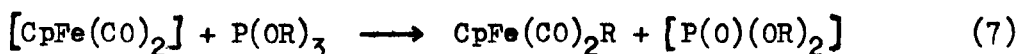
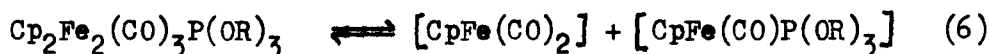
The complexes (8a,b) and (11) were isolated as air stable yellow crystalline solids (8a) or as yellow oils (8b), (11) and were identified by analysis, infrared and nmr spectroscopy. Infrared and ^1H nmr data of (11) agree with published results and figures (10) and (11) show the ^1H and ^{13}C nmr spectra of (11) respectively. As with the ruthenium complexes (5a-c), the iron complexes (8a,b) exhibit a characteristic $\nu(\text{CO})$ acyl stretching frequency at ca. 1600cm^{-1} , and the acyl ^{13}C nmr resonance at ca. 270 ppm. The ^1H and ^{13}C nmr spectra of (8a,b) are illustrated in figures (12)-(15). Of note is the ^1H nmr spectrum of (8b). Both the acyl CH_2 and the co-ordinated phosphite CH_2 are potential AB systems. While the latter forms a pair of quintets consistent with coupling to CH_3 and the phosphorus, the former appears as an apparent first order quartet. This is in contrast to (5b) where the AB nature of the CH_2 protons can be seen clearly.

The phosphonate complexes $\text{CpFe}(\text{CO})[\text{P}(\text{OR})_3]\text{P}(\text{O})(\text{OR})_2$ (9a,b) have been synthesised previously by the reaction of $\text{CpFe}(\text{CO})_2\text{Cl}$ with $\text{P}(\text{OR})_3$, which also yields some $\text{CpFe}(\text{CO})_2\text{P}(\text{O})(\text{OR})_2$. The products are probably produced via an Arbusov rearrangement of a $\text{CpFe}(\text{CO})_2[\text{P}(\text{OR})_3]\text{Cl}$ intermediate.⁹ $\text{CpFe}(\text{CO})_2-(\eta^1-\text{Cp})$ undergoes reaction with $\text{P}(\text{OMe})_3$ to yield $\text{CpFe}(\text{CO})[\text{P}(\text{OMe})_3]\text{P}(\text{O})(\text{OMe})_2$ and methyl cyclopentadiene.^{19,20} The latter reaction is thought to proceed via an Arbusov rearrangement of the intermediate $\text{CpFe}(\text{CO})[\text{P}(\text{OMe})_3](\eta^1-\text{Cp})$ in which a free double bond of the $\eta^1-\text{Cp}$ ligand acts as a nucleophile and has a precedent in the rearrangement of $\text{CpMo}(\text{CO})_2(\text{SbMe}_2)\text{P}(\text{OMe})_3$ to $\text{CpMo}-(\text{CO})_2(\text{SbMe}_3)\text{P}(\text{O})(\text{OMe})_2$, although this reaction is thought to proceed intermolecularly.¹⁰

The phosphonate complexes $\text{CpFe}(\text{CO})[\text{P}(\text{OR})_3]\text{P}(\text{O})(\text{OR})_2$ were isolated as yellow solids (9a) or as yellow oils (9b) and were characterised by analysis, infrared and nmr spectroscopy. ^{31}P nmr spectra show a doublet at ca. 180 ppm and a doublet at ca. 125 ppm assignable to co-ordinated phosphite and

phosphonate respectively. The ^1H nmr spectra of (9a,b) exhibit a slightly broadened triplet for the cyclopentadienyl resonance consistent with the AX Y nature of the system where $J_{\text{AX}} \approx J_{\text{AY}}$. The inequivalence of the phosphonate alkyl groups can be detected in the spectra, which are illustrated in figures (16) and (17).

A scheme accounting for these results is shown by the following reactions;



Equations (6), (7) and (9) are equivalent to the equations (2), (3) and (4) mentioned earlier for the ruthenium dimer (1) reactions with phosphites and the mechanism proposed is essentially the same, involving radical intermediates. Note the ready reaction of any mono-substituted ruthenium dimer of the type $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{P}(\text{OR})_3$ produced in the reaction of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (1), with $\text{P}(\text{OR})_3$ in refluxing xylene.

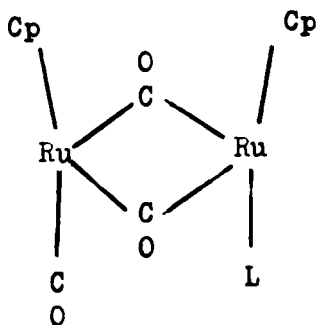
(c). Reaction of $\text{Cp}_2\text{M}_2(\text{CO})_4$ (M = Ru, Fe) with tertiary phosphines.

Reaction of PPr_3 or PPhMe_2 with $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (1) in refluxing xylene followed by chromatography on alumina using dichloromethane as eluent yields a mixture of the complexes $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PR}_3$ (12a,b) and $\text{CpRu}(\text{CO})(\text{PR}_3)\text{Cl}$ (13a,b). The proportion of (13a,b) formed increases with increasing excess of PR_3 and longer reaction time. Reaction of isolated $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PR}_3$ (12a,b) with PR_3 proceeds smoothly to yield ultimately $\text{CpRu}(\text{CO})(\text{PR}_3)\text{Cl}$ (13a,b) and in the case of PPhMe_2 the $\text{CpRu}(\text{PPhMe}_2)_2\text{Cl}$ derivative as well. Complexes (13a,b) and (14) were characterised by analysis, infrared and nmr spectroscopy.

They were identical to samples prepared by carbonyl substitution of $\text{CpRu}(\text{CO})_2\text{Cl}$. In the ^1H nmr spectrum of (13b) the methyl resonances are observed as two doublets due to the proximity of the chiral ruthenium atom. The methyl resonances of (14) occur as two multiplets, each having the characteristic

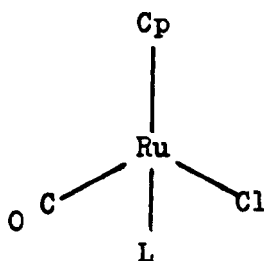
shape (broad inner peak flanked by two sharp singlets) of the $X_3AA'X'_3$ system previously observed for $CpRu(PPh_2Me)_2Cl$.¹² The 1H nmr spectra of the complexes (13a,b) and (14) are illustrated in figures (18)-(20).

If dibromomethane is used as the chromatography eluent in the reaction of $Cp_2Ru_2(CO)_4$ (1) with PPr_3 the analogous bromide $CpRu(CO)(PPr_3)Br$ (15) is isolated. Thus (13a,b) are not initial reactions products. Analysis of the crude reaction mixtures shows a band in the infrared spectrum at ca. $1930cm^{-1}$ and 1H nmr resonances at ca. -12δ (doublet, $J = ca. 35$ Hz) and -12.7δ (triplet, $J = ca. 36.2$ Hz) (only for $PPhMe_2$) which identify the initial reaction products as the hydrides $CpRu(CO)(PR_3)H$ (16a,b) and $CpRu-(PPhMe_2)_2H$ (17). The hydrides (16a,b) may be prepared unambiguously in solution by reaction of $CpRu(CO)_2H$, synthesised in situ from $Ru_3(CO)_{12}$ and cyclopentadiene,²¹ with one equivalent of PR_3 . Although identified by infrared and nmr spectroscopy, the hydrides could not be isolated analytically pure and were characterised by conversion to the chlorides (13a,b), by stirring in chloroform. Prolonged reaction of $CpRu(CO)_2H$ with $PPhMe_2$ yielded a mixture of $CpRu(CO)(PPhMe_2)H$ and $CpRu(PPhMe_2)_2H$; although characterised spectroscopically the latter could also not be isolated in the pure state, and was converted into $CpRu(PPhMe_2)_2Cl$ (14), by stirring in chloroform. The hydrides (16a,b) and (17) exhibit characteristic high field proton resonances in the nmr spectrum; the pattern of the methyl resonances for (16b) and (17) is also analogous to the pattern observed for the chlorides (13b) and (14).



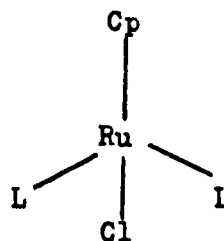
(12a). $L = PPr_3$

(12b). $L = PPhMe_2$

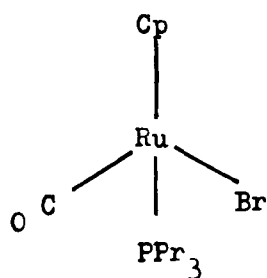


(13a). $L = PPr_3$

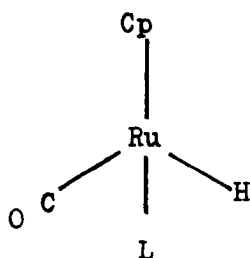
(13b). $L = PPhMe_2$



(14). $L = PPhMe_2$

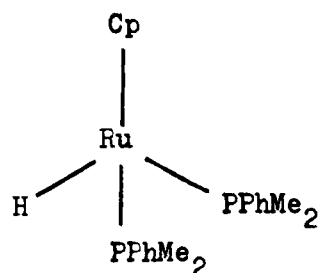


(15)



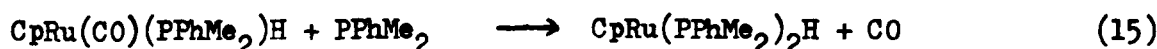
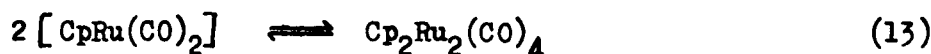
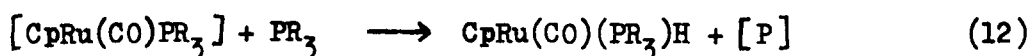
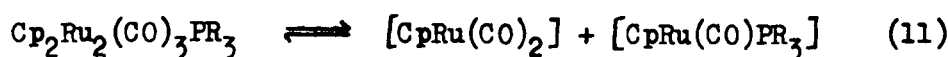
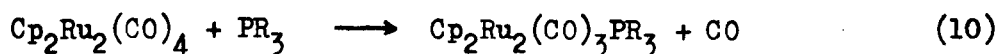
(16a). L = PPr₃

(16b). L = PPhMe₂



(17)

The pathway proposed for this reaction is shown below.



Thermolysis of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPhMe}_2$ (12b) in toluene in the absence of excess phosphine yields mainly $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{H}$ (identified by ^1H nmr) and $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (identified by infrared and ^1H nmr spectroscopy). Heating of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPhMe}_2$ (12b) in d^8 -toluene in the absence of excess phosphine yields in addition to $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ a compound exhibiting a cyclopentadienyl resonance at 4.84 δ assignable to the deuteride $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{D}$, since no high field resonance is observed. Addition of chloroform converts this to the chloride (13b). These reactions carried out, in situ, in the nmr tube thus show that no $\text{CpRu}(\text{CO})_2\text{H}$ is formed, and that the formation of $\text{CpRu}(\text{CO})-(\text{PPhMe}_2)\text{H}$ is not the result of intramolecular decomposition. The thermal decomposition in the absence of excess phosphine is not totally clean however; small additional peaks in the cyclopentadienyl region may be observed, and the ^1H nmr spectrum of the residue in CDCl_3 shows a multiplet at ca. 6.64 δ which may be indicative of an o-metallation product.²² reaction of (12b) with PPhMe_2 in either d^8 -toluene or toluene yields exclusively a mixture of $\text{CpRu}-$

$(\text{CO})(\text{PPhMe}_2)\text{H}$ and $\text{CpRu}(\text{PPhMe}_2)_2\text{H}$, showing that in the presence of excess phosphine, hydrogen abstraction from the solvent and o-metallation are not competitive with equation (12).

Analysis of aliquots from the reaction of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ with PPhMe_2 using both ^{31}P and ^1H nmr spectroscopy show that the only metal containing products formed are $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{H}$, $\text{CpRu}(\text{PPhMe}_2)_2\text{H}$, and $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPhMe}_2$. The fate of the organic phosphorus radical of equation (12) has not been completely determined. The ^{31}P nmr spectrum of the crude reaction products does show several small additional peaks in the region -45 to -47 ppm characteristic of a free phosphine and the reaction is accompanied by the formation of some brown phosphorus containing insoluble organic material.

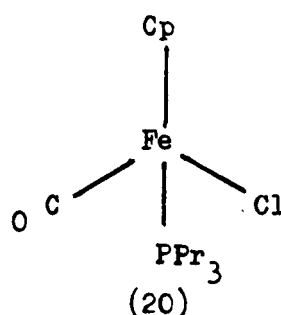
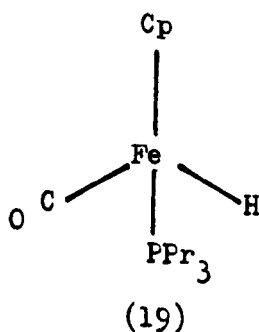
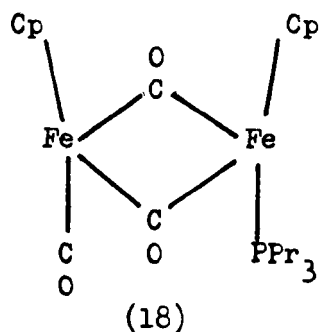
Complete conversion to $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{H}$ and $\text{CpRu}(\text{PPhMe}_2)_2\text{H}$ is observed on reaction of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPhMe}_2$ with excess PPhMe_2 ; whether this is a result of recycling through $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (1) (equations (13) and (10)) or direct substitution of the $\text{CpRu}(\text{CO})_2$ radical (equation (14)) cannot be determined; the enhanced lability of $17e^-$ species with respect to carbonyl substitution has been demonstrated however.²³

Reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (1a) with PPr_3 in refluxing benzene yields the mono-substituted dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPr}_3$ (18).¹⁵ Further reaction of isolated $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPr}_3$ (18) with an excess of PPr_3 in refluxing xylene results in the formation of $\text{CpFe}(\text{CO})(\text{PPr}_3)\text{H}$ (9%) (19) and ferrocene (35%). The hydride was identified by nmr spectroscopy; the high field ^1H nmr resonance characteristic of the hydride is found at -14.02 δ (doublet, $J_{\text{PH}} = 76.2 \text{ Hz}$) in d^6 -benzene. The complex $\text{CpFe}(\text{CO})(\text{PPr}_3)\text{H}$ (19) could not be isolated in the pure state, and was converted to the chloride $\text{CpFe}(\text{CO})(\text{PPr}_3)\text{Cl}$ (20) by reaction with chloroform. The chloride was characterised by analysis, infrared and nmr spectroscopy.

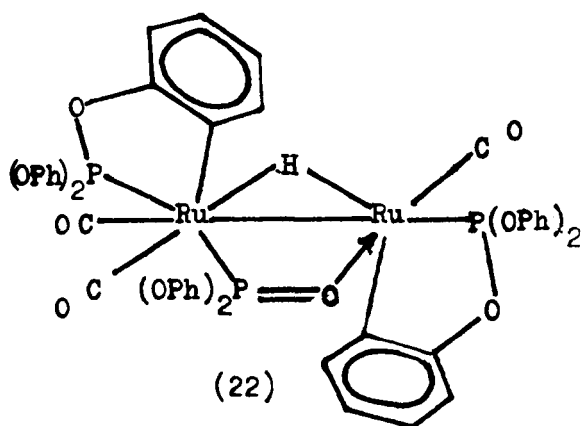
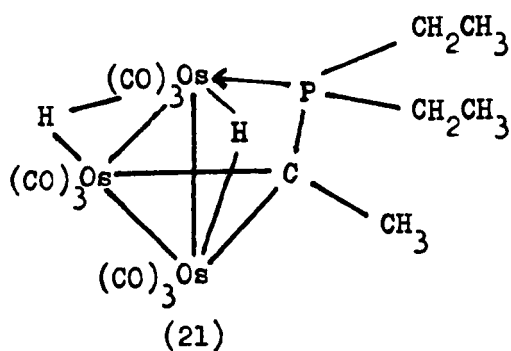
Authentic $\text{CpFe}(\text{CO})(\text{PPr}_3)\text{Cl}$ was prepared by the carbonyl substitution of $\text{CpFe}(\text{CO})_2\text{Cl}$ by PPr_3 under uv irradiation in near quantitative yield.

Thermolysis of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPr}_3$ (18) in xylene in the absence of excess

phosphine resulted in the formation of $\text{CpFe(CO)(PPr}_3\text{)H}$ (3%)(19), ferrocene (31%), and $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (16%).

