ISONITRILE DERIVATIVES OF POLYNUCLEAR METAL CARBONYLS

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fulfilment of the requirements for the Degree of
Doctor of Philosophy

by

Pradeep Mathur

Department of Chemistry
University of Keele
Staffordshire
United Kingdom

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The work in this thesis unless otherwise stated, was carried out by the author under the supervision of Dr.J.A.S.Howell. No part of the work incorporated in the thesis has been incorporated in a thesis submitted for a Higher Degree at any University.

CONTENTS

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ABSTRACT

The synthesis of a number of transition metal carbonyl complexes and their isonitrile derivatives has been carried out. The fluxional character of some of the isonitrile substituted derivatives has been studied by means of infrared and variable temperature n.m.r. spectroscopy.

The complexes, $Cp_2Fe_2(CO)_3(CS)$ and $Cp_2Fe_2(CO)_2(CS)_2$, the thiocarbonyl analogues of $Cp_2Fe_2(CO)_4$, and their isonitrile substituted derivatives have been prepared and fully characterised. The fluxional behaviour of these complexes, in which the CS group is found exclusively in the bridging position, has been studied.

The attempted preparation of mixed metal carbonyl complexes containing isonitrile groups has been discussed. Although no mixed metal isonitrile derivative was obtained, the products isolated may be explained by mechanisms involving free radicals, electron transfer and ligand exchange reactions.

A general method for polynuclear carbonyl complexes containing the CNR_2 group has been discussed and n.m.r. studies carried out on complexes of the type $HFe_3(CO)_{10}CNR_2$, indicate a restricted rotation about the C-N bond. An independent fluxional behaviour of the CO groups is also discussed. The preparation and fluxional behaviour of $HFe_3(CO)_9CHNPr^i$ and $Fe_3(CO)_{11}(CNR)$ is also discussed.

CHAPTER 1

Introduction

Since the discovery of the first transition metal carbonyl complex, tetracarbonylnickel[1], the field of transition metal carbonyls has undergone massive expansion. Tetracarbonylnickel had almost immediate industrial application and this helped to initiate the search for carbonyls of other metals. In the 20 years following the discovery of $Ni(CO)_4$, iron[2], cobalt and molybdenum[3] carbonyls were synthesised and their properties studied. Since then the discovery of new metal carbonyls has continued and is still in progress.

An excellent review by Calderazzo[4] gives a comprehensive survey of transition metal carbonyl chemistry upto 1966. The early work on carbonyl chemistry mainly dealt with the exploration of the reactivity and stability of these compounds in order to prepare a large number of compounds containing carbonyl and other ligands. The readily measurable C—O stretching frequencies were found to be extremely convenient and useful to study a variety of bonding schemes and chemical properties. The carbonyl complexes have been found to act as templates to allow novel reactions upon the ligands and in their ability to stabilise organic molecules[5]. Although the early discoveries of metal carbonyls were largely a result of chance rather than predicted reactions, in recent years many rational methods of preparing metal carbonyls have been reported[4,6,7,8]. As a result, new mononuclear and polynuclear carbonyl complexes are being prepared at an ever increasing rate.

Structural studies based on X-ray, electron and neutron diffraction techniques, as well as data based on infrared, Raman, e.s.r., n.m.r., Mossbauer and microwave spectroscopy, dipole moment studies, magnetic susceptibility measurements, and mass spectrometry have contributed to provide much useful information about the various structures of metal carbonyl complexes[9,12]. The structure adopted by polymetallic carbonyls depends significantly on temperature, solvent and substitution by other ligands, and all of the techniques listed above provide information relating to the structures adopted. In addition, ligands such as CO, NO and CNR have been found to exhibit fluxional behaviour, i.e., exchange between non-equivalent sites in the molecule, and n.m.r. spectroscopy provides a unique tool to study this phenomenon. Infrared studies[10] carried out on complexes of the type $[LCo(CO)_3]_2$ indicate that in solution, when L = $AsPr^i_3$, $AsBu^i_3$, the complex exists solely in the non-bridged form. In contrast, when L = PEt_3, $AsEt_3$ or $SbEt_3$, the bridged tautomers increase in importance in passing from phosphorus to antimony. In recent years, the use of fourier transform n.m.r. spectroscopy has become increasingly significant in following stereochemical non-rigidity in metal carbonyl and related complexes. N.m.r. techniques have been used to show the bridged and non-bridged carbonyl structural interconversions undergone by $Cp_2Fe_2(CO)_4$ (henceforth Cp represents cyclopentadienyl) in solution[11,18,19], as shown in Fig. 1.

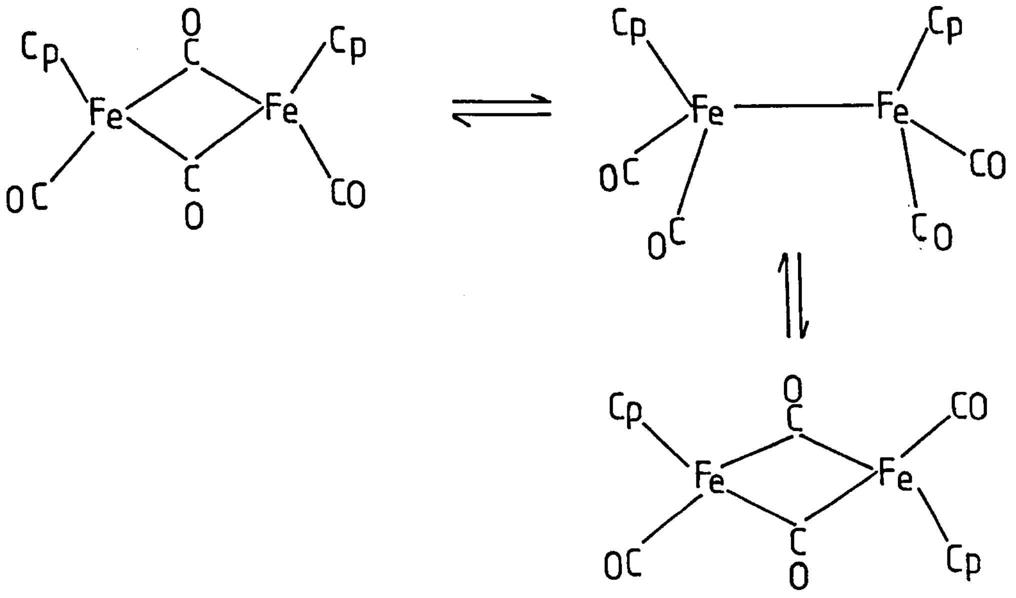


Fig. 1.

Isonitriles[14,15] and nitrosyls[16] have been shown to undergo similar bridge-terminal site exchange, and there are likely to be a wider range of ligands that undergo this type of exchange between different sites.

Several metal carbonyl compounds can be prepared by direct interaction of carbon monoxide and the metal. Thus $Ni(CO)_4$ may be prepared by reaction of finely divided nickel metal with carbon monoxide at atmospheric pressure[17]. However, iron, cobalt, molybdenum and ruthenium only combine with carbon monoxide at elevated temperatures and pressures to give the corresponding carbonyl compounds, $Fe(CO)_5$, $[Co(CO)_4]_2$, $Mo(CO)_6$ and $Ru(CO)_5$ respectively. A much more convenient method for the preparation of many metal carbonyls is based on the reaction of carbon monoxide with a metal compound in the presence of a reducing agent. Some of the more commonly used reducing agents include excess carbon monoxide, hydrogen, sodium, magnesium, aluminium, zinc, copper, Grignard reagents, aluminium alkyls, lithium aluminium hydride and sodium benzophenoneketyl. The following reactions illustrate the applications of some of these reducing agents.

(i) $OsO_4 + 9CO \rightarrow Os(CO)_5 + 4CO_2$

(ii) $2CoCO_3 + 8CO + 2H_2 \rightarrow [Co(CO)_4]_2 + 2CO_2 + 2H_2O$

(iii) $VCl_3 + 4Na + 2\,\text{diglyme} + 6CO \rightarrow [Na(\text{diglyme})_2][V(CO)_6] + 3NaCl$

(iv) $CrCl_3 + 4Al + 6CO \rightarrow Cr(CO)_6 + AlCl_3$

(v) $WCl_6 + 3Zn + 6CO \rightarrow W(CO)_6 + 3ZnCl_2$

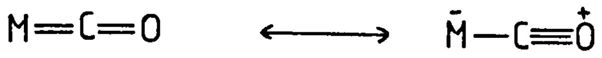
In some cases, iron pentacarbonyl has been used as the source of carbon monoxide in the preparation of metal carbonyls. Tungsten hexacarbonyl has been prepared by treatment of tungsten hexachloride with iron pentacarbonyl in an autoclave containing hydrogen under pressure.

The versatility of carbon monoxide as a ligand is evident from the diversity it shows in bonding to metal atoms. It can be found bonded to one, two or three metal atoms, and although it is usually the carbon atom of the carbon monoxide that coordinates to metal atoms, the ligand can coordinate through its oxygen atom also. An outline of the several ways in which carbon monoxide can coordinate to one or more metal atoms is given below.