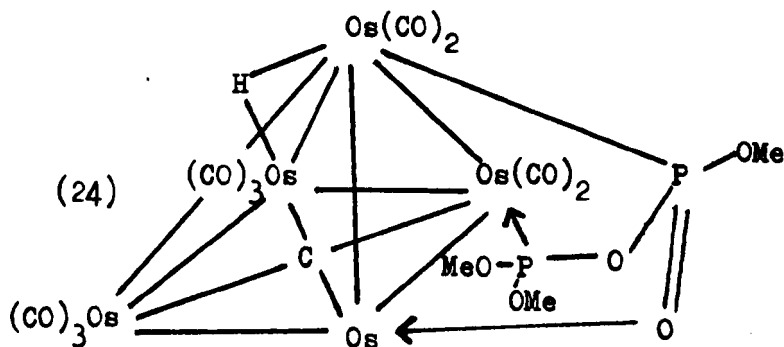
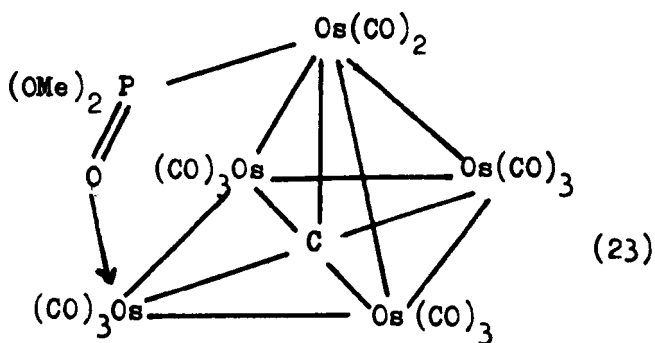


The mechanism for this reaction can be described by the equations (10)-(14), substituting Fe for Ru. The presence of ferrocene indicates another thermal reaction competing with the formation of the hydride. It is known that $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ decomposes into $\text{Cp}_4\text{Fe}_4(\text{CO})_4$ and ferrocene upon thermolysis in xylene, albeit over a period of 14 days.²⁸ More recently it has been found that addition of PPh_3 to the thermolysis of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ increases the yield of $\text{Cp}_4\text{Fe}_4(\text{CO})_4$ and reduces the reaction time.²⁹ The latter reaction is thought to proceed through the formation of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPh}_3$ as an intermediate, which then decomposes at a lower temperature than $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ to form the products. Since ruthenocene is not formed in the thermolysis of mono-substituted ruthenium complexes $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PR}_3$ the reaction involving this particular decomposition is not competitive with the formation of the hydride $\text{CpRu(CO)(PR}_3\text{)H}$.



The C - H bond cleavage observed in the reactions between $\text{Cp}_2\text{M}_2(\text{CO})_3\text{PR}_3$

(M = Fe, Ru) and excess PR_3 is consistent with the presence of the radical intermediates of equations (11) and (12), and it is of interest to compare these reactions to transformations of phosphine and phosphite co-ordinated to trinuclear clusters of the iron group. A similar hydrogen transfer has been observed in the thermolysis of $\text{Os}_3(\text{CO})_{11}\text{P}(\text{Et})_3$ to yield (21).²⁴ Thermolysis of $\text{Ru}_3(\text{CO})_{11}\text{P}(\text{OPh})_3$ ²⁵ and $\text{Os}_3(\text{CO})_{11}\text{P}(\text{OMe})_3$ ²⁶ yield polymetallic species (22) - (24) containing co-ordinated phosphonate. Thus it may be tempting to speculate that these formal oxidative additions to metal-metal bonds may proceed via the intermediacy of radical species in which the integrity of the cluster is maintained by the presence of more than one metal-metal bond. In a recent kinetic study it has been shown that the reaction of $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ with PBu_3 to yield mono-nuclear fragments proceeds via a rate determining loss of CO to yield a $\text{Ru}_3(\text{CO})_8(\text{PBu}_3)_3$ species; one structure proposed for this intermediate is a di-radical arising from the cleavage of one Ru - Ru bond.



(d). The structure and fluxional behaviour of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PR}_3$ (12a, b).

It was originally intended to prepare the complexes $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PR}_3$ (12a,b) to compare their structure and fluxional behaviour with that of the $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CNR})$ series.³ The two infrared bands at 1943 and 1762 cm^{-1} in the spectrum of (12a) may be assigned to terminal and bridging carbonyl vibrations indicating the presence of only $\text{Cp}(\text{CO})\text{Ru}(\mu\text{CO})_2\text{Ru}(\text{PR}_3)\text{Cp}$ isomers. This is in contrast to the parent dimer (1) where concentrations of the non-bridged isomers may be detected in solution.² The conversion of a totally bridged species can be explained in electronic terms. Alkyl phosphines are better σ -donors and poorer π -acceptors than carbon monoxide. This will result in increased negative charge on the cluster. Carbon monoxide is a better π -acceptor in a bridged position compared to a terminal position, and the negative charge built up on the cluster by co-ordination of phosphine may be relieved by two terminally bound carbonyls migrating to bridging positions. The increased acceptor property of carbon monoxide in (12a,b) compared to (1) can be seen clearly in the infrared spectrum. The bridged isomers of the parent dimer (1) adsorb at ca. 1790 cm^{-1} in the bridging CO region whereas the substituted dimers at 1760 cm^{-1} in the bridging CO region.

The complexes $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PR}_3$ ¹⁵ exhibit analogous spectra indicating the presence of either the cis or the trans isomers, although a definite assignment is not possible. The complexes show fluxional behaviour involving bridge - terminal carbonyl exchange. Thus in the ^{13}C nmr spectrum of (12b) the two carbonyl signals observed at -70°C (figure 21) broaden and coalesce to give a single broadened resonance at 238.2 ppm at $+25^\circ\text{C}$. In the absence of detectable concentrations of both geometric isomers, little information can be gained with respect to the mechanism of exchange, except to note that the activation energy for the exchange process is considerably less than that observed for the similar $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PR}_3$ complexes.²⁹ Proton nmr spectra of (12a,b) are illustrated in figures (22) and (23).

Experimental

$\text{Cp}_2\text{Ru}_2(\text{CO})_4$ was prepared from $\text{Ru}_3(\text{CO})_{12}$ using the method of Knox.²¹ $\text{CpRu}(\text{CO})_2\text{Cl}$ was prepared by the reaction of $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ with TiCp ,³⁰ which also yields amounts of $\text{Cp}_2\text{Ru}_2(\text{CO})_4$. $\text{CpFe}(\text{CO})_2\text{Cl}$,³¹ PPr_3 ,³² were prepared by literature methods; all other starting materials were obtained commercially. All experiments were carried out under nitrogen using dried and degassed solvents. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer using 1.0mm NaCl cells, n.m.r. spectra on a JEOL FX-100 spectrometer, and mass spectra on an AEI MS 12 instrument. ^{13}C spectra were run in the presence of $\text{Cr}(\text{acac})_3$ as relaxation agent.

Preparations and Reactions.

- (a) Reaction between $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ and $\text{P}(\text{OEt})_3$. The dimer (500mg) was reacted in refluxing xylene (15cm^3) with a 5:1 molar excess of $\text{P}(\text{OEt})_3$. The reaction was followed to complete disappearance of dimer (ca. 6hrs) and the solvent was removed under reduced pressure. The residue was chromatographed on silica-gel which had been deactivated previously with diethyl ether and washed with benzene. Using benzene as eluent, a first colourless band was collected which gave the product $\text{CpRu}(\text{CO})_2\text{Et}$ (2b) as a clear oil (200mg; 36%). This material was characterised further by its reaction with PPh_3 as described below. The remaining products were eluted from the column as a light brown band using methanol. The residue obtained after evaporation of the solvent was further purified by preparative thin layer chromatography on silica plates using methanol/diethyl ether (5/95%) as eluent. A small amount of $\text{CpRu}(\text{CO})_2\text{Et}$ (2b) was eluted with the solvent front, while two slower moving colourless bands were collected to yield $\text{CpRu}[\text{P}(\text{OEt})_3]_2\text{P}(\text{O})(\text{OEt})_2$ (3b) (250mg; 18%) and $\text{CpRu}(\text{CO})\text{P}(\text{OEt})_3\text{P}(\text{O})(\text{OEt})_2$ (4b) (150mg; 14%) in order of elution.

In reactions with $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OBu})_3$, refluxing was con-

tinued for an additional three hours after disappearance of dimer (1) to yield (2a,c) and (3a,c) as the only isolated products after work up.

- (b) Reaction between $\text{CpRu}(\text{CO})_2\text{Me}$ and PPh_3 . $\text{CpRu}(\text{CO})_2\text{Me}$ (2a) (100mg), prepared as in (a) or from $\text{Na}[\text{CpRu}(\text{CO})_2]$ and methyl iodide, was reacted with a 6:1 molar excess of PPh_3 in refluxing xylene (15cm^3) until reaction was 50% complete as judged by infrared spectroscopy. The solvent was removed and the residue was chromatographed on silica preparative thin layer chromatography plates using CH_2Cl_2 as eluent. A fast moving band yielded starting material and PPh_3 ; the second light yellow band gave the product $\text{CpRu}(\text{CO})-(\text{PPh}_3)\text{COMe}$ (5a) (90mg) as light yellow crystals after evaporation from dichloromethane/pet-ether (40:60).

Heating for prolonged periods of time (ca. 2-3 weeks) results in almost complete consumption of starting material; the product isolated after chromatography as above is the alkyl derivative $\text{CpRu}(\text{CO})(\text{PPh}_3)\text{Me}$ (6).

Complexes (5b,c) may be prepared similarly by reaction of $\text{CpRu}(\text{CO})_2\text{R}$ (2b,c) ($\text{R} = \text{Et}, \text{Bu}$) with a 5:1 molar excess of PPh_3 in refluxing xylene for 48 hours followed by chromatography on grade (II) alumina using dichloromethane as eluent.

- (c) Reaction between $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ and PPr_3 . The dimer (1) (250mg) was reacted with a 2:1 molar excess of PPr_3 in refluxing xylene to complete disappearance of (1) as judged by infrared spectroscopy. The nmr spectrum of an aliquot taken at this point (d^6 -benzene) showed the presence of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPr}_3$ (12a) and $\text{CpRu}(\text{CO})(\text{PPr}_3)\text{H}$. The solvent was removed under reduced pressure and the residue chromatographed on grade (II) alumina using dichloromethane as eluent. The first orange band collected yielded $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPr}_3$ (12a) (125mg) as orange crystals after recrystal-

lisation from $\text{CH}_2\text{Cl}_2/\text{pet-ether}$ (40:60). The second yellow band eluted gave $\text{CpRu}(\text{CO})(\text{PPr}_3)\text{Cl}$ (13a) (170mg) as yellow crystals after recrystallisation from $\text{CH}_2\text{Cl}_2/\text{pet-ether}$ (40:60). If CH_2Br_2 is used as eluent, the second band yields $\text{CpRu}(\text{CO})(\text{PPr}_3)\text{Br}$ (15) isolated as orange crystals.

Reaction of (1) with PPhMe_2 was carried out in the same way to yield a mixture of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPhMe}_2$ (12b) and $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{-Cl}$ (13b).

- (d) Reaction between $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPhMe}_2$ and PPhMe_2 . $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPhMe}_2$ (100mg) was reacted with a 5:1 molar excess of PPhMe_2 in refluxing toluene (10cm^3). After eight hours starting material had disappeared and infrared and nmr analysis indicated the presence of $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{H}$ (16b) and $\text{CpRu}(\text{PPhMe}_2)_2\text{H}$ (17). The solvent was removed under reduced pressure and the residue chromatographed on grade (III) alumina using dichloromethane as eluent. The first yellow band to develop gave $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{Cl}$ (13b) (50mg) and the second yellow band gave $\text{CpRu}(\text{PPhMe}_2)_2\text{Cl}$ (14) (30mg) identical with samples prepared as in (e).
- (e) Reaction between $\text{CpRu}(\text{CO})_2\text{Cl}$ and PR_3 . $\text{CpRu}(\text{CO})_2\text{Cl}$ (250mg) was reacted with a 2:1 molar excess of PPr_3 for 12 hours in refluxing toluene. The solvent was removed and the residue was chromatographed on grade (III) alumina using dichloromethane as eluent. The product was eluted as a yellow band yielding yellow crystals of $\text{CpRu}(\text{PPr}_3)\text{Cl}$ (13a) (200mg). $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{Cl}$ (13b) was prepared in the same way.

Reaction of $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{Cl}$ (13b) (200mg) with a 2:1 molar excess of PPhMe_2 in refluxing toluene for twelve hours, followed by chromatography, gave $\text{CpRu}(\text{PPhMe}_2)_2\text{Cl}$ (14) as a yellow solid in low yield (20mg).

- (f) Reaction of $\text{CpRu}(\text{CO})_2\text{H}$ with PR_3 . A heptane solution of CpRu-

$(\text{CO})_2\text{H}$ (1.67 mmols) was prepared by the method of Knox.¹⁹ At 80 C, PPr_3 (2.0 mmols) was added and the solution was stirred for 15 minutes. Infrared and n.m.r analysis indicated complete conversion to $\text{CpRu}(\text{CO})(\text{PPr}_3)\text{H}$ (16a). The solvent was removed and the residue dissolved in chloroform and then stirred overnight. The solvent was evaporated and the residue chromatographed on grade (III) alumina using benzene as eluent. Collection of the yellow band and recrystallisation from dichloromethane/pet-ether (40:60) gave $\text{CpRu}(\text{CO})(\text{PPr}_3)\text{Cl}$ (13a) (400mg). A solution of $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{H}$ (16b) was prepared in the same way and converted to $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{Cl}$ (13b).

Prolonged reaction (ca. 2 hours) between $\text{CpRu}(\text{CO})_2\text{H}$ and PPhMe_2 yields a mixture of $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{H}$ (16b) and $\text{CpRu}(\text{PPhMe}_2)_2\text{H}$ (17) as judged by n.m.r analysis. Evaporation of heptane, followed by stirring in chloroform and chromatography of the residue yields $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{Cl}$ (13b) and $\text{CpRu}(\text{PPhMe}_2)_2\text{Cl}$ (17).

All products were identical with samples prepared as in (e).

- (g) Reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OMe})_3$ with $\text{P}(\text{OMe})_3$. The substituted dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OMe})_3$ (1.0g) and a 3:1 excess of $\text{P}(\text{OMe})_3$ were reacted in refluxing xylene. The reaction was followed until complete disappearance of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OMe})_3$ as judged by infrared spectroscopy (ca. 30 minutes) and the solvent was removed under reduced pressure. The residue was first chromatographed upon silica-gel preparative thin layer chromatographic plates using dichloromethane as eluent. The yellow band that developed was collected and gave the product $\text{CpFe}(\text{CO})\text{P}(\text{OMe})_3$ Me. Collection of the residue and further chromatography, as above, using a (1:1) mixture of dichloromethane/ethyl acetate as eluent, developed a second yellow band which upon recrystallisation yielded CpFe -

(CO) $\text{P}(\text{OMe})_3$ COMe. Collection of the residue and further chromatography, as above, using a (1:1) mixture of methanol/diethyl ether, yielded a further yellow band which upon purification yielded $\text{CpFe}(\text{CO}) \text{P}(\text{OMe})_3 \text{P}(\text{O})(\text{OMe})_2$.

Reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OEt})_3$ with $\text{P}(\text{OEt})_3$ was carried out similarly, and the same work up routine was used to produce $\text{CpFe}(\text{CO}) \text{P}(\text{OEt})_3 \text{COEt}$ and $\text{CpFe}(\text{CO}) \text{P}(\text{OEt})_3 \text{P}(\text{O})(\text{OEt})_2$.

- (h) Reaction of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPr}_3$ with PPr_3 . The dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPr}_3$ (500 mg) was reacted with a 3:1 excess of PPr_3 in refluxing xylene (15 cm^3). The reaction was monitored by infrared spectroscopy, and upon completion (ca. 10 hours) the solvent was removed. The residue was chromatographed upon grade (IV) alumina using dichloromethane/pet-ether (40:60) as eluent. The first orange band to develop gave ferrocene (116 mg, 35%) and a second green band of product $\text{CpFe}(\text{CO})(\text{PPr}_3)\text{Cl}$ (46.5 mg, 9%) followed.
- (i) Thermolysis of $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPr}_3$ in xylene. The dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{PPr}_3$ (500 mg) was refluxed in xylene (15 cm^3) for ca. 10 hours. The solvent was removed and the residue chromatographed upon grade (IV) alumina. Elution with a (1:1) mixture of dichloromethane/pet-ether (40:60) yielded first, ferrocene (250 mg) followed by $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (60 mg). Further elution with dichloromethane produced a band green in colour containing $\text{CpFe}(\text{CO})(\text{PPr}_3)\text{Cl}$ (20 mg).
- (j) Reaction between $\text{CpFe}(\text{CO})_2\text{Cl}$ and PPr_3 . The chloride $\text{CpFe}(\text{CO})_2\text{Cl}$ (1.0 g, 400 mmols) in tetrahydrofuran (250 cm^3) was reacted with PPr_3 (1.0 g, 600 mmols) in the presence of uv radiation for six hours. The reaction was followed by infrared spectroscopy. Evaporation of the solvent followed by chromatography upon grade (IV) alumina using dichloromethane as eluent yielded green crystalline $\text{CpFe}(\text{CO})(\text{PPr}_3)\text{Cl}$ (400 mg).