The carbon monoxide ligand can be terminally attached to one metal atom forming a linear or nearly linear M—C—O unit, as shown below.

$$M=C=O$$

The metal carbon bonds in compounds containing CO coordinated to a single metal atom are found to be much shorter than the metal carbon bonds of metal alkyls. For example, in the molybdenum complex, $(\eta^5 - C_5H_5)Mo(CO)_3Et$,[20] the carbonyl ligands are attached to the molybdenum by molybdenum carbon bonds of length 1.97 Å, whereas the single molybdenum carbon bond to the ethyl group is 2.38 Å long. This can be interpreted by describing the M—CO bonding as a resonance hybrid of the mesomeric forms I and II (Fig. 2).



$$M=C=O \longleftrightarrow \overset{-}{M}-C\equiv\overset{+}{O}$$

I II

Fig. 2.

Therefore, the bond order of M—C is expected to be between 1 and 2, and that of C—O between 2 and 3.

The more commonly used description of M—CO bonding is the molecular orbital formulation (Fig. 3).

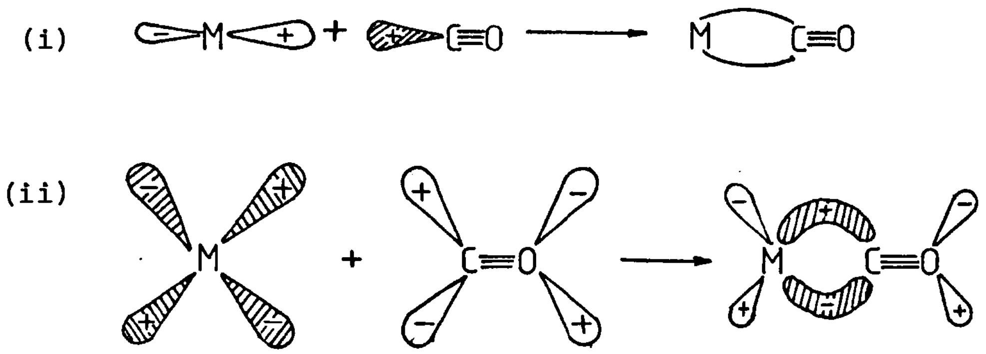


Fig. 3.

The lone pair electrons on carbon are donated to a suitable vacant metal orbital, and the electron drift from the ligand to the metal assumed to occur in this process is compensated for by back π-donation from metal to ligand from a filled metal d atomic orbital into the ligand π* orbital. This bonding mechanism is synergic, since the drift of metal electrons into CO orbitals will tend to make the ligand as a whole negative and this increases its basicity through the σ-orbital of carbon. Simultaneously, the drift of electrons to the metal in the σ bond will make the CO positive, hence increasing the acceptor capability of the π-orbitals. Thus the σ bond and π bond formation mutually strengthen each other. The synergic nature of the M—CO bond implies that the carbonyl ligand remains essentially neutral; however, closer consideration of the orbitals involved in the bonding shows that on coordination carbon monoxide acquires a significant negative charge. This results from the fact that the σ donation from CO to metal involves less charge transfer from CO to metal while the back π-donation involves a greater charge transfer from metal to CO than is commonly supposed.

Infrared stretching frequencies of CO vibrations provides evidence for the multiple nature of the M—CO bonds, as predicted according to the bonding description given above. Assuming that the valence of C remains constant, any increase in M—C bond order should cause an equal decrease in the C—O bond order which will be reflected by a drop in the CO stretching frequency. Therefore, by direct comparison of the stretching frequency of CO in metal carbonyl complexes with that of free carbon monoxide, the extent of back bonding from metal to carbonyl group can be noted. Whereas free carbon monoxide has a stretching frequency of 2143 cm^{-1}, terminal carbonyl groups in neutral metal carbonyl complexes have stretching frequencies in the range 2150-1850 cm^{-1}. Although the extent to which electronic charge is transferred to the ligand may vary from one system to another, there is no variation in the number of electrons formally donated from ligand to metal. The terminal carbonyl ligand can be regarded as a 2-electron ligand, that being the number it donates to the metal atom.

In di- or polynuclear metal carbonyl complexes, a carbonyl ligand can adopt a doubly bridging mode of coordination, still functioning as a 2-electron donor (Fig. 4).

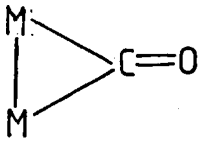


Fig. 4.

The 'lone pair' orbital on carbon can overlap with a suitable in-phase combination of empty metal orbitals. Simultaneously, an out of phase combination of filled metal orbitals can interact with the carbon monoxide π^* antibonding orbital (Fig. 5). As a consequence of this type of bonding, the carbon-oxygen bond order is reduced to approximately two. Infrared stretching frequencies of bridging carbonyls generally fall in the range 1850-1750 cm^{-1}, indicating even more reduced carbon-oxygen bond order than in the case of the terminally attached carbonyls. Very often the bridging carbonyl groups occur in pairs and any pair can be regarded as having an alternative non-bridged arrangement with a terminal carbonyl on each metal (Fig. 6).

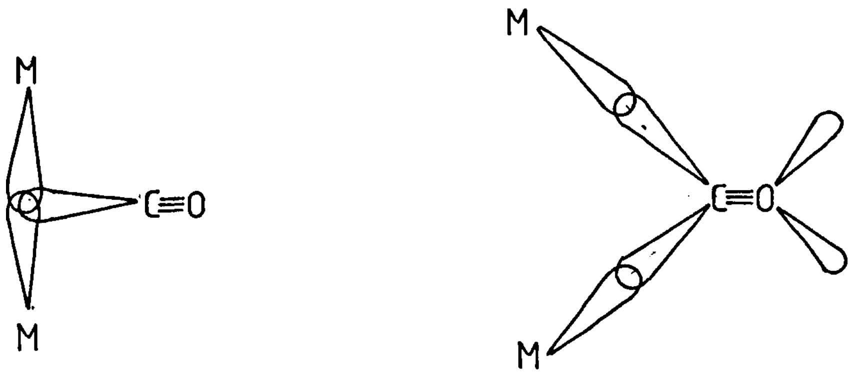


Fig. 5.

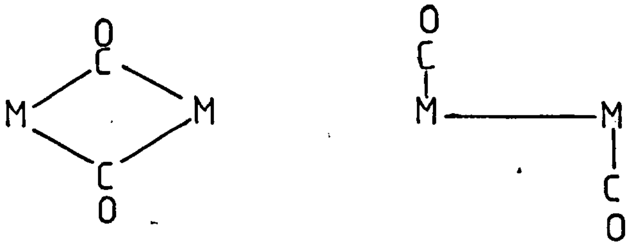


Fig. 6.

The relative stability of the non-bridged structure over the bridged structure increases on descending any group in the Periodic Table; the larger the metal atoms the greater is the likelihood for a non-bridged structure. Hence, whereas $Fe_3(CO)_{12}$ has two bridging carbonyl groups, $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ contain only terminally bound carbonyl ligands. Metal atom size plays an important role when one considers the attachment of carbonyl ligands to different metal atoms along a horizontal period of the Periodic Table. Thus the dinuclear

$Mn_2(CO)_{10}$ contains only terminally attached carbonyl ligands because of the large size of the Mn atoms, whereas $Co_2(CO)_8$ exists as an equilibrium mixture of the bridged and non-bridged structures. Similarly, although $Fe_2(CO)_9$ and $Cp_2Rh_2(CO)_3$ have structures as shown in Fig. 7(i) and Fig. 8(i) respectively, the alternate structures shown in Fig. 7(ii) and Fig. 8(ii) are also possible. In the second form of structure each Fe

(i) (ii)

Fig. 7. $Fe_2(CO)_9$

(i) (ii)

Fig. 8. $Cp_2Rh_2(CO)_3$

atom of $Fe_2(CO)_9$ is bound to the other by a M—M bond and bridged by a single CO group. The alternate structure for $Cp_2Rh_2(CO)_3$ has three bridging CO groups and no M—M bond as in

$Cp_2Rh_2(CO)(CH_2)_2$ (Fig. 9). Substitution of a carbonyl group of $Fe_2(CO)_9$ gives a complex with a monobridged structure (Fig. 10).

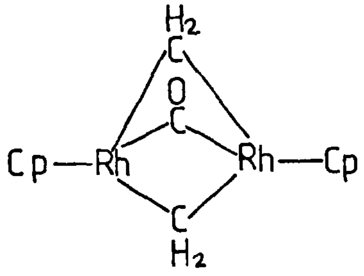


Fig. 9. $Cp_2Rh_2(CO)(CH_2)_2$

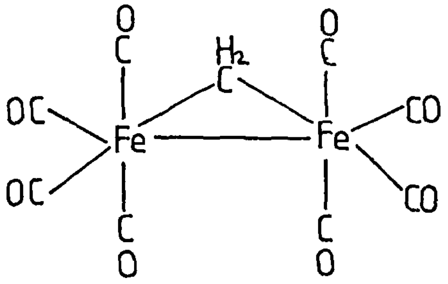


Fig. 10. $Fe_2(CO)_8CH_2$

Generally, the doubly bridging carbonyl groups are symmetrical, the metal carbon distances being equal, but in a few cases unsymmetrical bridging carbonyls are found to occur, such as in $Fe_3(CO)_{12}$ (Fig. 11)[21] and the phosphine substituted $Fe_3(CO)_{11}$ PPh_3 (Fig. 12)[22].

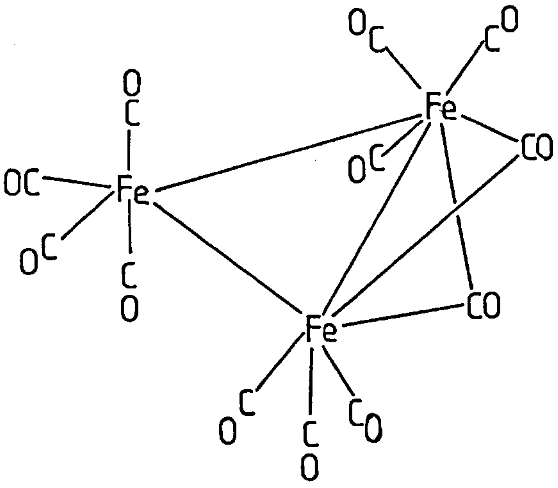


Fig. 11. $Fe_3(CO)_{12}$

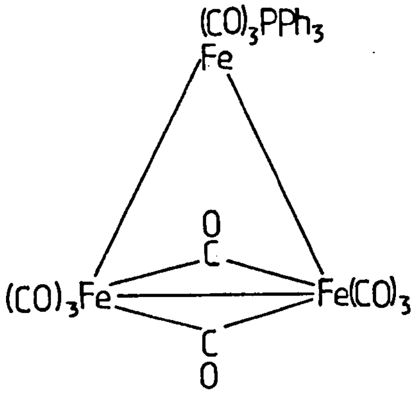


Fig. 12. $Fe_3(CO)_{11}(PPh_3)$

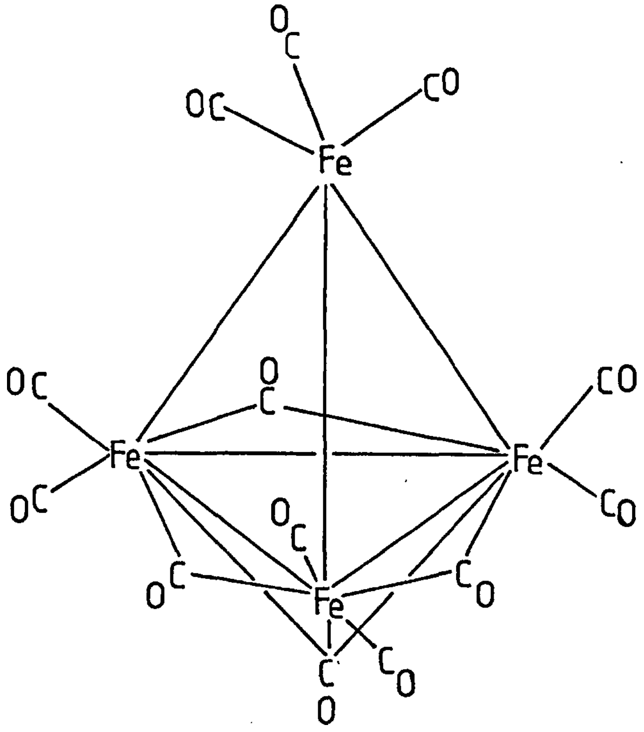


Fig. 13. $[Fe_4(CO)_{13}]^{2-}$

In the dianion $[Fe_4(CO)_{13}]^{2-}$ (Fig. 13), three of the carbonyls form very asymmetric bridges with the three basal iron atoms while a fourth carbonyl triply bridges these three iron atoms[82].

The carbonyl ligand has been shown to scramble between bridging and terminal sites with great ease[23], and this lends much support to the suggestion that the difference between the strength of attachment in the bridging and terminal sites is very small. A study of the bond energies of the dinuclear iron carbonyl, $Fe_2(CO)_9$, which has six terminal and three bridging carbonyl ligands is in accord with this conclusion[24].

A slightly different type of bonding between metal and bridging carbonyl group exists for the dihapto doubly bridging carbonyl group. This type of a bridging carbonyl can be found in $Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2$ [25]. The bonding scheme, as shown in Fig. 14 consists of a donation

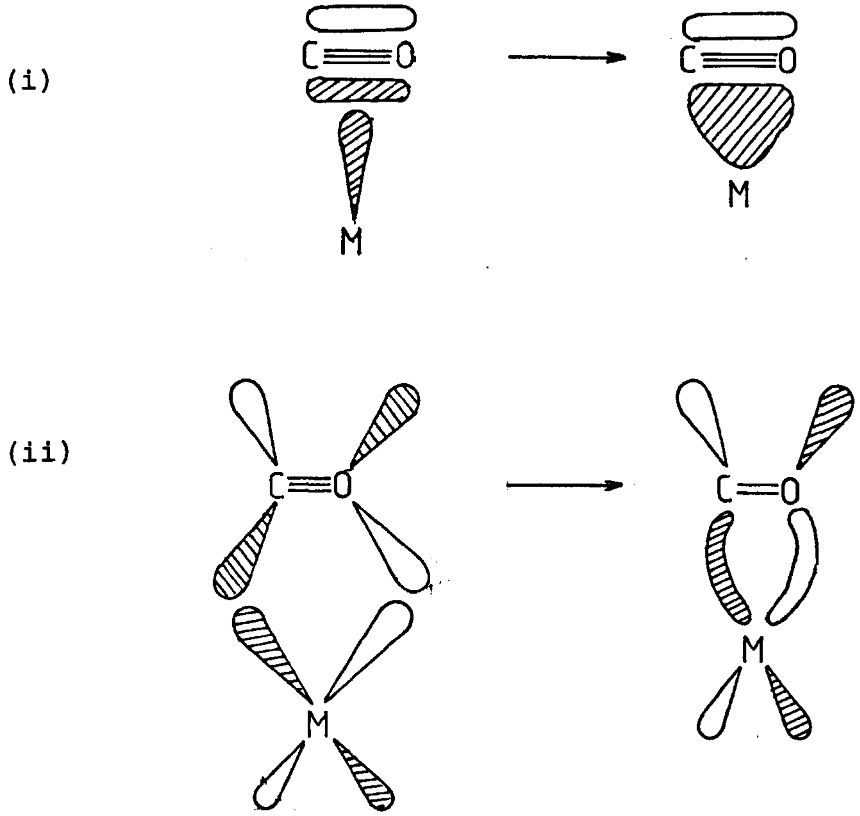


Fig. 14.

of electrons from the ligand π molecular orbital to a suitable metal orbital and simultaneously, a donation of electrons from metal to ligand π^* antibonding molecular orbital.

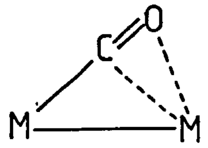


Fig. 15.

Thus, in this type of bonding, both the carbon and the oxygen atoms form an attachment to one of the metal atoms and hence facilitating quite an extensive reduction of the carbon oxygen bond order.

The structure of $Cp_2V_2(CO)_5$ (Fig. 16) shows the presence of two semibridging carbonyl groups. The formation of the V → V bond gives a highly polar electron distribution which is redressed by partial transfer of electron density from a filled d orbital of one metal atom into one of the π* orbitals of a CO group that is principally bonded to the adjacent metal atom (Fig. 17). A consequence

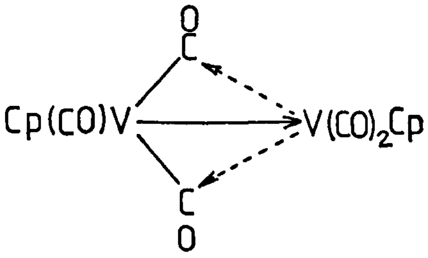


Fig. 16. $Cp_2V_2(CO)_5$

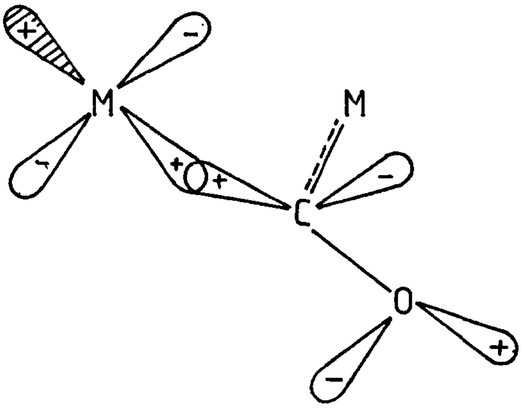


Fig. 17.

of this type of bonding is the substantial bent nature of the M-C-O bond (160-170°).