TABLE 1
Analytical Data (%)

<u>Compound</u>	<u>Found</u>		<u>Calculated</u>	
	<u>C</u>	<u>H</u>	<u>C</u>	<u>H</u>
(3a)	29.0	5.4	29.8	5.5
(3b)	40.3	7.1	39.7	7.1
(3c)	51.9	9.4	51.7	9.0
(4b)	39.2	6.5	38.6	6.1
(5a)	62.7	4.7	62.5	4.6
(5b)	63.2	5.0	63.2	4.9
(5c)	64.3	5.4	64.3	5.4
(6)	63.8	4.9	63.7	4.9
(8a)	41.5	5.3	41.8	5.4
(8b)	48.7	6.7	48.4	6.7
(9a)	35.3	5.7	34.6	5.2
(9b)	42.9	7.0	42.5	6.6
(11)	42.1	6.2	41.7	5.9
(12a)	46.4	5.5	46.0	5.4
(12b)	45.3	3.7	45.5	3.8
(13a)	45.7	6.5	46.2	6.7
(13b)	45.8	4.4	45.7	4.4
(14)	53.2	6.0	52.8	5.7
(15)	42.2	6.0	41.3	6.0
(20)	52.2	7.7	52.3	7.6

TABLE 2
Infrared Data (cm⁻¹)

<u>Compound</u>	M - <u>CO</u> ^a	M - <u>COR</u> ^b	P = 0 ^c
(3a)			1175
(3b)			1155
(3c)			1145
(4b)	1978		1140
(5a)	1935	1596	
(5b)	1933	1596	
(5c)	1928	1600	
(6)	1928		
(8a)	1939	1619	
(8b)	1935	1619	
(9a)	1967		
(9b)	1965		
(11)	1943, 1929		
(12a)	1943 (t), 1762 (b)		
(12b)	1940 (t), 1740 (b)		
(13a)	1953		
(13b)	1959		
(14)	1958		
(16a)	1927		
(16b)	1931		
(20)	1955		

a. hexane solution.

b. nujol mull.

c. thin film.

t = terminal carbonyl, b = bridging carbonyl.

TABLE 3
Proton n.m.r Data

<u>Compound</u>	<u>Cp</u>	<u>Other</u>
(3a)	5.02 (q; $J_{PH} = 1$ Hz)	P(O)(OCH ₃) ₂ 3.49 (d; $J_{PH} = 10.5$ Hz) P(OCH ₃) ₃ 3.61 (m)
(3b)	4.88 (q; $J_{PH} = 0.9$ Hz)	P(O)(OCH ₂ CH ₃) ₂ 3.78 - 4.03 (m) P(OCH ₂ CH ₃) ₃ P(O)(OCH ₂ CH ₃) ₂ 1.15 (m) P(OCH ₂ CH ₃) ₃
(3c)	4.95 (q; $J_{PH} = 1$ Hz)	P(O)(OCH ₂ CH ₂ CH ₂ CH ₃) ₂ 3.97 (m) P(OCH ₂ CH ₂ CH ₂ CH ₃) ₃ P(O)(OCH ₂ CH ₂ CH ₂ CH ₃) ₂ 1.42 (m) P(OCH ₂ CH ₂ CH ₂ CH ₃) ₃ P(O)(OCH ₂ CH ₂ CH ₂ CH ₃) ₂ 0.90 (m) P(OCH ₂ CH ₂ CH ₂ CH ₃) ₃
(4b)	5.16 (t; $J_{PH} = 0.9$ Hz)	P(O)(OCH ₂ CH ₃) ₂ 3.80 - 4.07 (m) P(OCH ₂ CH ₃) ₃ P(O)(OCH ₂ CH ₃) ₂ 1.23 (m) P(OCH ₂ CH ₃) ₃
(5a)	4.99 (d; $J_{PH} = 0.4$ Hz)	CH ₃ 2.08 (d; $J_{PH} = 0.5$ Hz) PPh ₃ 7.40 (m)
(5b)	4.98 (d; $J_{PH} = 0.4$ Hz)	CH ₂ 2.4 (m) CH ₃ 0.52 (t) PPh ₃ 7.40 (m)
(5c)	4.95 (d; $J_{PH} = 0.4$ Hz)	CH ₂ CH ₂ CH ₂ CH ₃ 2.35 (m) CH ₂ CH ₂ CH ₂ CH ₃ 0.73 - 1.40 (m) PPh ₃ 7.40 (m)
(6)	4.80 (d; $J_{PH} = 0.5$ Hz)	CH ₃ 0.07 (d; $J_{PH} = 5.3$ Hz) PPh ₃ 7.36 (m) (cont. over...)

TABLE 3 continued.

Compound	Cp		Other
(8a)	4.61 (d; $J_{PH} = 1$ Hz)	CH_3	2.5 (d; $J_{PH} = 0.9$ Hz)
		$P(OCH_3)_3$	3.6 (d; $J_{PH} = 11.35$ Hz)
(8b)	4.55 (d; $J_{PH} = 1$ Hz)	CH_2	2.81 (q; $J_{HH} = 7.3$ Hz)
		CH_3	0.82 (t)
		$P(OCH_2CH_3)_3$	3.92 (m)
		$P(OCH_2CH_3)_3$	1.23 (t; $J_{HH} = 7.0$ Hz)
(9a)	4.76 (t; $J_{PH} = 0.9$ Hz)	$P(O)(OCH_3)_2$	3.47 - 3.59 (m)
		$P(OCH_3)_3$	3.69 (d; $J_{PH} = 11.4$ Hz)
(9b)	4.69 (t; $J_{PH} = 0.9$ Hz)	$P(O)(OCH_2CH_3)_2$	3.80 - 4.20 (m)
		$P(OCH_2CH_3)_3$	
		$P(O)(OCH_2CH_3)_2$	1.08 - 1.30 (m)
		$P(OCH_2CH_3)_3$	
(11)	4.47 (d; $J_{PH} = 1$ Hz)	CH_3	0.18 (d; $J_{PH} = 4.9$ Hz)
		$P(OCH_3)_3$	3.55 (d; $J_{PH} = 11.3$ Hz)
(12a)	5.22, 4.99	$CH_2CH_2CH_3$	1.40 (m)
		$CH_2CH_2CH_3$	1.03 (t)
(12b)	5.24, 4.71	CH_3	1.42 (d; $J_{PH} = 9.4$ Hz)
		Ph	7.45 (m)
(13a)	5.03 (d; $J_{PH} = 0.4$ Hz)	$CH_2CH_2CH_3$	1.22 - 1.98 (m)
		$CH_2CH_2CH_3$	1.03 (t)
(13b)	4.84	CH_3	1.94 (d)
			1.84 (d) ($J_{PH} = 12.6$ Hz)
		Ph	7.44 (m)
(14)	4.27	CH_3	1.51 (m)
			1.67 (m)
		Ph	7.27 (m)
(15)	5.04 (d; $J_{PH} = 0.4$ Hz)	$CH_2CH_2CH_3$	1.33 - 2.01 (m)
		$CH_2CH_2CH_3$	1.03 (t)

(cont. over...)

TABLE 3 continued

<u>Compound</u>		<u>Cp</u>	<u>Other</u>
(16a) ^a	4.84		$\text{CH}_2\text{CH}_2\text{CH}_3$ 1.41 (m) $\text{CH}_2\text{CH}_2\text{CH}_3$ 0.93 (m) Ru - $\underline{\text{H}}$ -12.1 (d; $J_{\text{PH}} = 33.2$ Hz)
(16b) ^a	4.82		CH_3 1.56 (d) 1.47 (d) ($J_{\text{PH}} = 9.4$ Hz) Ph 7.22 - 7.72 (m) Ru - $\underline{\text{H}}$ -11.7 (d; $J_{\text{PH}} = 35.1$ Hz)
(17) ^a	4.77		CH_3 1.44 (m) Ph 7.18 - 7.67 (m) Ru - H -12.68 (t; $J_{\text{PH}} = 36.2$ Hz)

^a in d⁶-benzene solution; all other spectra in d-chloroform.

TABLE 4
 ^{13}C and ^{31}P n.m.r. Data

<u>Complex</u>		<u>(^{13}C)^a</u>	<u>(^{31}P)^b</u>	
(2a)	Cp	87.4		
	CO	200.8		
	CH ₃	-33.2		
(3a)			P(O)(OMe) ₂	108.5 (t)
			P(OMe) ₃	158.4 (d)
(3b)			P(O)(OEt) ₂	106.9 (t)
			P(OEt) ₃	155.3 (d)
(3c)			P(O)(OBu) ₂	110.0 (t)
			P(OBu) ₃	155.6 (d)
(4b)			P(O)(OEt) ₂	94.5 (d)
			P(OEt) ₃	148.7 (d)
(5a)	Cp	88.7		
	<u>CO</u> R	254.0 ($J_{\text{PC}} = 12.2$)		
	CO	205.0 ($J_{\text{PC}} = 19.5$)		
	CH ₃	52.0 ($J_{\text{PC}} = 1.9$)		
(5b)	Cp	88.6		
	<u>CO</u> R	255.7 ($J_{\text{PC}} = 11.7$)		
	CO	205.4 ($J_{\text{PC}} = 19.5$)		
	CH ₂	58.5 ($J_{\text{PC}} = 2.9$)		
	CH ₃	9.4		
(5c)	Cp	88.4		
	<u>CO</u> R	255.8 ($J_{\text{PC}} = 12.2$)		
	CO	205.4 ($J_{\text{PC}} = 19.6$)		
	CH ₂	65.4 ($J_{\text{PC}} = 2.0$)		
	CH ₂	27.1		
	CH ₂	22.3		
	CH ₃	14.1		

Cont. over.....

TABLE 4 Continued

<u>Complex</u>		<u>(¹³C)</u>	<u>(³¹P)</u>
(6)	Cp	87.2	
	CO	206.6 ($J_{PC} = 22.0$)	
	CH ₃	-29.6 ($J_{PC} = 12.2$)	
(8a)	Cp	83.6	
	CO	217.4 ($J_{PC} = 46.3$)	
	<u>CO</u> R	269.8 ($J_{PC} = 36.7$)	
	CH ₃	51.6	
(8b)	Cp	83.7	
	CO	217.9 ($J_{PC} = 46.4$)	
	<u>CO</u> R	271.0 ($J_{PC} = 36.7$)	
	CH ₂	57.4 ($J_{PC} = 4.9$)	
	CH ₃	9.4	
	CH ₂ ^e	60.2	
	CH ₃ ^e	15.7 ($J_{PC} = 4.9$)	
(9a)			P(O)(OMe) ₂ 125.7
			P(OMe) ₃ 108.3
			$J_{PP} = 139.1$
(9b)			P(O)(OEt) ₂ 120.9
			P(OEt) ₃ 175.5
			$J_{PP} = 136.8$
(11)	Cp	82.6	
	CO	220.0 ($J_{PC} = 46.4$)	
	CH ₃	-26.2 ($J_{PC} = 34.3$)	
	CH ₃ ^e	51.3	
(12a) ^c	Cp	89.6, 90.5	
	CO _t	208.6	
	CO _b	258.6	
	CH ₂	30.6 ($J_{PC} = 23.0$)	
	CH ₂ CH ₂	17.7	

Cont over.....

TABLE 4 Continued

<u>Complex</u>	<u>(¹³C)</u>	<u>(³¹P)</u>
(12b) ^c Cp	87.5 coincident	
CO _t	204.5	
CO _b	255.1	
CH ₃	14.1 (d; J _{PC} = 19.5)	
Ph	126 - 136	
(13b)		PPhMe ₂ 22.3
(14)		PPhMe ₂ 16.4
(16b) ^d		PPhMe ₂ 31.5
(17) ^d		PPhMe ₂ 28.3

^a relative to tetramethylsilane.

^b relative to 85% phosphoric acid.

^c = 70°C in d²- dichloromethane.

^d in d⁶- benzene solution. all other spectra in d-chloroform.

^e alkyl components of phosphite ligands.

Figure 1

^1H n.m.r. of $\text{CpRu}(\text{CO})(\text{PPh}_3)\text{COMe}$ (5a)

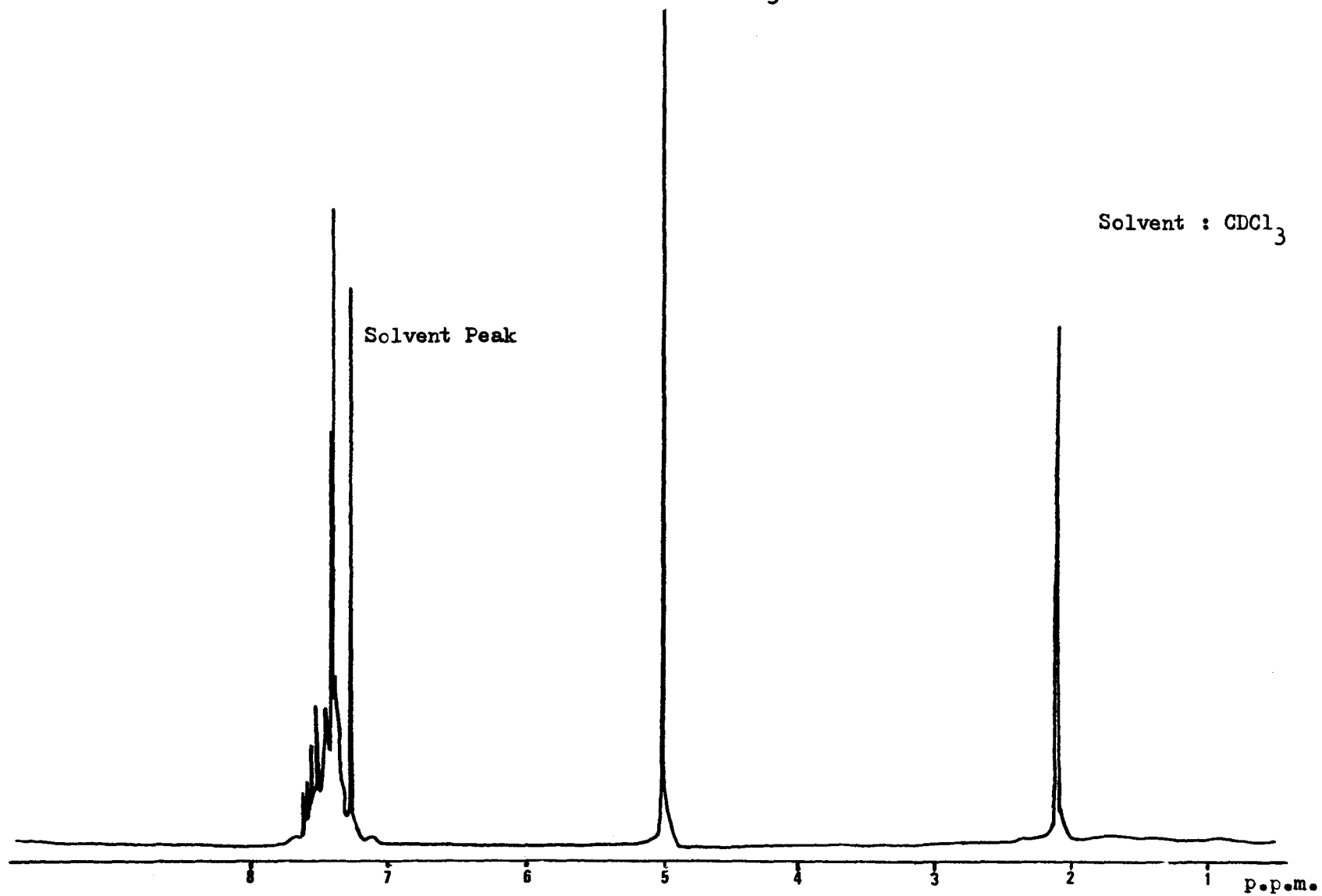


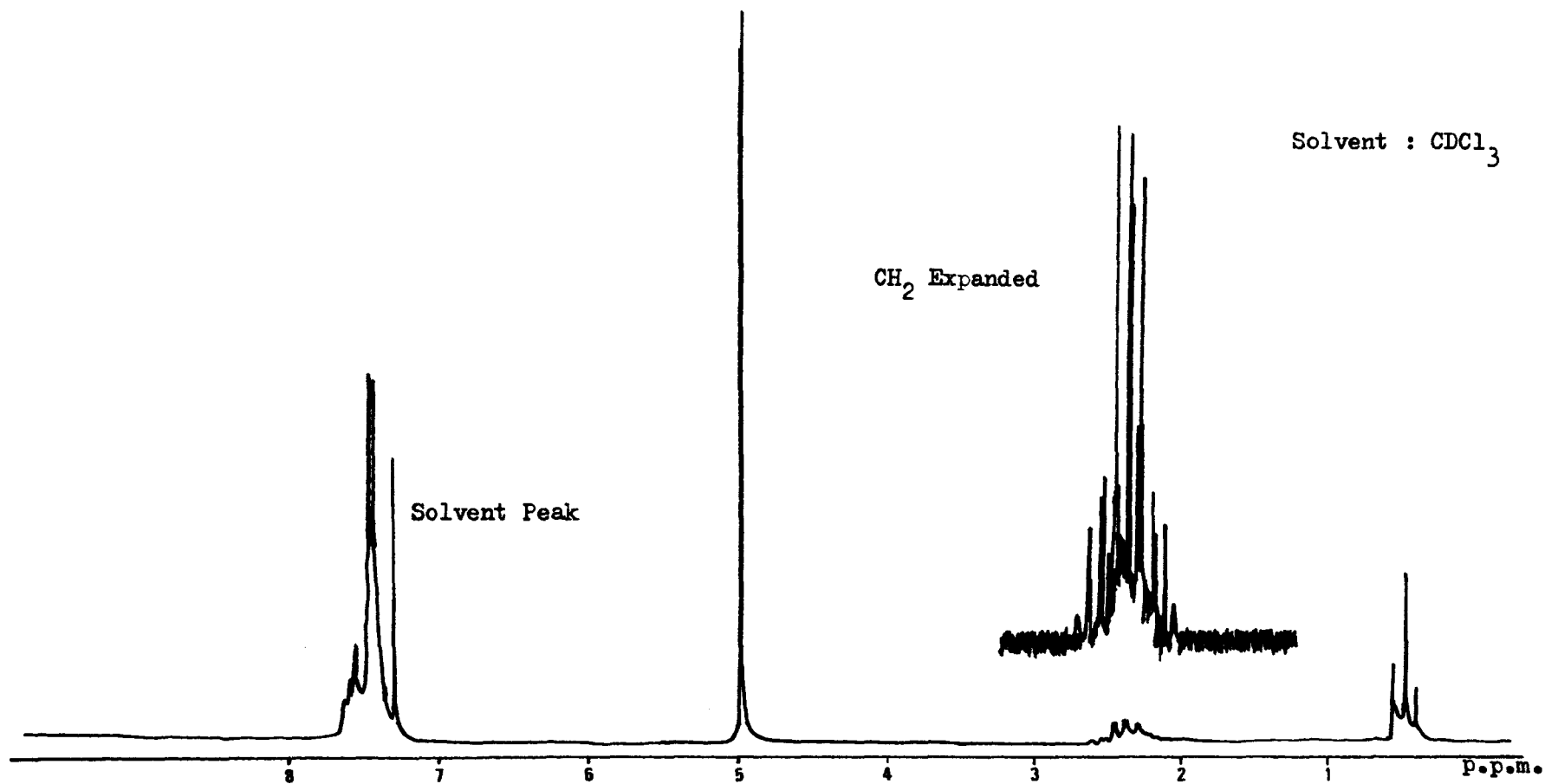
Figure 2 ^1H n.m.r. of $\text{CpRu}(\text{CO})(\text{PPh}_3)\text{COEt}$ (5b)