The carbonyl ligand may also be found triply-bridging three metal atoms (Fig. 18). The bonding in such a

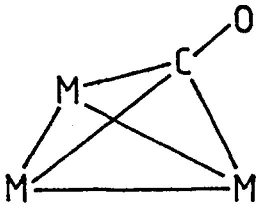
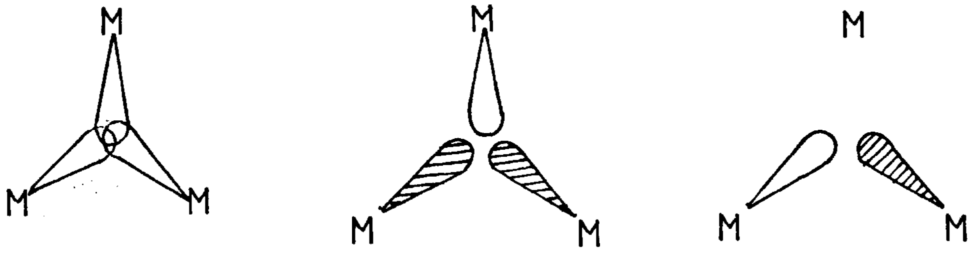


Fig. 18.



(i) (ii) (iii)

Fig. 19.

system involves interaction of the lone pair orbital on carbon with a suitable combination of empty metal orbitals (Fig. 19 (i)), and a simultaneous donation of electrons from a suitable combination of metal orbitals (Fig. 19 (ii) and (iii)) into the π* antibonding orbitals of carbon monoxide. The CO stretching frequencies of the triply-bridging carbonyls are even lower than those of the doubly-bridging carbonyl groups. The CO bond orders have been estimated to be just below two.

Recently, a quadruply-bridging carbonyl ligand has been reported[26]. The anion $[HFe_4(CO)_{13}]^-$ has a unique

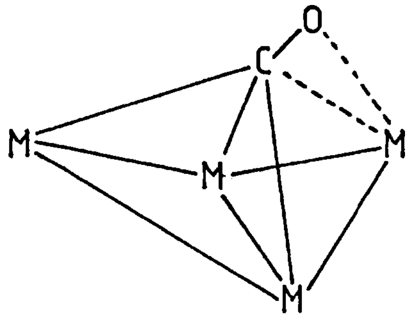


Fig. 20.

carbonyl group which bridges three of the metal atoms in the manner of a triply-bridging carbonyl and forms a π bond to the fourth metal atom, as shown in Fig. 20.

Due to the great variability shown by the carbonyl ligand in bonding to metal atoms, polynuclear metal carbonyl complexes may serve as reasonable models for metal surfaces in the processes of chemisorption and catalysis[27-33]. There is a close resemblance in the structure and bonding features of the ligands bound to metal atoms, both in the molecular clusters and on the metal surfaces. The common forms of carbonyl bonding in metal carbonyls, MCO, M_2CO, M_3CO, are all analogous to the carbonyl bonding in the possible intermediate chemisorbed states on metal surfaces. There are numerous examples of hydrido transition metal carbonyl clusters which serve as models for the intermediate states in the surface catalysed hydrogenation of carbon monoxide[34]. In these complexes, the hydrogen can co-ordinate to a terminal or a bridging site. The 1s atomic orbital of hydrogen can interact with a σ-bonding atomic orbital of a metal or a suitable combination of metal orbitals and so, it is capable of forming a 2-centre M-H or 3-centre M_2H bonds.

The catalytic hydrogenation of carbon monoxide can be regarded as consisting of the following stages:
(i) carbon-oxygen bond scission, (ii) oxygen-hydrogen bond formation, (iii) carbon-hydrogen bond formation and (iv) carbon-carbon bond formation, but not necessarily in this order. Each of these stages has a specific model in metal carbonyl cluster chemistry.

Prior to carbon-oxygen bond scission in hydrogenation reactions, chemisorption of carbon monoxide molecule on the metal surface takes place. An intermediate state is obtained in which the carbon-oxygen bond order is reduced, this may be achieved when both the carbon and oxygen atoms of the carbon monoxide molecule form linkages to surface metal atoms, thus facilitating the eventual bond scission. This type of an intermediate state has specific models in metal carbonyl clusters. For instance, the tetranuclear iron complex, $[HFe_4(CO)_{13}]^-$, has twelve terminally bound carbonyl ligands and one with the carbon and the oxygen atoms bonded to the metal atoms as shown in Fig. 20. As a result, a significant reduction of the carbon oxygen bond order of the bridging carbonyl group is obtained.

Once the carbon-oxygen bond scission has taken place on the metal surface, subsequent steps may involve carbon-hydrogen and carbon-carbon bond formation. In the formation of methane, for instance, there are likely to be intermediate states of CH, CH_2 and CH_3 species bound to surface metal atoms, and all these species together with a C (carbide) species are known in cluster chemistry.

An example of a cluster complex containing a carbide carbon atom is $Fe_5C(CO)_{15}$ (Fig. 21) in which the carbidic carbon atom projects out below the plane of the four basal metal atoms[35]. Recently, the ruthenium analogue, $Ru_5C(CO)_{15}$, prepared by carbonylation of $Ru_6C(CO)_{17}$ has been shown to have a similar structure[87].

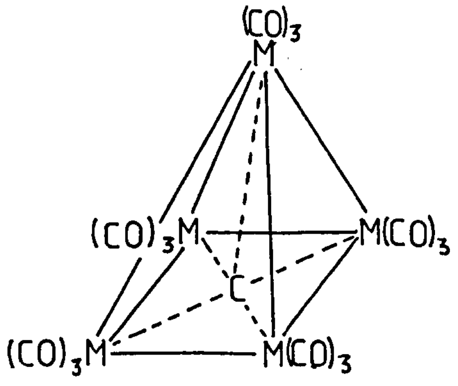


Fig. 21. $M_5C(CO)_5$, M=Fe, Ru.

Muetterties has isolated the carbide containing clusters $[HFe_4(CO)_{12}(\mu_4\text{-}C)]^-$ and $[Fe_4(CO)_{12}(\mu_4\text{-}C)]^{2-}$ (Fig. 22)[85]. The monoanion has a similar structure to that of the dianion with a hydride bridging the two basal Fe^B atoms.

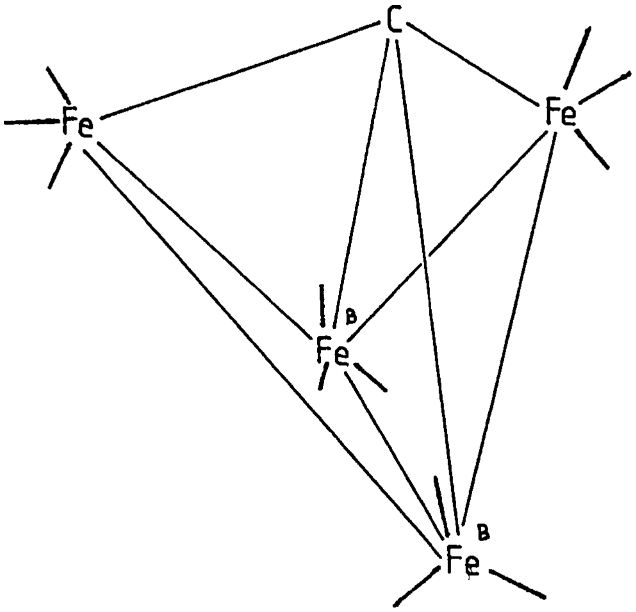


Fig. 22. $[Fe_4(CO)_{12}(\mu_4\text{-}C)]^{2-}$. The carbonyl groups are represented by the lines projecting from the Fe atoms.

The carbyne or CH species bound to metal clusters are well established. Treatment of the dianion $[Fe_4(CO)_{12}(\mu_4\text{-}C)]^{2-}$ with HCℓ yields the monoanion $[HFe_4(CO)_{12}(\mu_4\text{-}C)]^-$. Prolonged reaction of the hydride derivative with HCℓ gives a cluster containing a methylidyne group bonded to the iron atoms, as shown in Fig. 23[85,86].

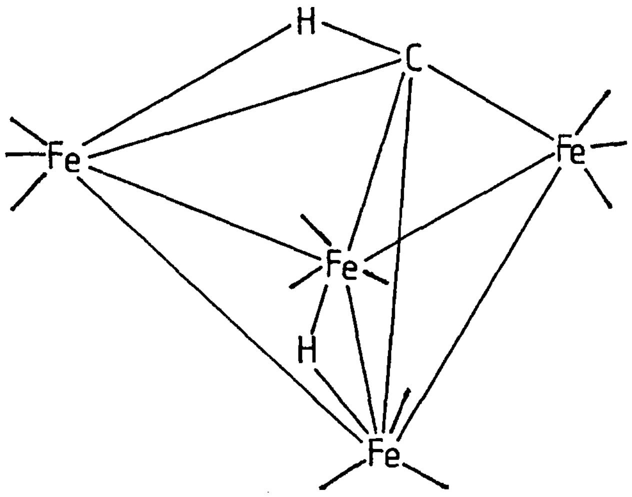


Fig. 23. $HFe_4(CH)(CO)_{12}$. The carbonyl groups are represented by the lines projecting from the Fe atoms.

The cluster complex $HCCo_3(CO)_9$ has the CH carbon atom bound to the three metal atoms (Fig. 24)[36], and it has

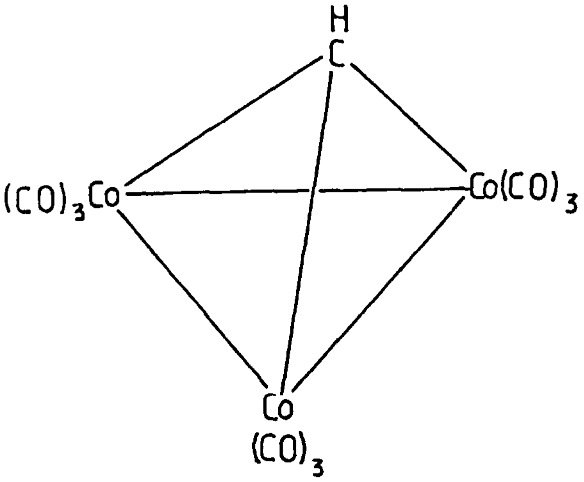
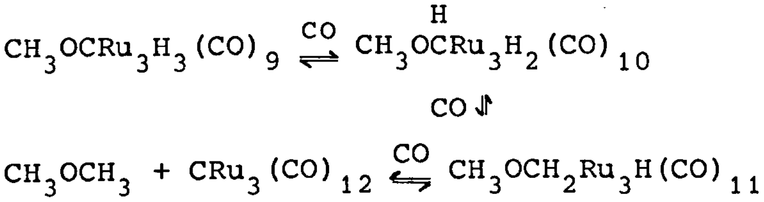


Fig. 24. $Co_3(CO)_9(CH)$.

been shown that the photochemical reaction of $Co_3(CO)_9(CH)$ and hydrogen leads to quantitative formation of methane and

$Co_4(CO)_{12}$. The complex $RCCo_3(CO)_9$ similarly reacts with hydrogen to form alkane, alkene and $Co_4(CO)_{12}$. In an atmosphere of CO and H_2, $CH_3OCRu_3H_3(CO)_9$ gives dimethyl ether, and Muetterties[31] suggests that the hydrogenation process involves intermediate carbene and alkyl derivatives, as outlined in Scheme 1.



$$\begin{tikzcd} CH_3OCRu_3H_3(CO)_9 \arrow[r, shift left, "CO"] & CH_3O\overset{H}{C}Ru_3H_2(CO)_{10} \arrow[l, shift left] \arrow[d, shift left, "CO"'] \\ CH_3OCH_3 + CRu_3(CO)_{12} \arrow[r, shift left, "CO"] & CH_3OCH_2Ru_3H(CO)_{11} \arrow[l, shift left] \arrow[u, shift left] \end{tikzcd}$$

Scheme 1.

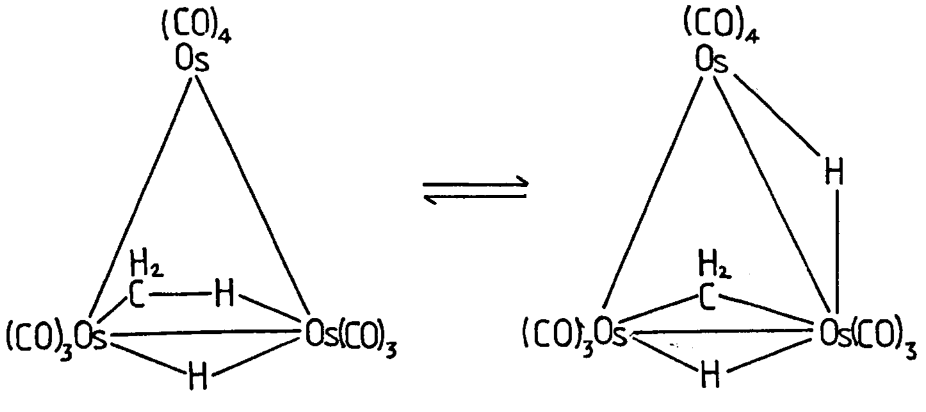
It is interesting to note here that $H_3Ru_3(COCH_3)(CO)_9$ and the analogous Os complex, $H_3Os_3(COCH_3)(CO)_9$ were prepared in two stages (Scheme 2), that involved conversion of the carbene bound species $HM_3(\mu_2\text{-}COCH_3)(CO)_{10}$ to the carbyne bound species $H_3M_3(\mu_3\text{-}COCH_3)(CO)_9$[31].

$$[HM_3(\mu_2\text{-}CO)(CO)_{10}]^- + CH_3SO_3CF_3 \rightarrow [HM_3(\mu_2\text{-}COCH_3)(CO)_{10}] + SO_3CF_3^-$$

$$[HM_3(\mu_2\text{-}COCH_3)(CO)_{10}] + H_2 \overset{60^\circ}{\rightleftharpoons} H_3M_3(\mu_3\text{-}COCH_3)(CO)_9 + CO$$

Scheme 2.

$HOs_3(CO)_{10}CH_3$, formed from the reaction of diazomethane with $H_2Os_3(CO)_{10}$, exists as an equilibrium mixture of the forms I and II (Fig. 25), i.e., the methyl species $H(CH_3)Os_3(CO)_{10}$ and the carbene species $H_2(CH_2)Os_3(CO)_{10}$[37].



I

II

Fig. 25. $H(CH_3)Os_3(CO)_{10}$ and $H_2(CH_2)Os_3(CO)_{10}$.

The Os-C-H-Os interaction in the methyl derivative (I) can be compared with an intermediate state involving C-H bond breaking or bond formation during a catalytic hydrogenation process.

$Fe_2(CO)_8(\mu\text{-}CH_2)$ (Fig. 10), prepared by the interaction of diiodomethane with $[Fe_2(CO)_8]^{2-}$ is another example of a cluster containing a bridged CH_2 group.

The cluster complexes discussed above serve as reasonable models for the sequence of steps $C \rightarrow CH \rightarrow CH_2 \rightarrow CH_3 \rightarrow CH_4$ in the hydrogenation of surface carbon atom to methane. In this sequence it has been assumed that carbon-oxygen bond scission takes place prior to carbon-hydrogen bond formation. However, it is possible that direct hydrogenation of the chemisorbed carbon monoxide may precede or at least compete with the carbon-oxygen bond cleavage step. In the event of direct hydrogenation, an intermediate state with a COH species would be involved, and this too is established in cluster chemistry. $HFe_3(CO)_{10}(COH)$ (Fig. 26i), obtained by acidification of the anion $[HFe_3(CO)_{11}]^-$, contains an edge-bridging COH moiety[38].

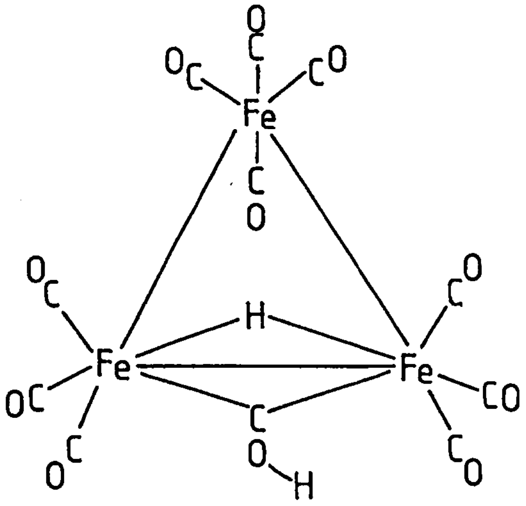


Fig. 26i. $HFe_3(CO)_{10}(COH)$

The analogous compound $Co_3(CO)_9(COH)$[39,91], which contains a face bridging COH ligand, is similarly obtained by protonation of $[Co_3(CO)_{10}]^-$. Recently, Wilkinson[96] has prepared the triiron cluster anion $[Fe_3(CO)_9(MeCO)]^-$ by the interaction of $[Fe_2(CO)_8]^{2-}$ with iodomethane. The oxygen atom of the acyl group is regarded as contributing three electrons to the cluster via donation from the lone pair to Fe^1 (Fig. 26ii.