Figure 3

^1H n.m.r. of $\text{CpRu}(\text{CO})(\text{PPh}_3)\text{COBu}$ (5c)

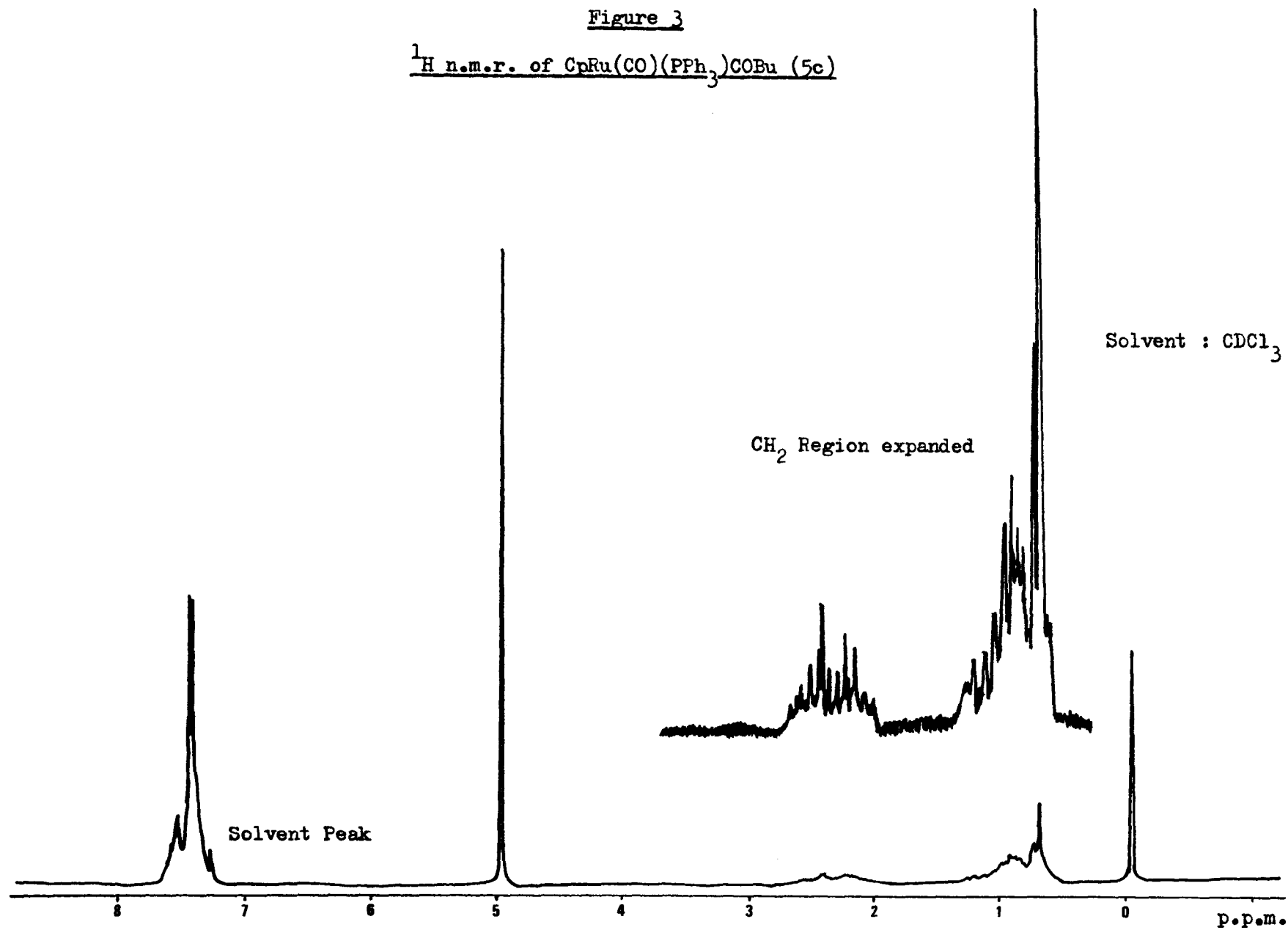


Figure 4

Computer Simulation of an ABX₃P System

$$\begin{aligned}
 J_{AB} &= -18\text{Hz} \\
 J_{AX} &= J_{BX} = 8.1\text{Hz} \\
 J_{PA} &= J_{PB} = 0.4\text{Hz} \\
 A &= H_a = 2.3\delta \\
 B &= H_b = 2.53\delta \\
 P &= P = 100\delta \\
 X_3 &= H_3 = 0.51\delta
 \end{aligned}$$

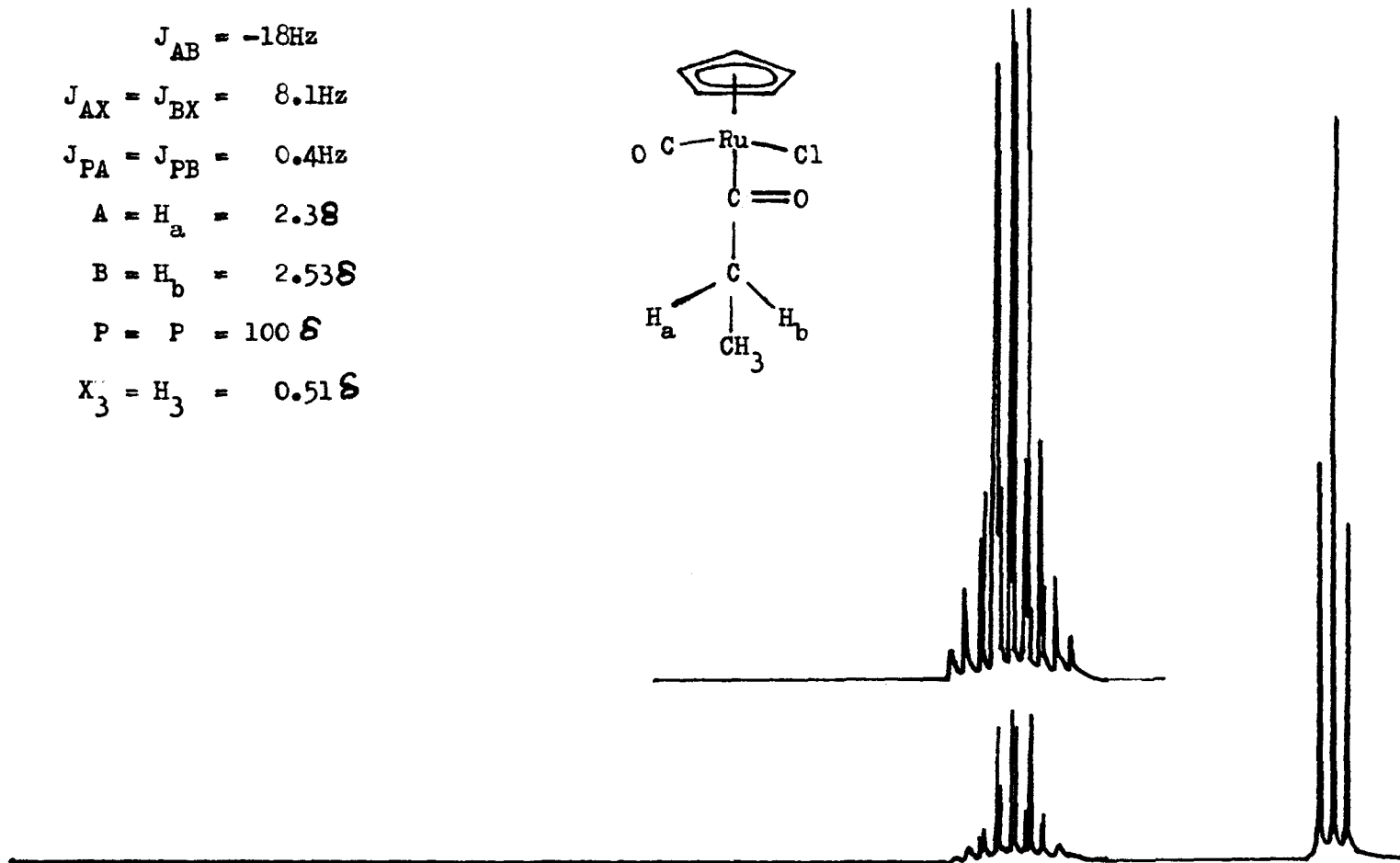
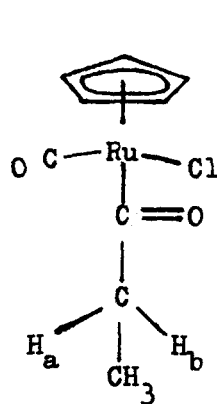


Figure 5

^1H n.m.r. of $\text{CpRu}(\text{CO})(\text{PPh}_3)_2\text{Me}$ (6)

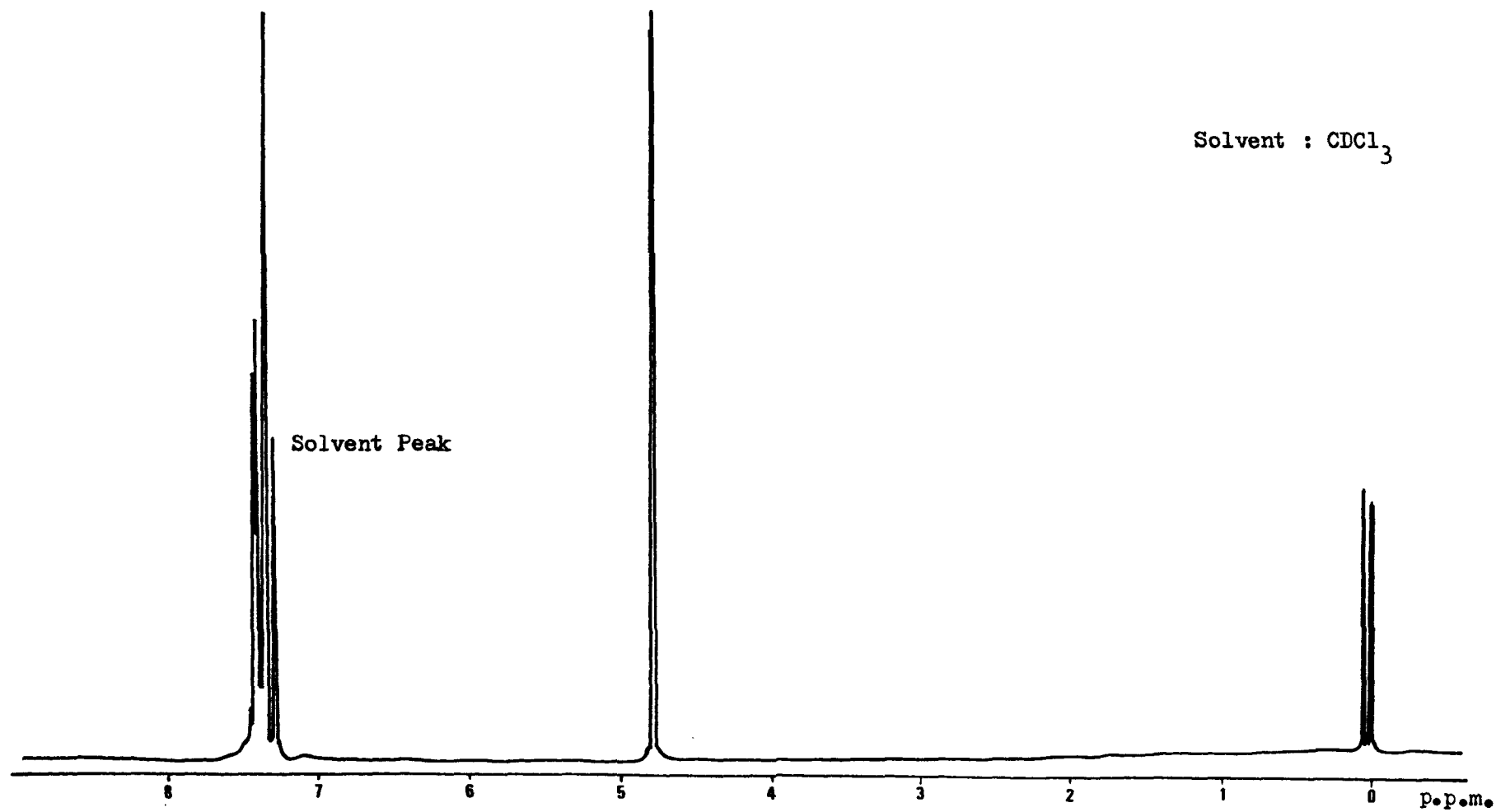


Figure 6

^1H n.m.r. of $\text{CpRu}[\text{P}(\text{OR})_3]_2\text{P}(\text{O})(\text{OR})_2$ (3a; R = Me)

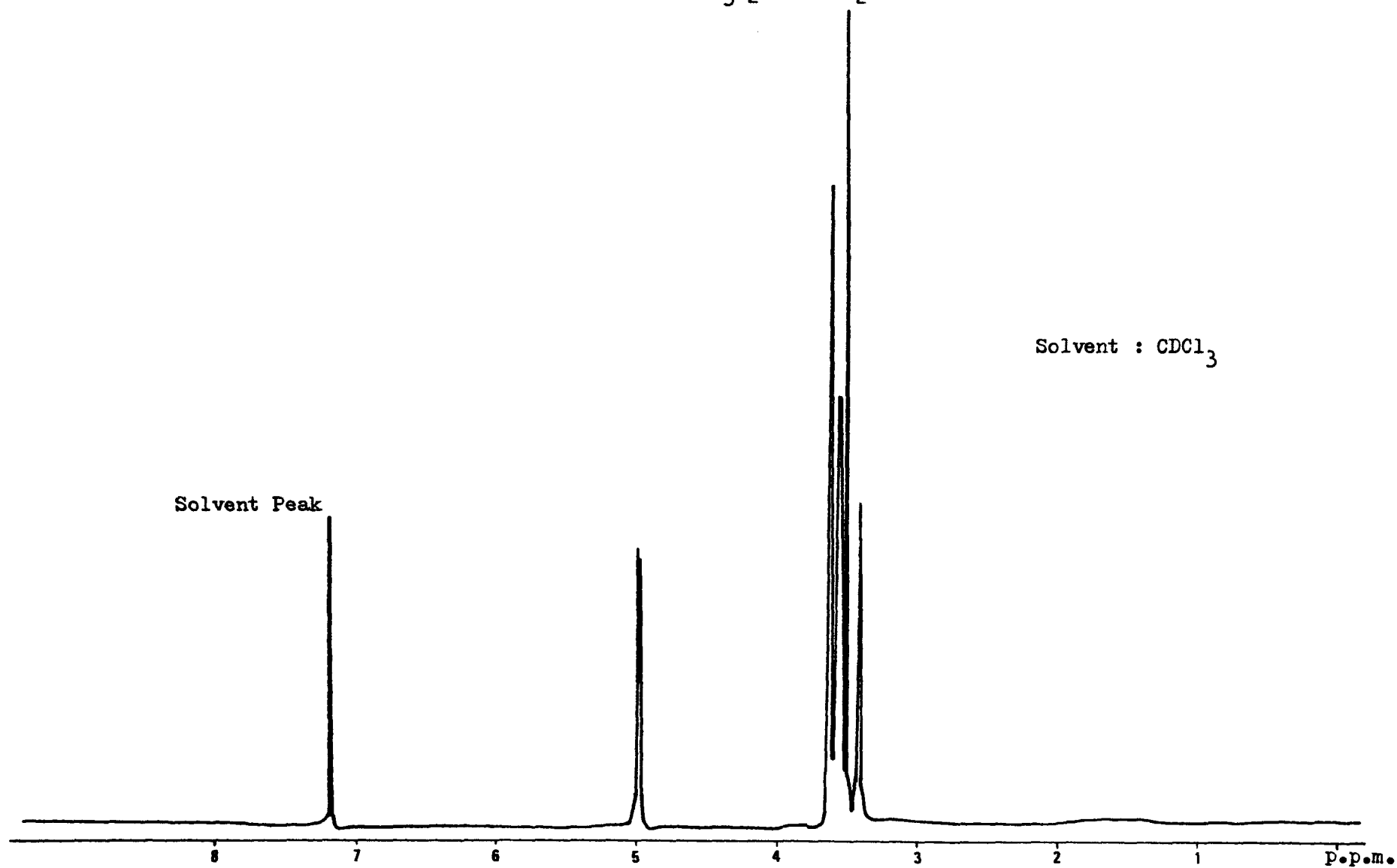


Figure 7

^1H n.m.r. of $\text{CpRu}[\text{P}(\text{OEt})_3]_2\text{P}(\text{O})(\text{OEt})_2$ (3b)