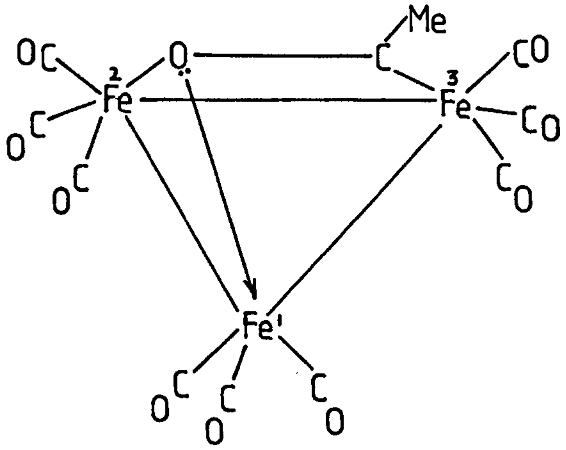
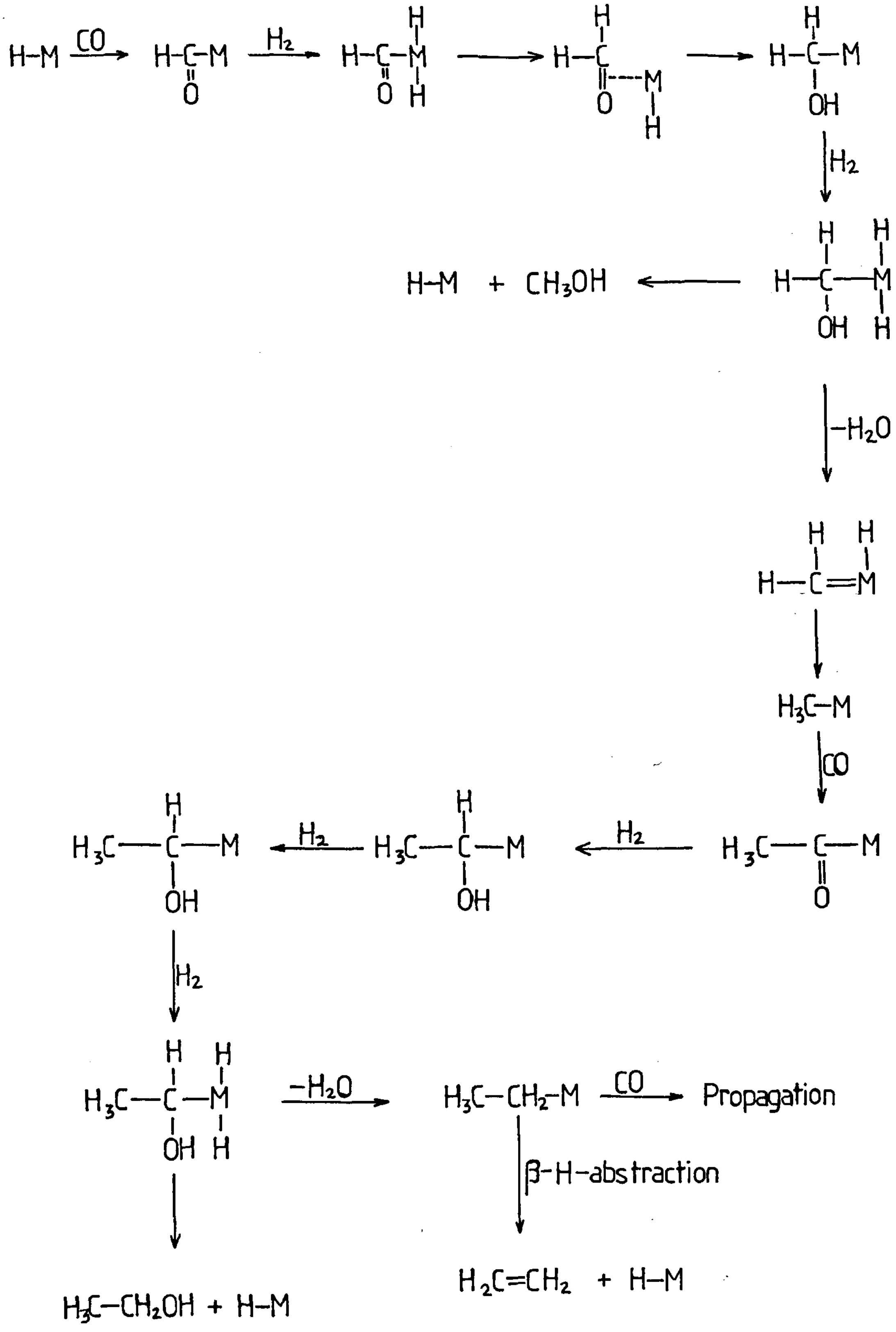


Fig. 26ii. $[Fe_3(CO)_9(MeCO)]^-$

Polynuclear metal complexes have a distinct advantage over mononuclear metal complexes in serving as models for various catalytic intermediate states. The μ_2-CO, μ_3-CO and η^2-OC type of interactions in polynuclear carbonyl complexes are more effective than the M-CO bonding in the mononuclear complexes in reducing the carbon-oxygen bond order, a requirement for carbon monoxide hydrogenation. For the Fischer-Tropsch reaction, a plausible scheme which involves formation of various intermediate states has been proposed, and each of these intermediate states has an established organometallic precedent[40].

The scheme involves the successive formation of formyl, formaldehyde, hydroxymethyl, carbene, and alkyl metal intermediates.

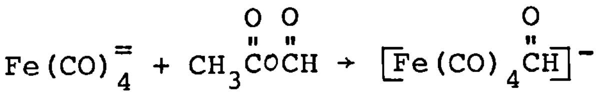
The formyl derivative, $[HCOFe(CO)_4]^-$ has been isolated and fully characterised. The complex has been



Scheme 3.

Mechanism of the Fischer Tropsch Reaction.

prepared by formylation of a nucleophilic saturated metal carbonyl, and isolated as the bis (triphenylphosphiniminium) salt[41].

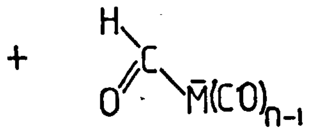


$$Fe(CO)_4^{=} + CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}H \rightarrow [Fe(CO)_4\overset{O}{\overset{\|}{C}}H]^-$$

Scheme 4.

A different method for the synthesis of metal formyl compounds involves the reaction of metal carbonyl compounds with trialkylborohydrides[42].

$$H\bar{B}(OR)_3 + M(CO)_n \rightarrow B(OR)_3$$



Scheme 5.

The interaction of $RuHC\ell(PPh_3)_3$ with sodium methoxide has been shown to give two compounds that are formulated as having Ru-CHO and $Ru-OCH_2$ groups[43].

Sweet and Graham have recently isolated and characterised models for the formyl, hydroxymethyl and alkylmetal intermediates in the Fischer Tropsch synthesis[44]. The formation of these derivatives is based on the systematic and controlled reduction of $[CpRe(CO)_2NO]^+$ (Scheme 6).

$$\begin{tikzcd}
CpRe(CO)_2NO^+ \arrow[r, "BH_4^-"] \arrow[dr, "2BH_4^-"'] & CpRe(CO)(CHO)NO \arrow[d, "BH_4^-"] \\
CpRe(CO)(CH_3)NO + & CpRe(CO)(CH_2OH)NO \arrow[d, "BH_4^-"] \\
& CpRe(CO)(CH_3)NO
\end{tikzcd}$$

Scheme 6.

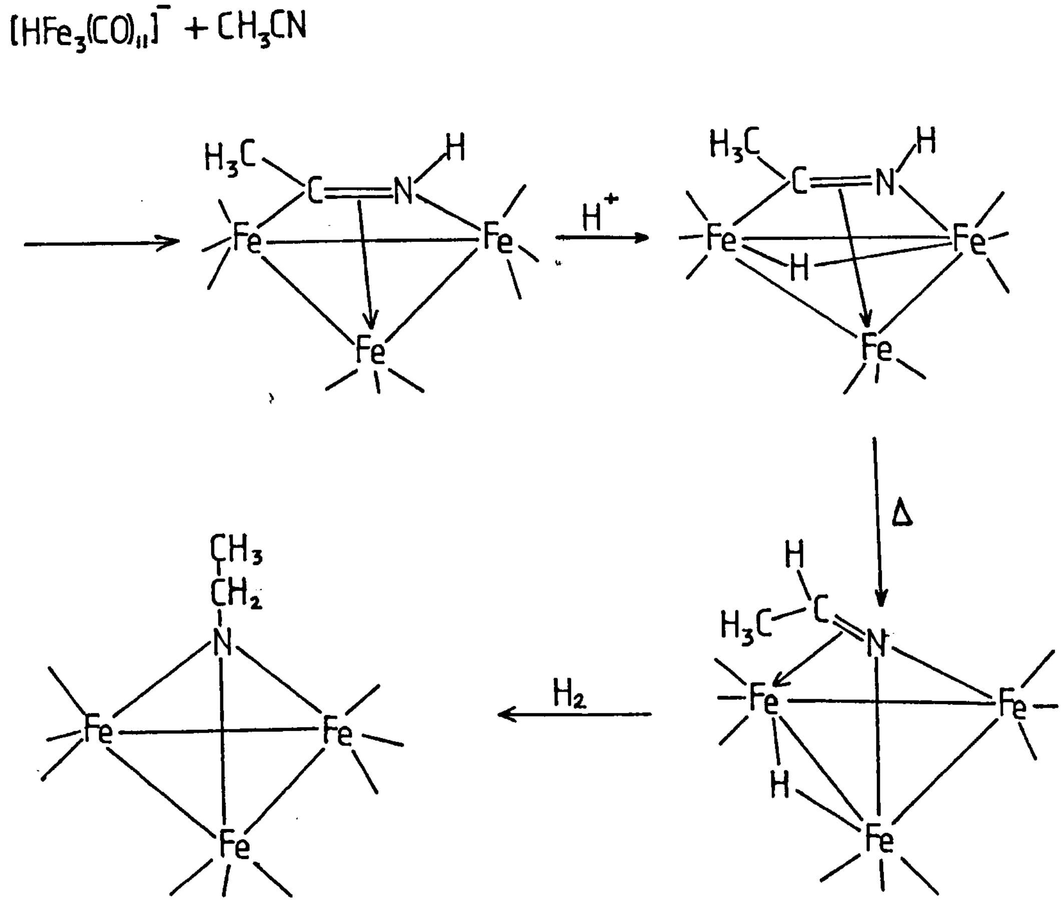
Polynuclear formyl complexes, $[Ir_4(CO)_{11}(CHO)]^-$ and $[M_3(CO)_{11}(CHO)]^-$ (M=Os, Ru) have been identified in the reaction of $Ir_4(CO)_{12}$ and $M_3(CO)_{12}$, with $LiBHEt_3$[89,90].