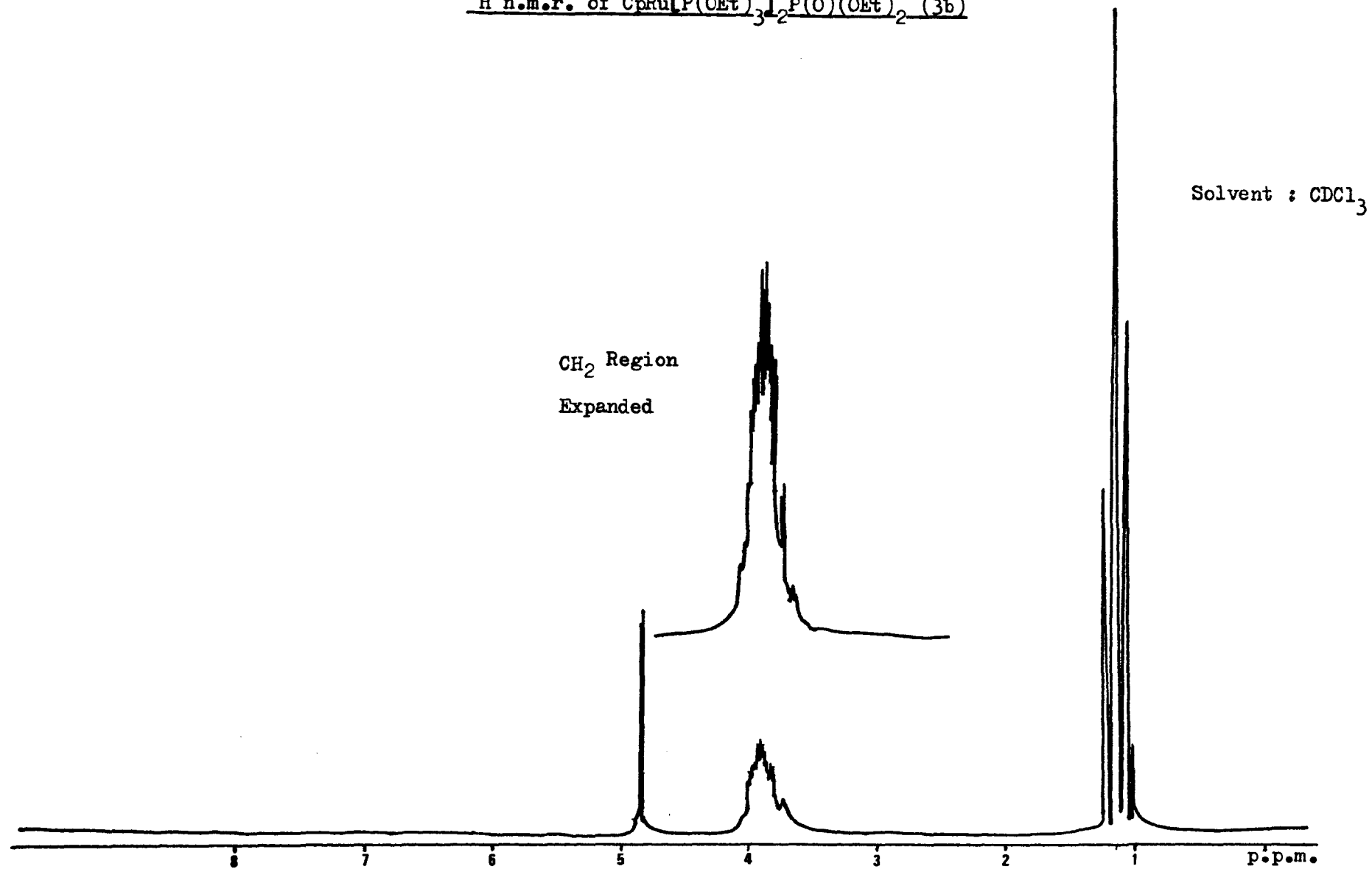


Figure 8

^1H n.m.r. of $\text{CpRu P}[(\text{OBu})_3]_2\text{P}(\text{O})(\text{OBu})_2$ (3c)

Solvent : CDCl_3

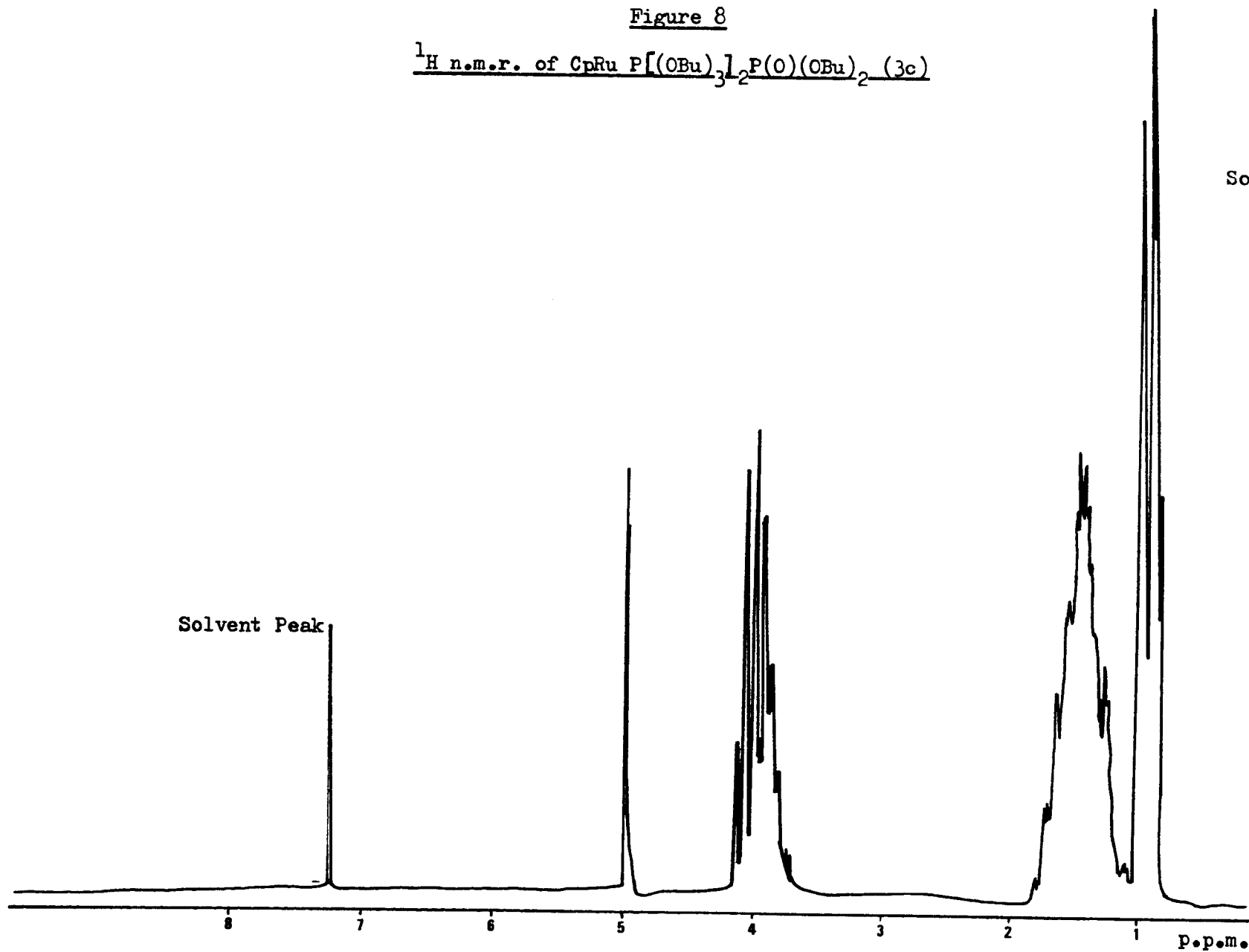


Figure 9

^1H n.m.r. of $\text{CpRu}(\text{CO})\text{P}(\text{OEt})_3\text{P}(\text{O})(\text{OEt})(4\text{b})$

Solvent : CDCl_3

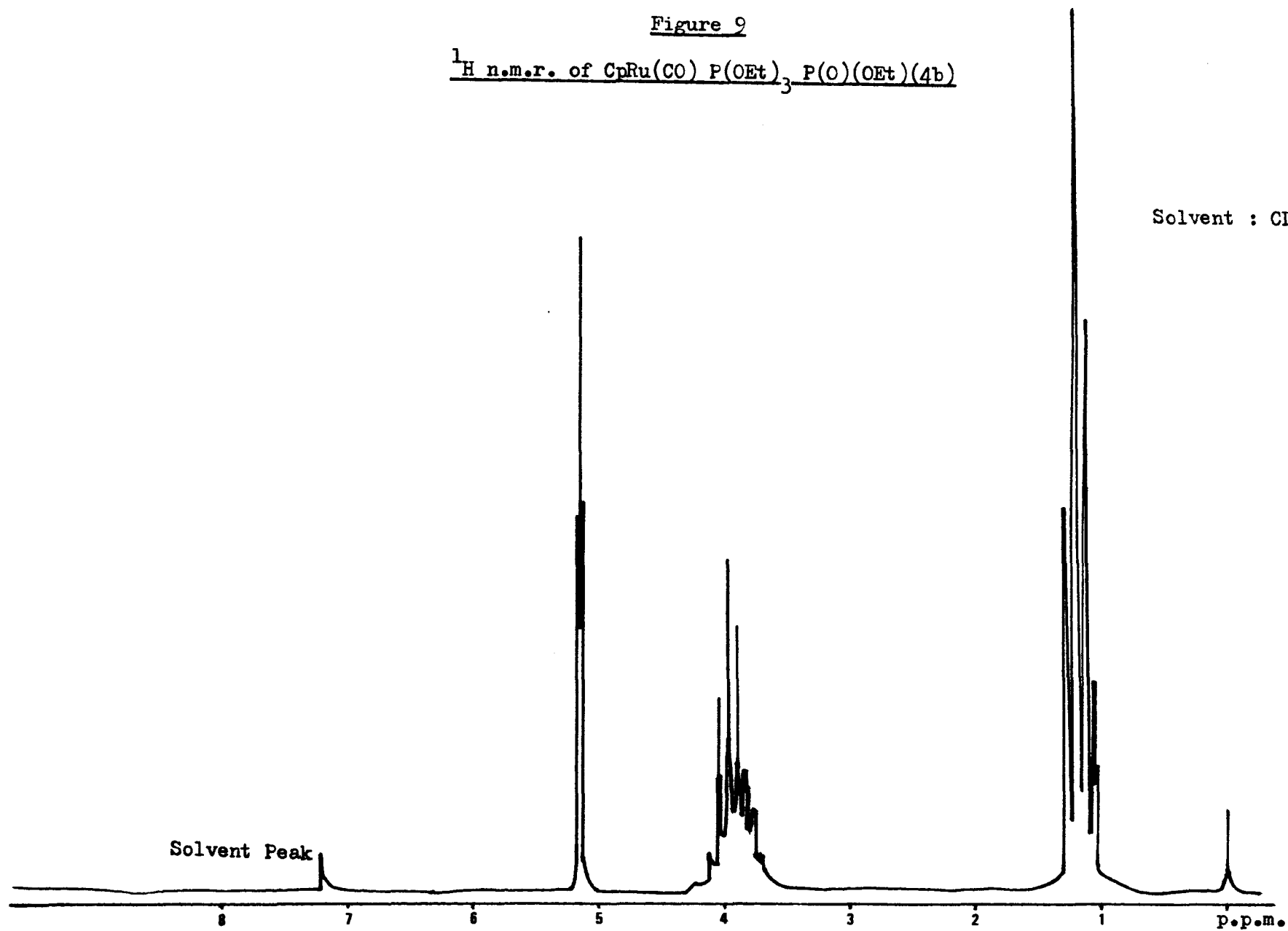


Figure 10

^1H n.m.r. of $\text{CpFe(CO)P(OMe)}_3\text{Me}$ (11)

Solvent : CDCl_3

Solvent Peak

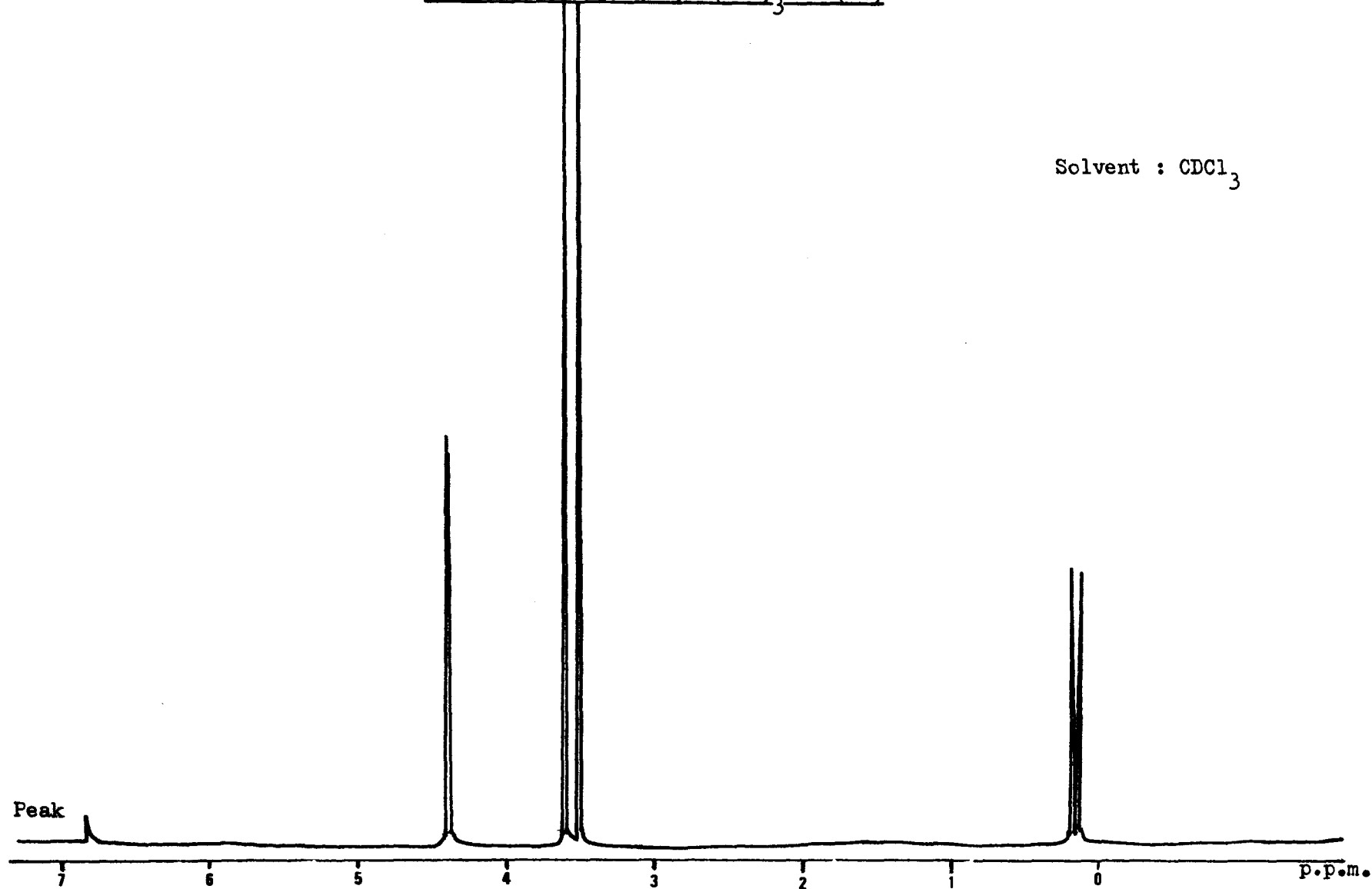


Figure 11

^{13}C n.m.r. of $\text{CpFe}(\text{CO})\text{P}(\text{OMe})_3\text{Me}$ (11)

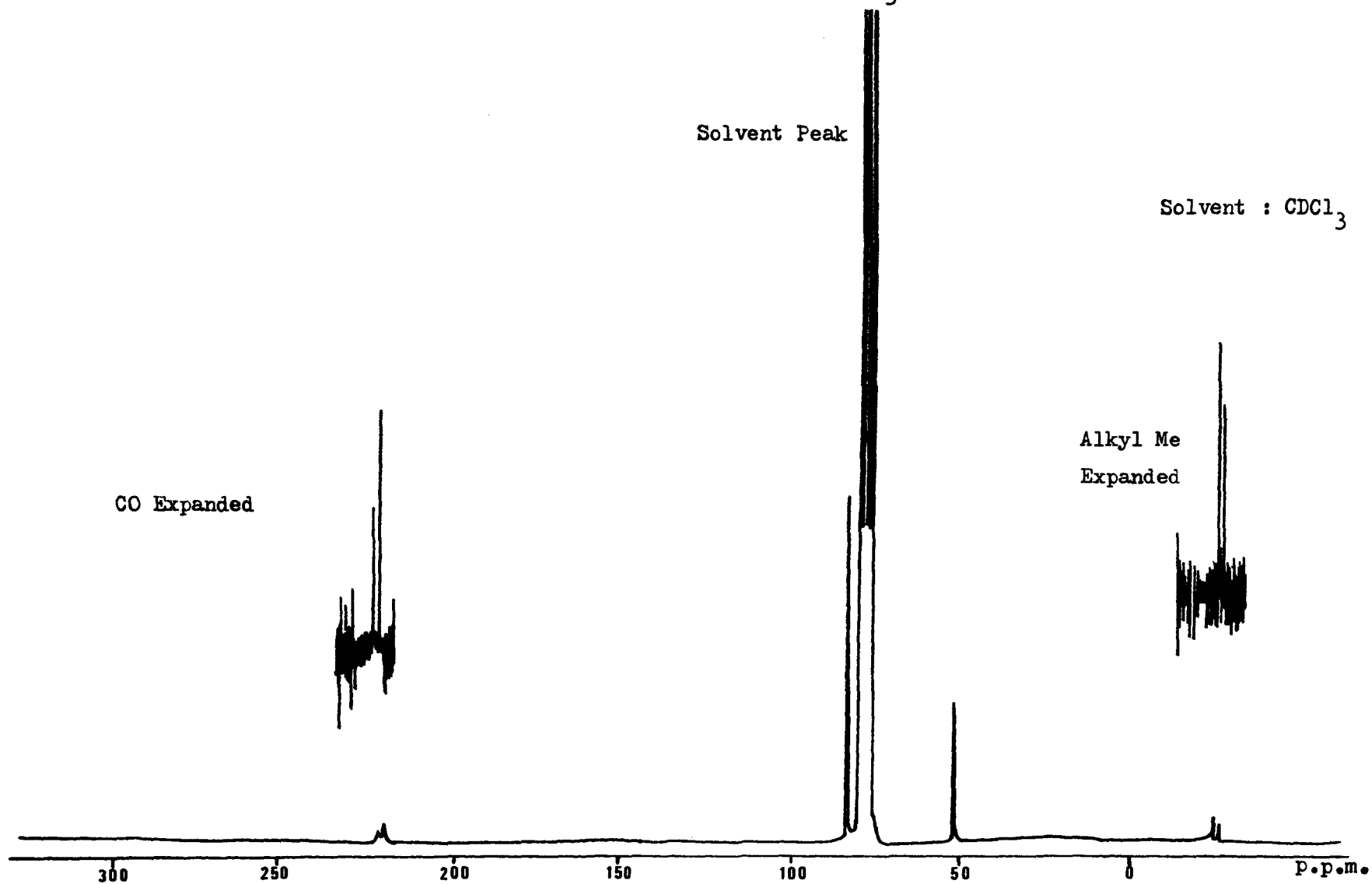


Figure 12

^1H n.m.r. of $\text{CpFe(CO)P(OMe)}_3\text{COMe}$ (8a)

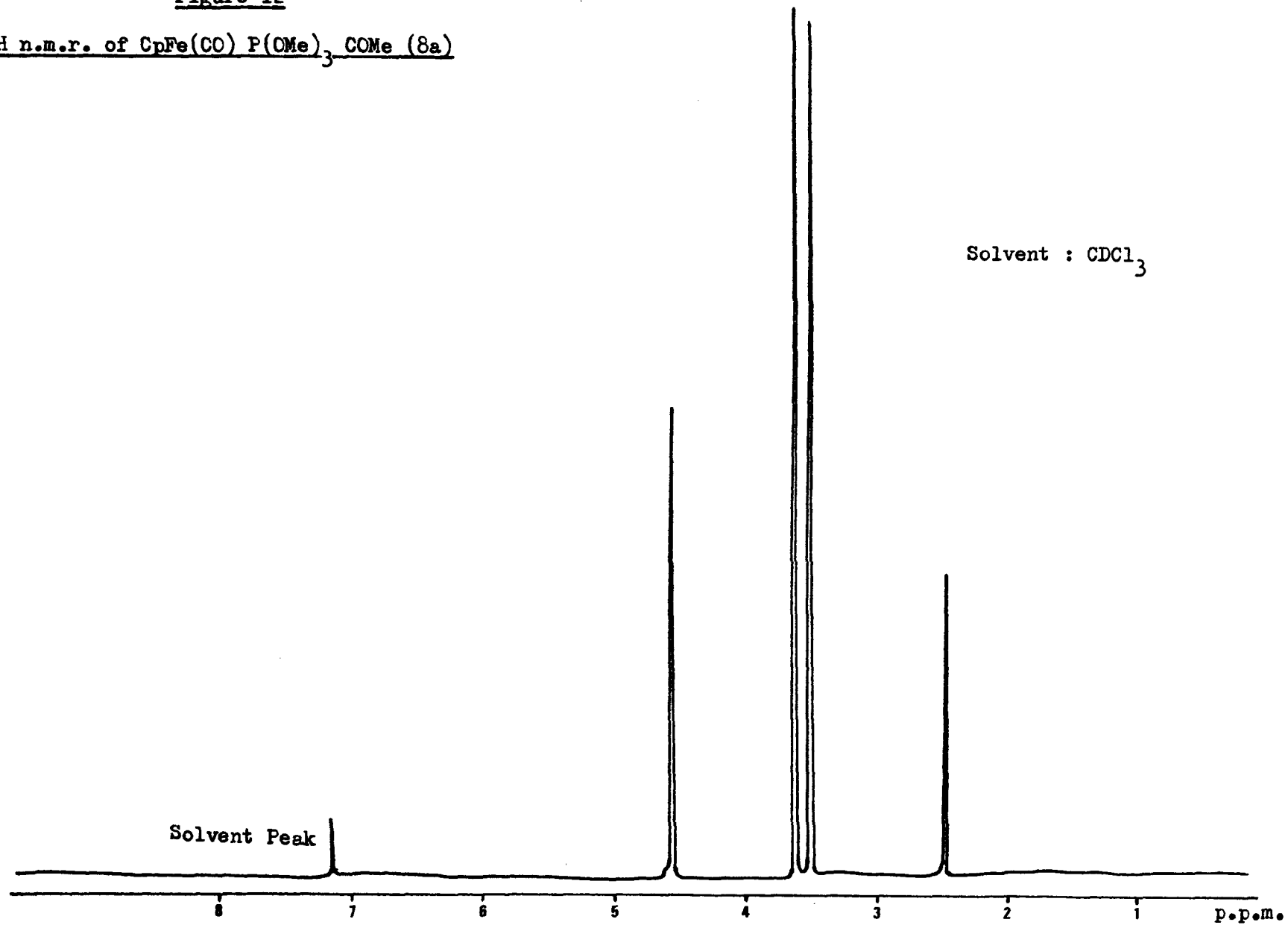


Figure 13

^{13}C n.m.r. of $\text{CpFe}(\text{CO})[\text{P}(\text{OMe})_3]\text{COMe}$ (8a)

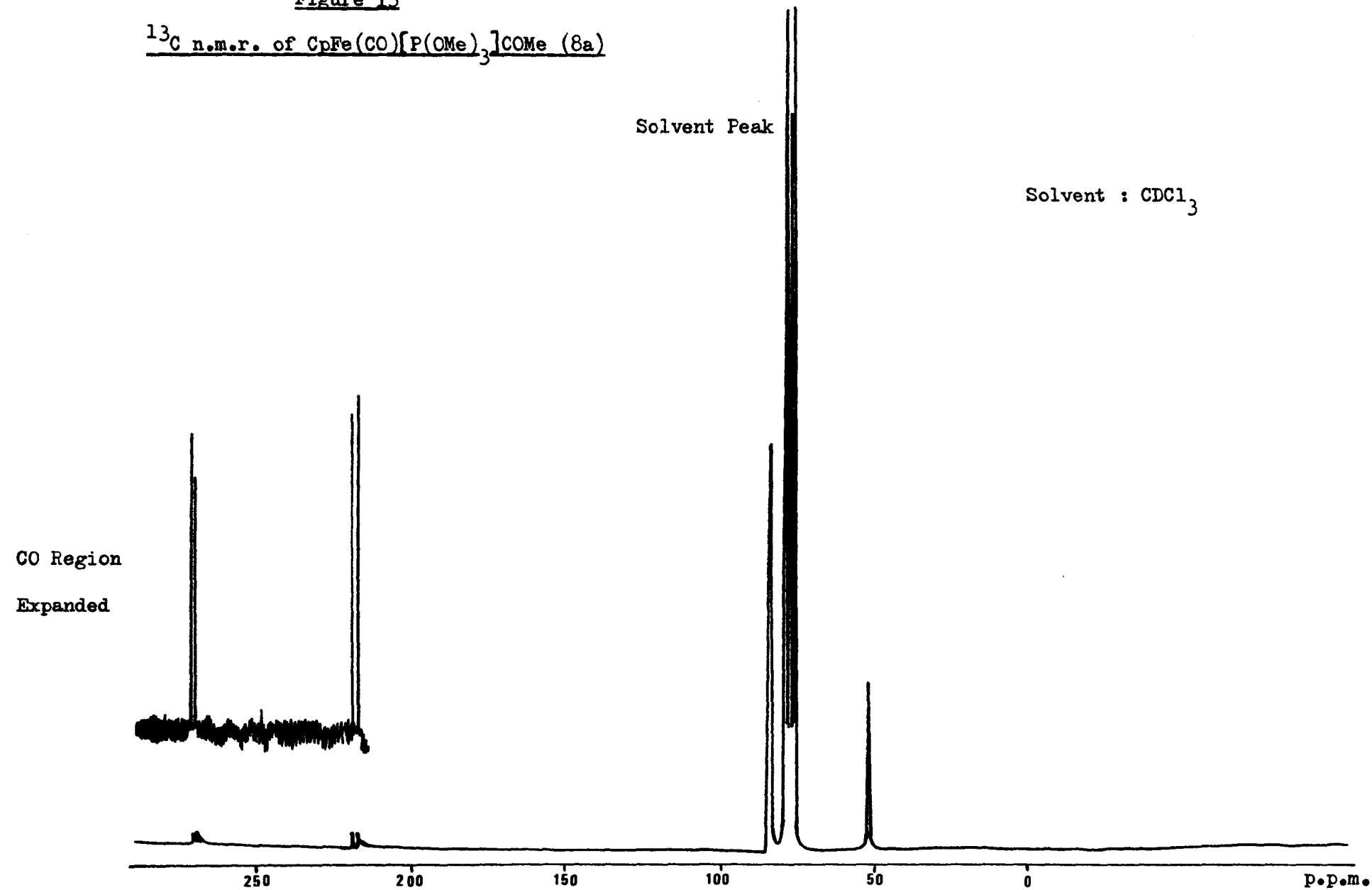


Figure 14

^1H n.m.r. of $\text{CpFe(CO)P(OEt)}_3\text{COEt}$ (8b)

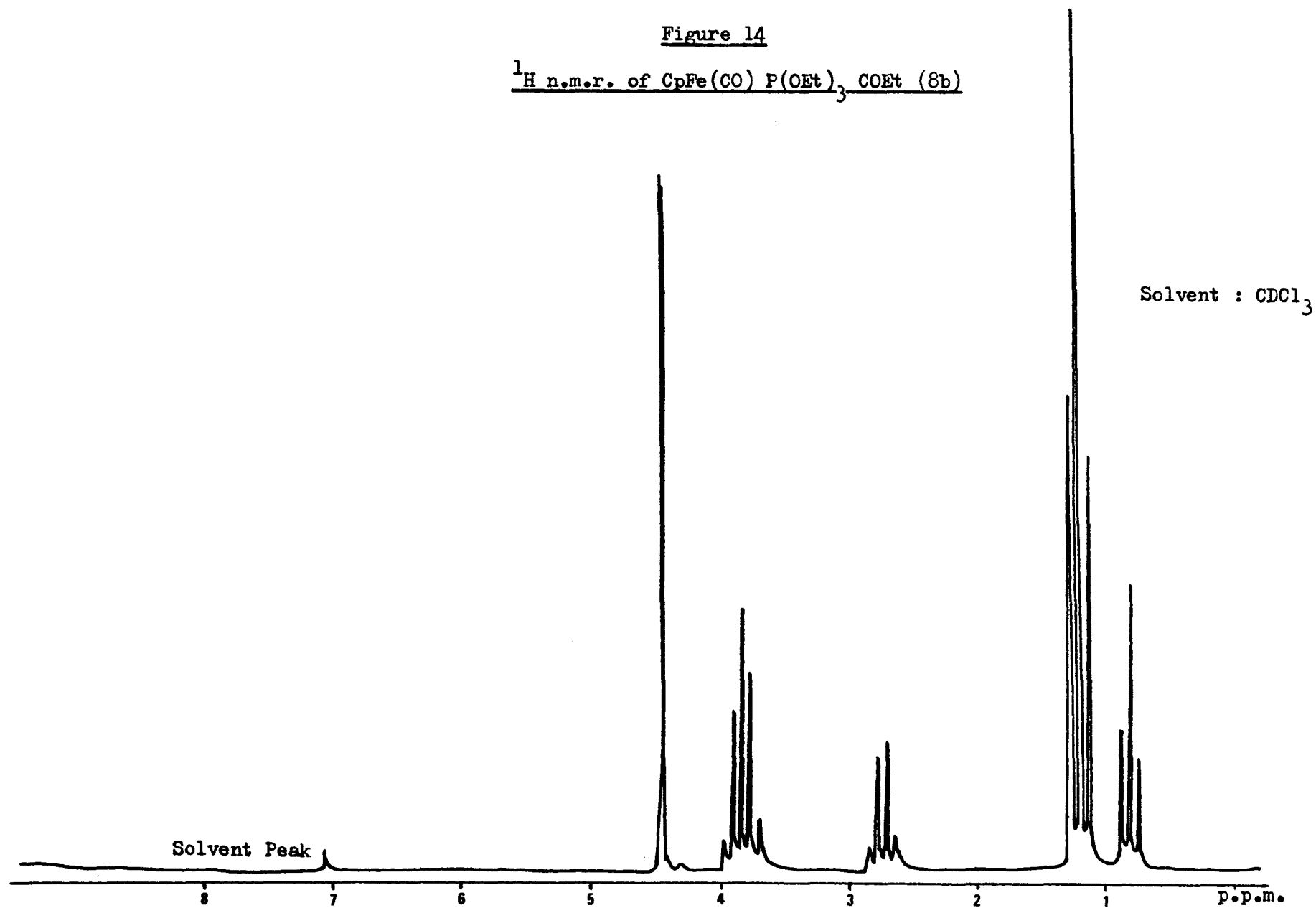


Figure 15

^{13}C n.m.r. of $\text{CpFe}(\text{CO})\text{P}(\text{OEt})_3\text{COEt}$ (8b)