The treatment of $Os(CO)_2(PPH_3)_2$ with 40% aqueous formaldehyde solution gives in good yield the complex $Os(CO)_2(\eta^2\text{-}CH_2O)(PPh_3)_2$, a mononuclear model for the formaldehyde intermediate in the Fischer Tropsch synthesis[45].

Polynuclear carbonyl models for some of the possible intermediates have already been mentioned. Thus, the carbene and alkylmetal intermediates are represented in cluster chemistry by $H_2Os_3(CH_2)(CO)_{10}$ (Fig. 25 I) in which the carbene ligand is seen to bridge two metal atoms, and $HOs_3(CH_3)(CO)_{10}$ (Fig. 25 II) in which two of the osmium atoms are bridged by a methyl group.

In recent years, many examples of homogeneously catalysed reactions have been reported in which metal carbonyl clusters and their derivatives act as catalysts. A very recent review by Whyman gives a very good account of the applications of metal clusters in catalysis[46]. Metal clusters have been used in a wide range of reactions, such as hydrogenation, isomerisation, hydroformylation, cyclisation and oxidation. The reader is referred to the review by Whyman for examples of all these reactions. Of particular importance are those catalytic reactions which lead to the reduction of the normally difficult CO and CN triple bonds.

Kaesz[47] has carried out the preparation of a series of complexes (Scheme 7) which represent a possible reduction pathway for acetonitrile over a triiron cluster.



Scheme 7.

As a result of the great applicability of metal carbonyl complexes, in recent years much work has been carried out in the search for metal complexes with ligands similar to the carbonyl group. Since Baird and Wilkinson[48] reported the first thiocarbonyl complexes, trans- $RhX(CS)(PPh_3)_2$ and $RhX_3(CS)(PPh_3)_2$ (X=Cℓ, Br), the synthesis and characterisation of other transition metal thiocarbonyl complexes has received much attention[59]. This is mainly due to the similarity of the thiocarbonyl group to the more common carbonyl group in terms of electronic structure and bonding. The ground state electronic configurations for the CO and CS molecules are:

CO $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4$

CS $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2(6\sigma)^2(7\sigma)^2(2\pi)^4$.

A molecular orbital calculation, carried out by Richards[49], indicates that the thiocarbonyl ligand is favoured over the carbonyl ligand in terms of both σ and π bonding. The calculations show that while the 7σ and 2π orbitals of CS molecules are almost degenerate, the 7σ orbital is localised largely on the carbon atom and the 2π is a bonding orbital distributed on both the C and the S atoms. The two electrons in the 7σ orbital can therefore be regarded as a lone pair available to bond to a metal atom. This is analogous to the bonding of CO to a metal atom, in which it is the lone pair of the 5σ orbital that is used. On comparing the energies of the 7σ orbital of CS and the 5σ orbital of CO (7σ orbital of CS: -0.4705 a.u, 5σ orbital of CO: -0.5704 a.u.) it is evident that the pair of electrons on the 7σ orbital of CS should be more readily available than those on the 5σ orbital of CO. Also, the energy of the empty 3π antibonding orbital on CS (+0.0848 a.u.) is much lower than that of the empty 2π antibonding orbital on CO (+0.1507 a.u.). As a result of the more favourable σ donor and π acceptor capabilities of the thiocarbonyl group over the carbonyl group, metal thiocarbonyl bonds are predicted to be stronger than the corresponding carbonyl bonds[50,51].

In contrast with metal carbonyl complexes, it is only recently that the first carbon bridged thiocarbonyl complex was prepared (Fig. 27)[52]. The complex $[CpMn(NO)(CS)]_2$

exists as a mixture of the cis and trans isomers. Thiocarbonyl analogues,

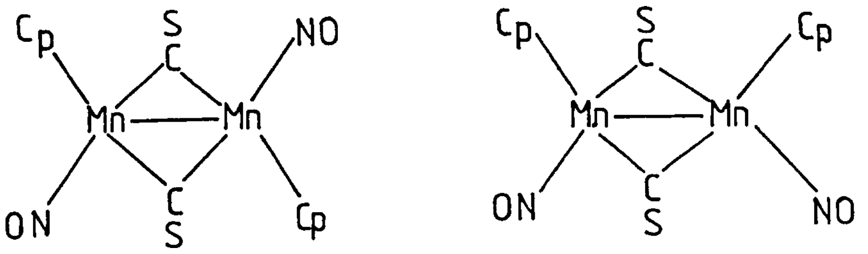


Fig. 27. $Cp_2Mn_2(CS)_2(NO)_2$.

$[CpM(CO)(CS)]_2$ (M=Fe[53], Ru[54]), of the wellknown $[CpM(CO)_2]_2$ have been prepared and shown to contain the CS groups exclusively in the bridging positions (Fig. 28). The

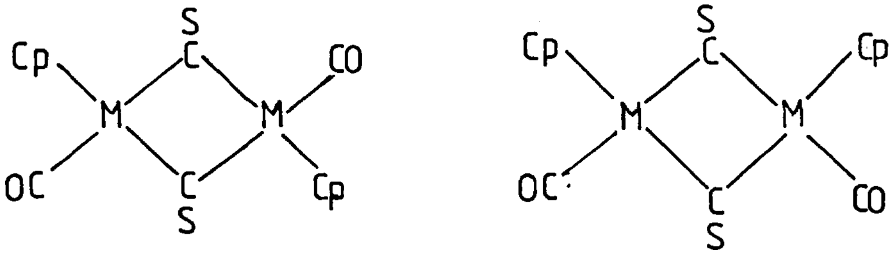


Fig. 28. $Cp_2M_2(CO)_2(CS)_2$

monothio compounds $Cp_2M_2(CO)_3CS$ (M=Fe[55], Ru[54]) have also been shown to exist with the thiocarbonyl group bridging the two metal atoms. The preferential adoption of the bridging site can be explained by the low stability of the π bonds between C and S[56]. Loss of the little π bond stabilisation is more than compensated by the stabilisation gained by forming a bond to a second metal atom upon migration of CS from terminal to a bridging position. The evidence for a weak CS π bonding is supported by several reactions of the thiocarbonyl ligand with nucleophiles to give products with diminished CS π bonding[57,58,92].

The triangular cobalt cluster, $Cp_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$[92] (Fig. 29) has a triply bridging thiocarbonyl group, the bonding of the CS to the three metal atoms being analogous to that of the triply bridging carbonyl groups discussed before.

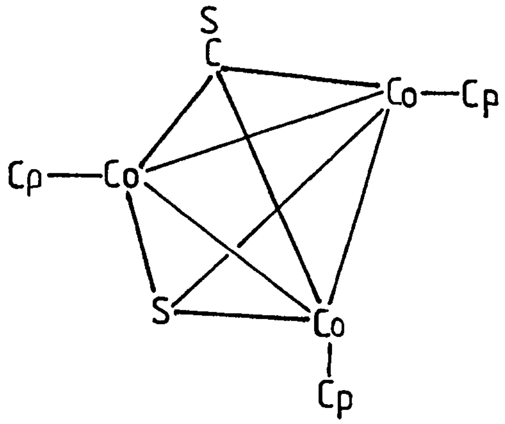


Fig. 29. $Cp_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$.