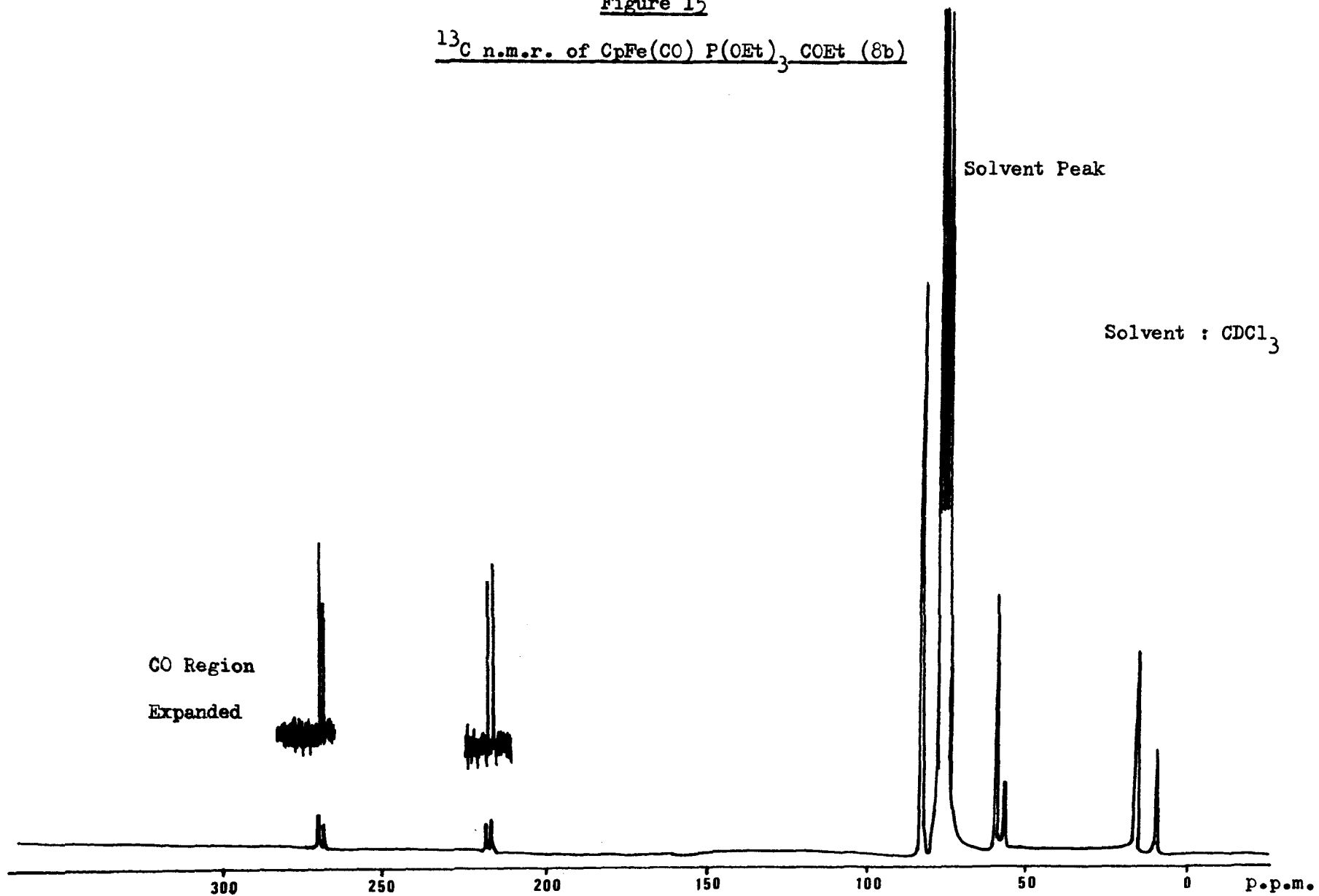


Figure 16

^1H n.m.r. of $\text{CpFe}(\text{CO})[\text{P}(\text{OMe})_3]\text{P}(\text{O})(\text{OMe})_2$ (9a)

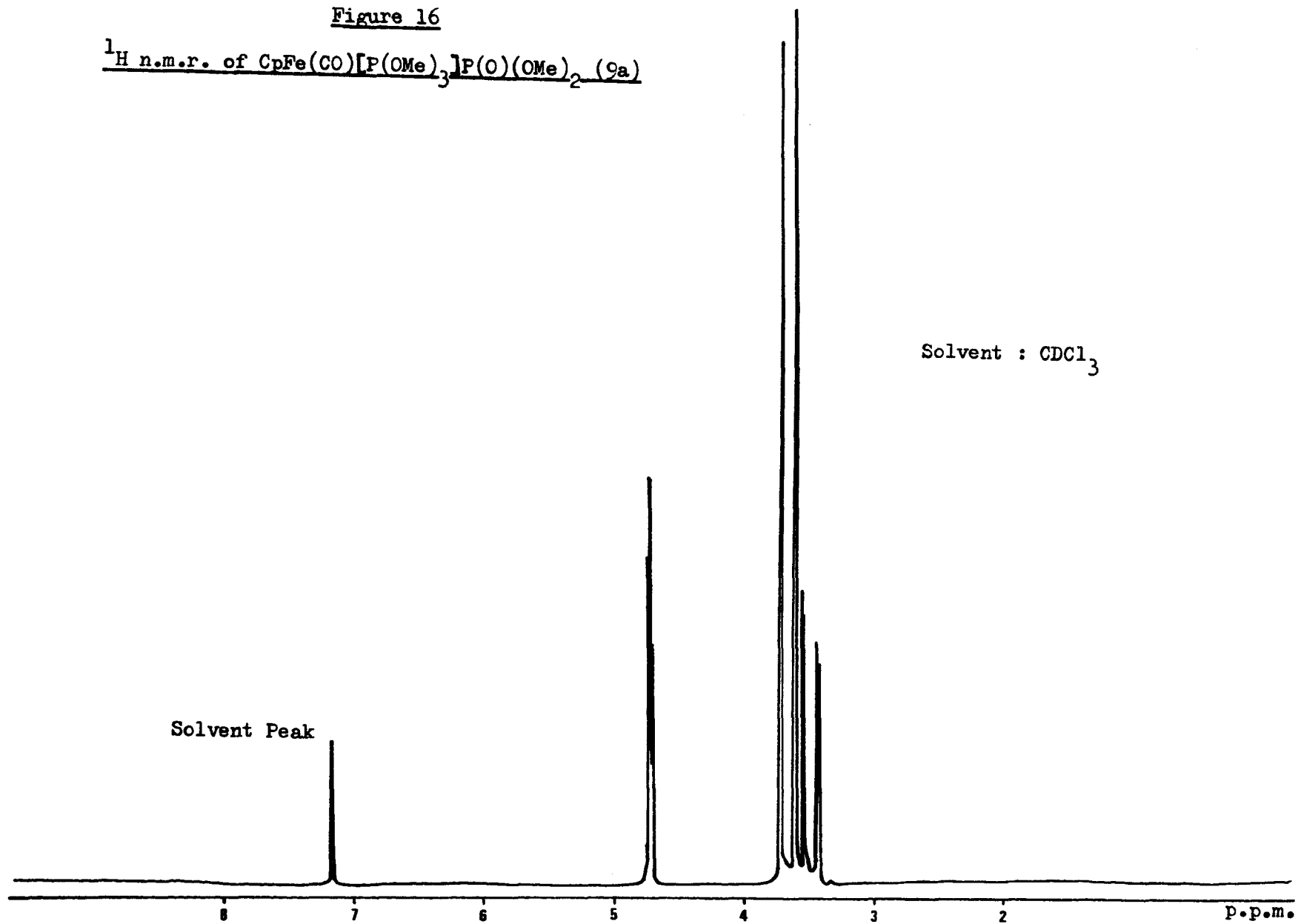
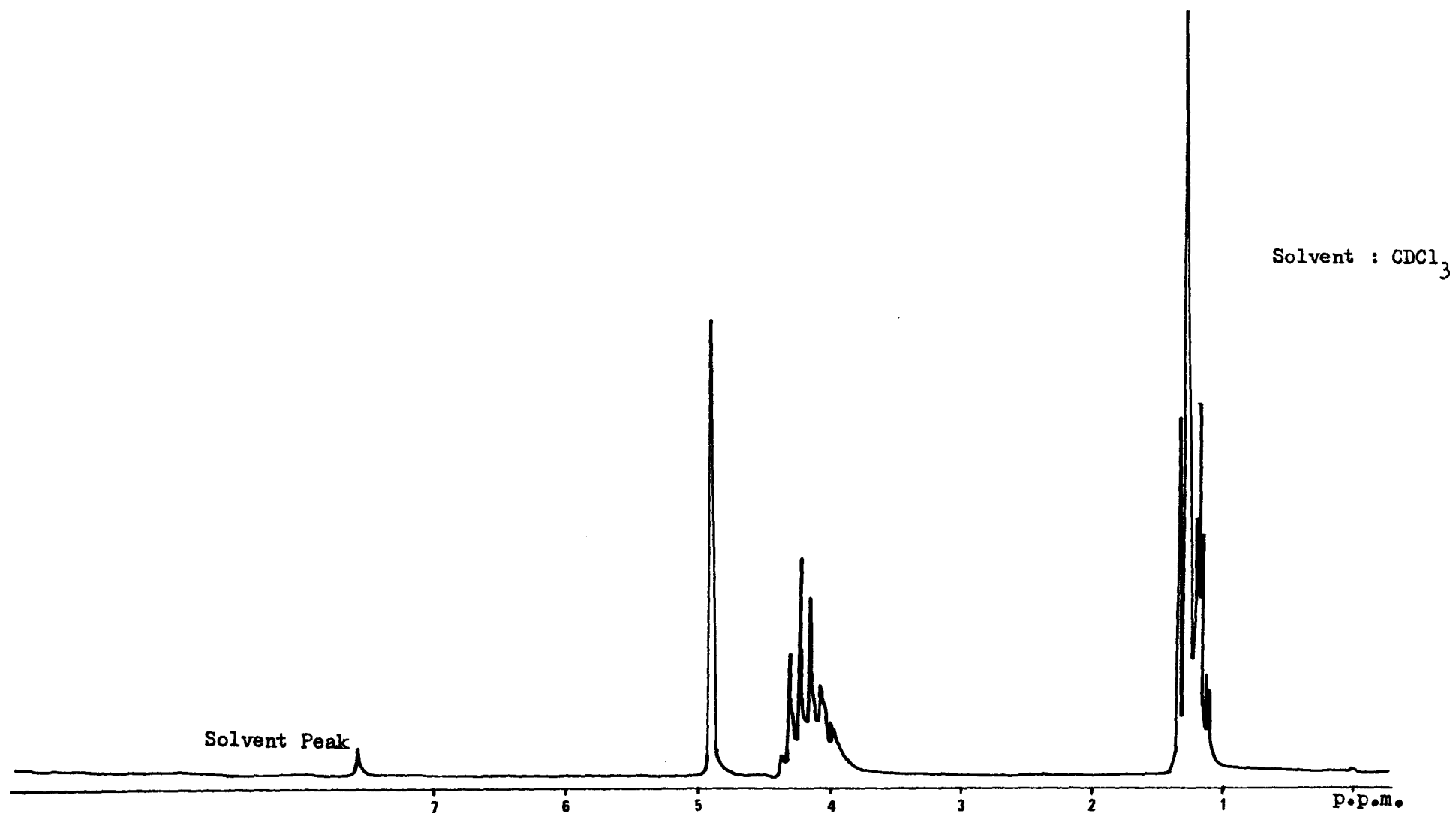


Figure 17

^1H n.m.r. of $\text{CpFe(CO)[P(OEt)}_3\text{]P(O)(OEt)}_2$ (9b)



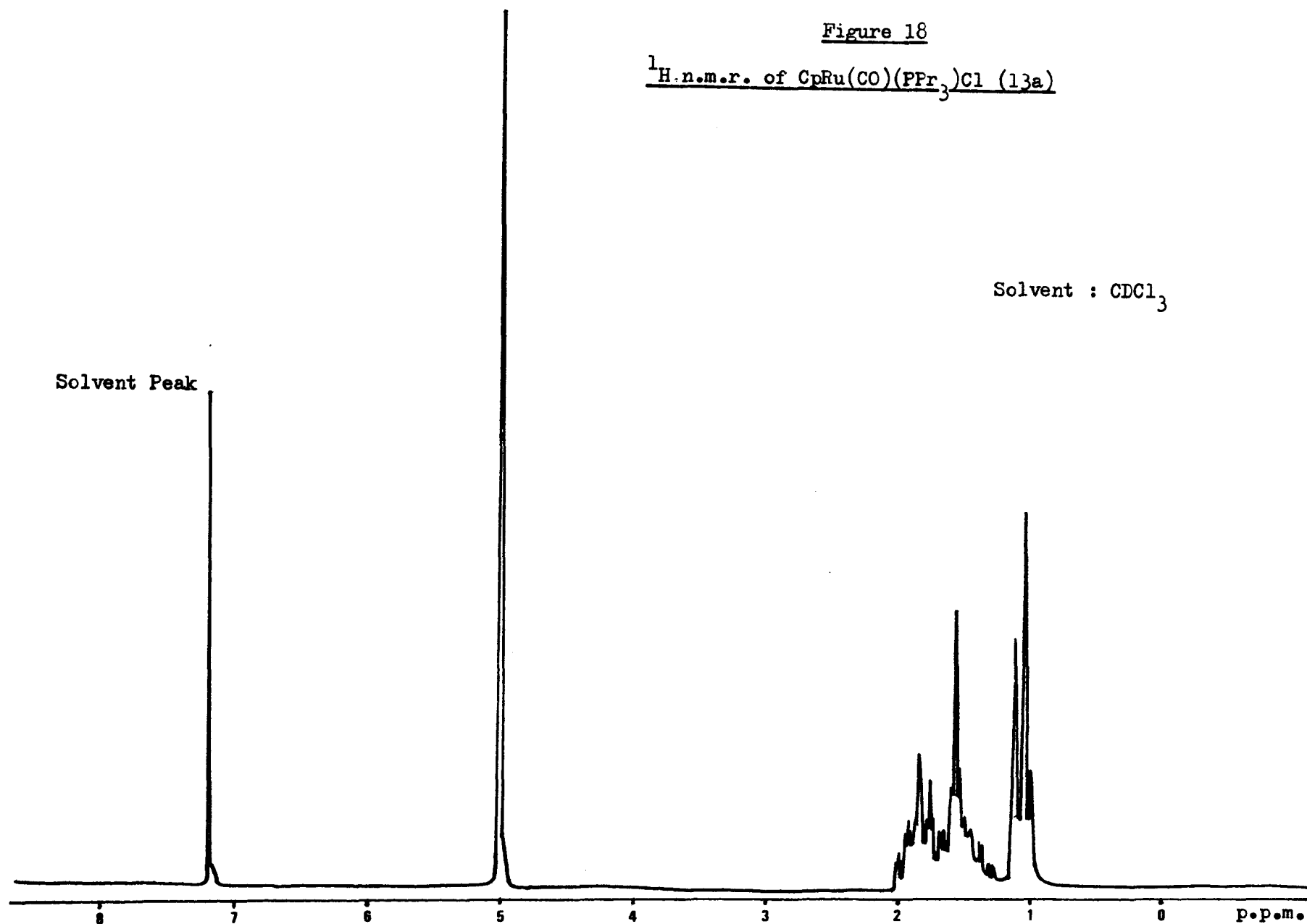


Figure 19

^1H n.m.r. of $\text{CpRu}(\text{CO})(\text{PPhMe}_2)\text{Cl}$ (13b)

Solvent : CDCl_3

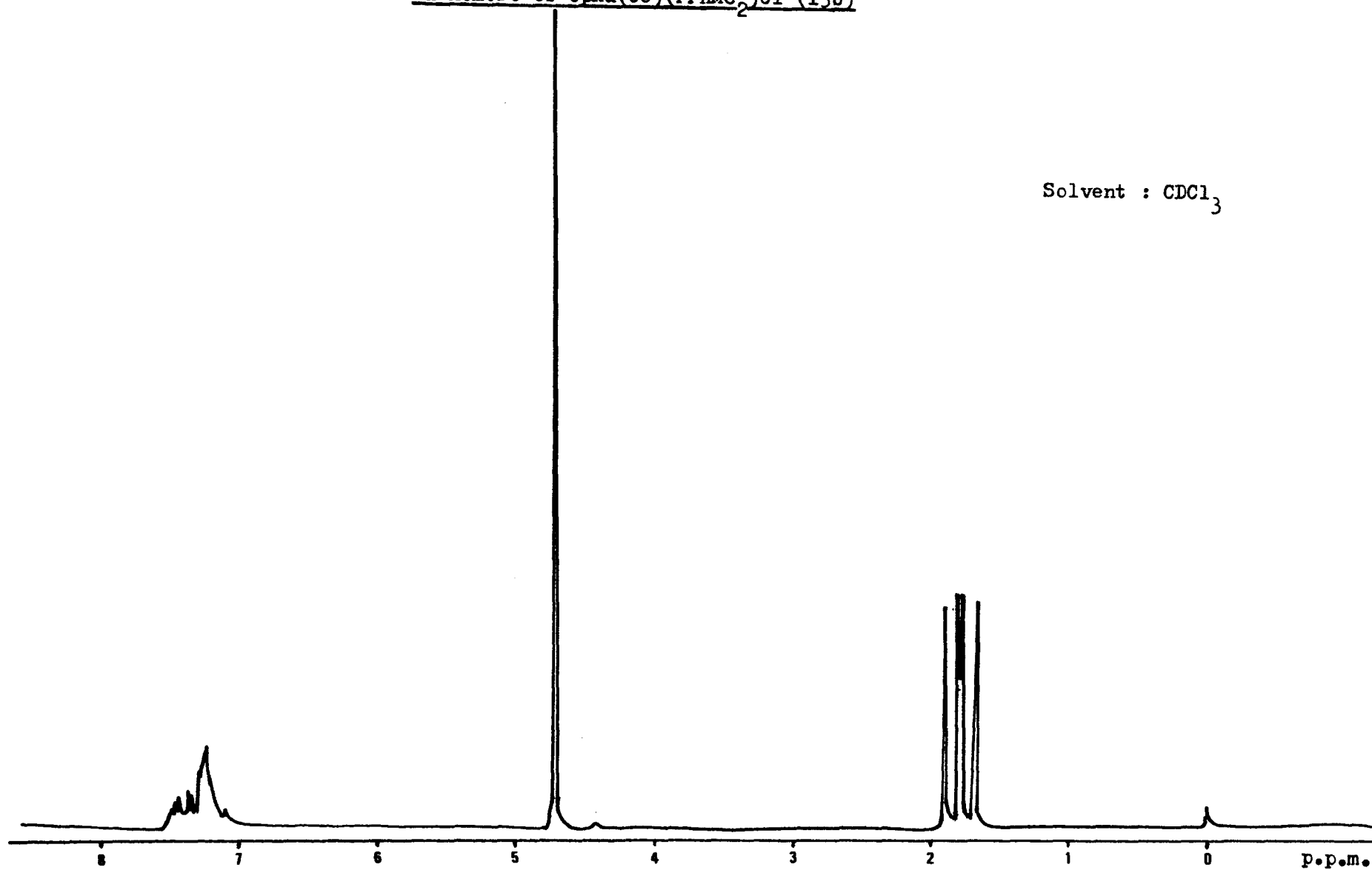


Figure 20

^1H n.m.r. of $\text{CpRu}(\text{PPhMe}_2)_2\text{Cl}$ (14)

Solvent : CDCl_3

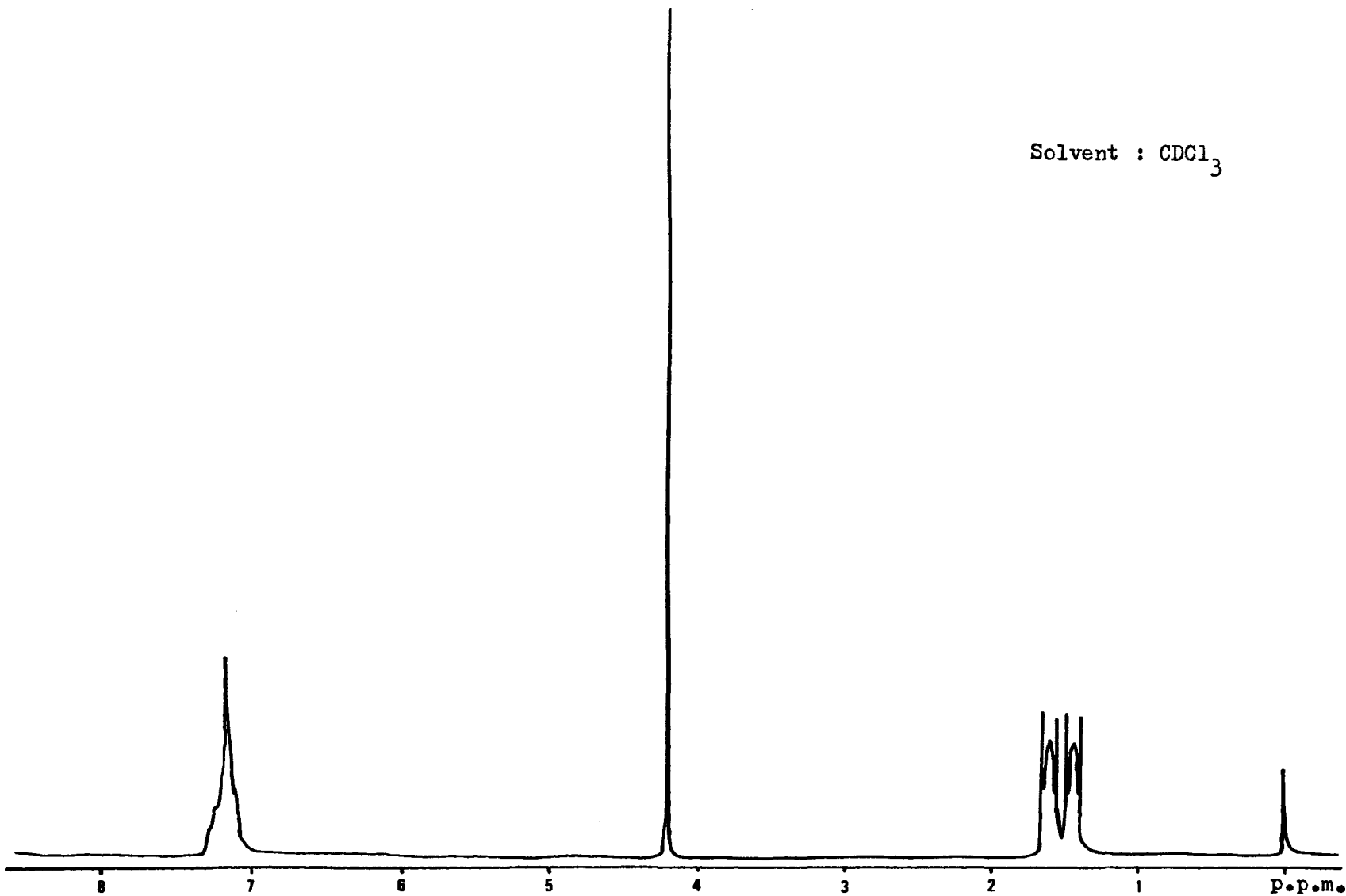


Figure 21

^{13}C n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPhMe}_2$ (12b)

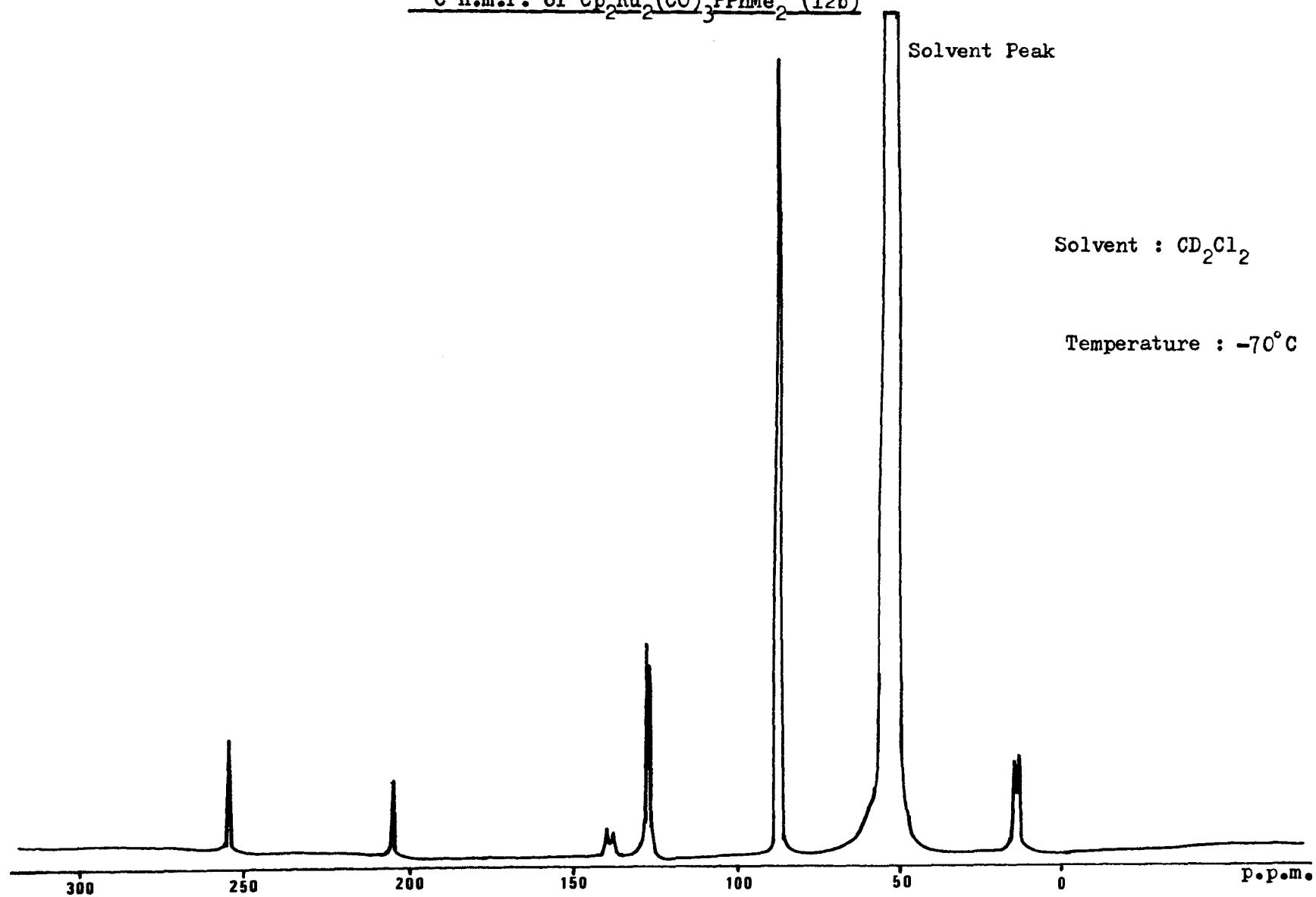


Figure 22

^1H n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPr}_3$ (12a)

Solvent : CDCl_3

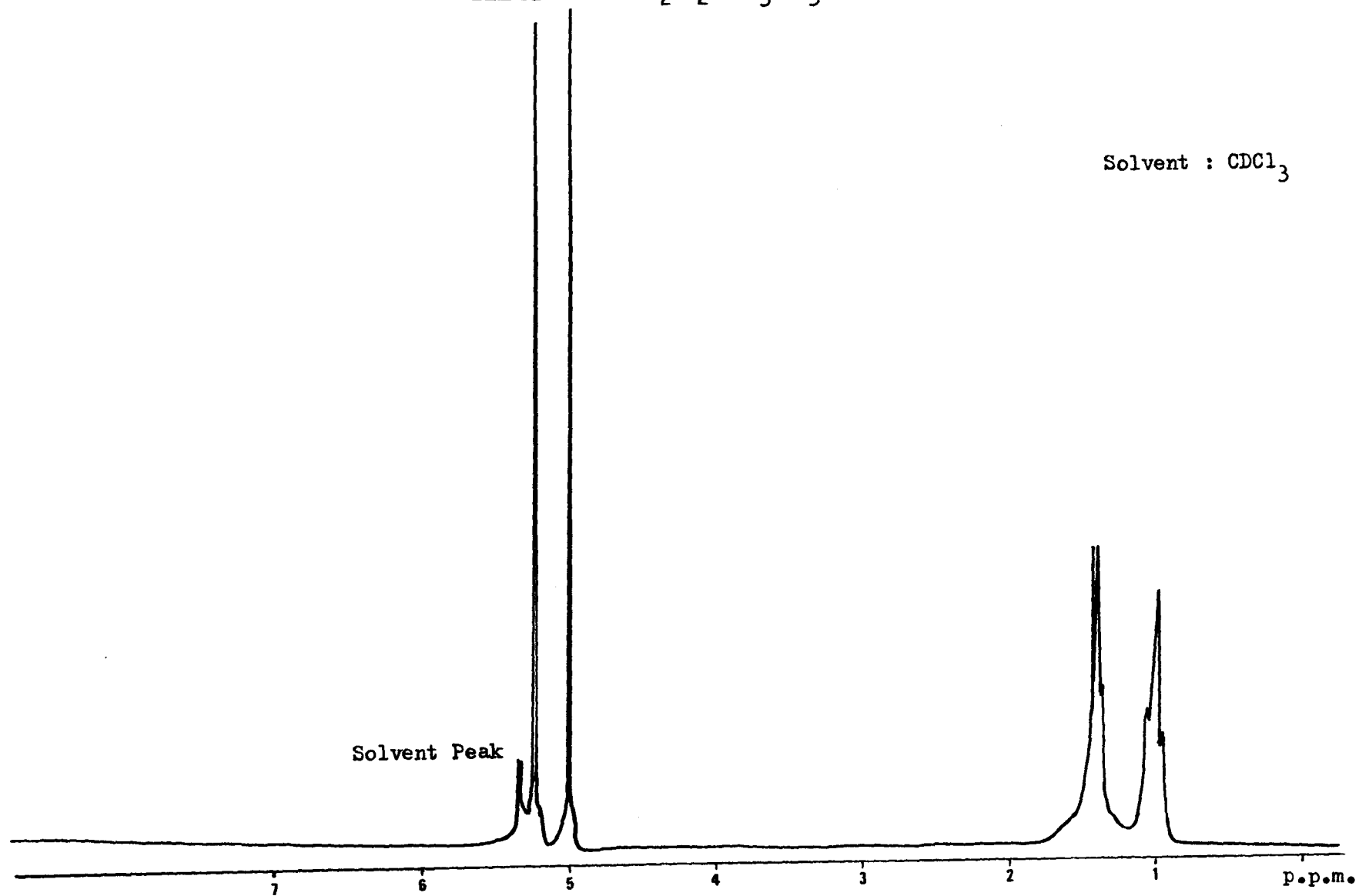
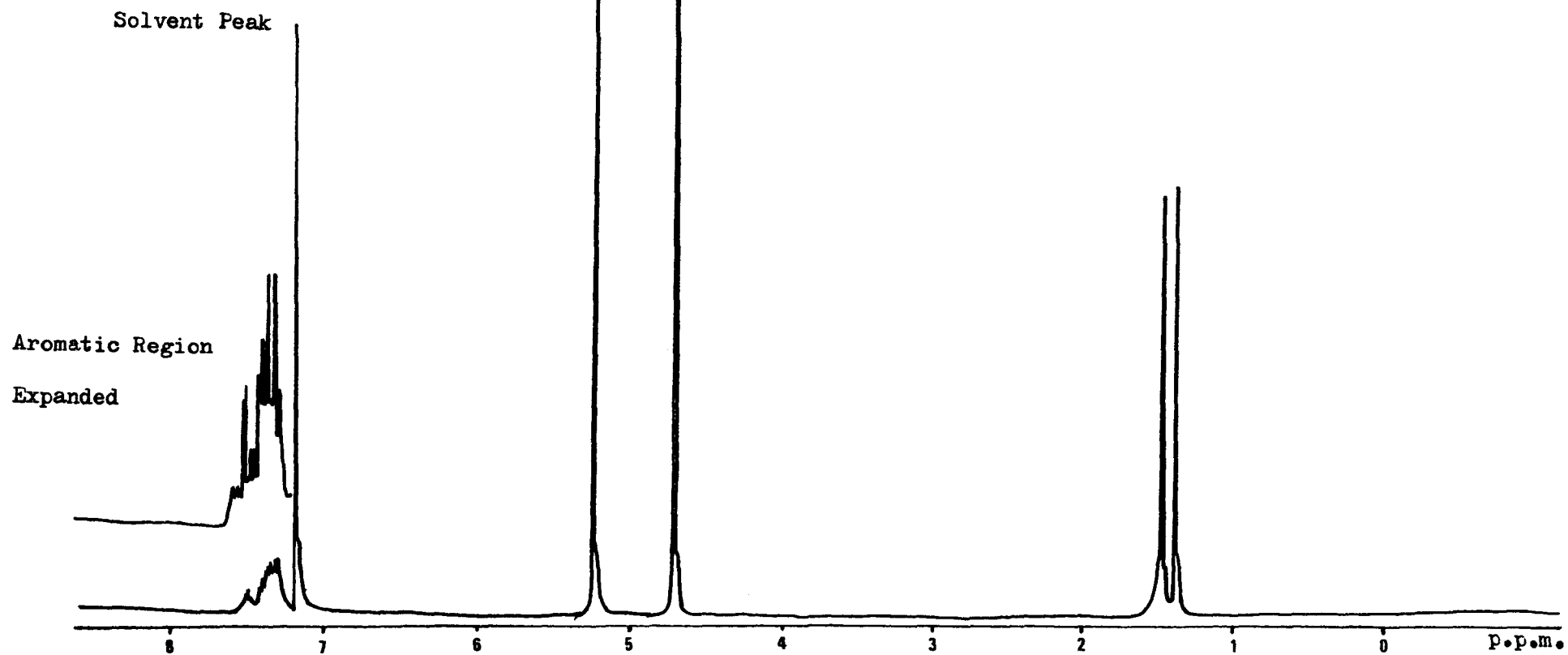


Figure 23

^1H n.m.r. of $\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PPhMe}_2$ (12b)

Solvent : CDCl_3



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