The tetranuclear cluster $[Fe_4(CO)_{12}(CS)S]$ (Fig. 30)[95], formed by reaction of $Fe_3(CO)_{12}$ with CS_2, has the thiocarbonyl ligand terminally bound to one Fe atom via sulphur, while the C atom caps in a μ_3 mode the Fe_3 triangle formed by the remaining three Fe atoms.

The phosphorus derivatives of the type PX_3 [X=halide, (OR)] can act as complexing agents in much the same way as CO. The particularly good bonding capabilities of PX_3 were first reported by Chatt after his preparation of the complex $(PF_3PtCl_2)_2$[60]. It was suggested that the donor σ bond formed between the ligand and the metal was reinforced

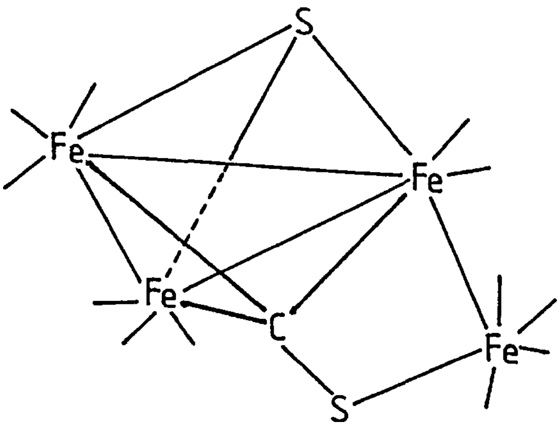


Fig. 30. $Fe_4(CO)_{12}(CS)(S)$. The carbonyls are represented by the lines projecting from the Fe atoms.

by electron transfer from the d orbitals of the metal to the empty d orbitals of P, analogous to that of CO in which there is electron drift from the metal d orbitals into the empty π^* antibonding orbitals. Thus, phosphorus derivatives of the type PX_3 came to be classified as π acceptor ligands, and this seemed a reasonable way of explaining the fact that like CO, PF_3 will form complexes with metals in low oxidation states but not with those in high oxidation states. Also, the Ni-P bond length in $Ni(PF_3)_4$ is about 10% shorter than other Ni-P bond lengths, implying a multiple metal-phosphorus bond. The highly electronegative fluorine atoms in PF_3 would certainly make the phosphine a good π acceptor; however, it has been a point of much dispute about the π-acceptor capabilities of other P(III) derivatives with less electronegative atoms or groups, such as PR_3 and PH_3.

Phosphines and phosphites can substitute a single carbonyl group of $[CpFe(CO)_2]_2$ to yield products of the general formula $[Cp_2Fe_2(CO)_3(PX_3)]$ in which the PX_3 always occupies a terminal position (Fig. 31)[61].

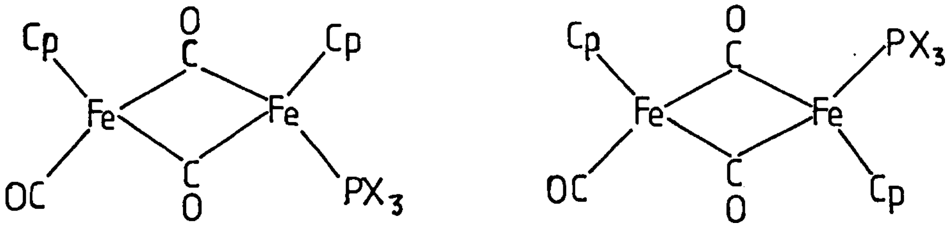


Fig. 31. $Cp_2Fe_2(CO)_3PX_3$.

The substitution of a terminal carbonyl group by a phosphorus donor ligand lowers the stretching frequencies of the remaining carbonyl groups.

In addition to the σ and π bonding, steric factors also play an important role as regards the overall complexing ability of a particular PX_3 ligand. Combining the three effects in approximately equal proportions, it is possible to arrange some of the more common PX_3 ligands in order of all-round complexing power, as follows:

$P(OR)_3 > PF_3 > PH_3 > PR_3 > P(OPh)_3 > PPh_3 \simeq PBu^t_3$[62].

As ligands co-ordinated to a metal, isonitrile and carbon monoxide are very similar in terms of metal ligand bonding. The two ligands are isoelectronic, and in terms of valence bond theory, the metal ligand bonding in both cases can be viewed as a combination of a σ bond, formed by donation of a lone pair of electrons on carbon to the metal, and a π bond, involving electron drift from the metal d orbitals into the empty π^*_{CO} or π^*_{CN} antibonding orbitals, (Fig. 32).

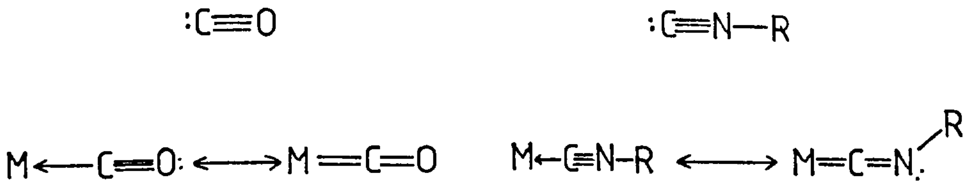


Fig. 32.

The net result is a multiple M-C bond and a reduced C-O or C-N bond order.

The simple valence bond description is convenient to highlight the basic similarity in bonding between the carbonyl and the isonitrile to metal atoms; however, it cannot explain some of the differences that exist between the two ligands when bound to metal atoms. An important difference is that whereas the co-ordination of carbon monoxide to a metal leads to a lower CO stretching frequency than that of free CO, as expected on the basis of a reduced CO bond order, the values for the CN stretching frequencies of co-ordinated isonitriles can be considerably higher than the values for the free isonitrile. Also, in contrast to the wide variety of carbonyl complexes with metals in low oxidation states (0, -1) that are known, it is also common for the isonitrile ligand to form complexes with metals in higher oxidation states (+1, +2). This implies that CO is a better π acceptor than CNR and so it is better able to stabilise the low oxidation states of the metals.

When an isonitrile co-ordinates to a metal in a positive oxidation state[63], the increase in the CN stretching frequency reflects the increase in the CN bond order, or in terms of molecular orbital theory, it can be said that there is no significant electron flow towards the π* antibonding orbitals of the isonitrile. In terms of valence bond theory, the rise in the CN stretching frequency can be interpreted in terms of the canonical structure I being significantly more important than II (Fig. 32). If the isonitrile is co-ordinated to a metal in a low oxidation state[64-66], the value of the CN stretching frequency is lower than that of the free ligand, and the reduction of the C-N bond order can be attributed to a significant electron flow from the metal into the π* antibonding orbitals of the isonitrile. In terms of valence bond picture, it can be said that in this case the canonical structure II (Fig. 32) is more important[67-69]. The nature of the R group in complexes of the type M-CNR influences the CN stretching frequencies. Thus, when R = Me, the ligand is a poorer π-acceptor than when R = Ph, and this is reflected by its higher CN stretching frequency[70].

Compounds of the type $M(CO)_xL_y$ can be suitably synthesised and by studying the infrared stretching frequencies of CO (and CN when L = CNR), it is possible to classify the various π-accepting ligands in order of their ability to act as π acceptors. When only a single isonitrile ligand is present, as in $Mo(CO)_5(CNR)$, the infrared data indicates that backbonding is virtually all towards the five carbonyl groups. When more than one isonitrile ligand is present some backbonding is accepted by these but it is always less than when only isonitriles are present[71]. Therefore, on the basis of the infrared studies, the isonitriles can be regarded as being poorer π acceptors than carbonyls when both types of ligands are present. Horrocks[72] has been able to classify the various π-accepting ligands in order of decreasing ability to withdraw electrons from the metal atom, as follows:

NO
CO
PF_3
$SbC\ell_3$
$AsC\ell_3$
$PC\ell_3$
$PC\ell_2C_6H_5$
$P(OPh)_3$
$P(OCH_3)_3$
Bu^tNC
$P(C_6H_5)_3$
$P(CH_3)_3$
$P(C_2H_5)_3$

This order has been confirmed on the basis of force constant measurements[73,74].

Like the carbonyl ligand, the isonitrile can also function either as a terminally bound ligand or as one bridging two metal atoms. The ability of isonitriles to act as bridging ligands was first demonstrated by the preparation of the diiron complex, $Cp_2Fe_2(CO)_3(CNPh)$ (Fig. 33)[75].

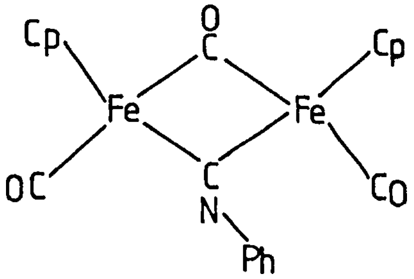


Fig. 33. $Cp_2Fe_2(CO)_3(CNPh)$.

The nickel complex $[CpNi(CNPh)]_2$, which had originally been reported to contain terminal isonitriles[76] has now been accepted to have a structure contain bridging isonitriles (Fig. 34)[75].

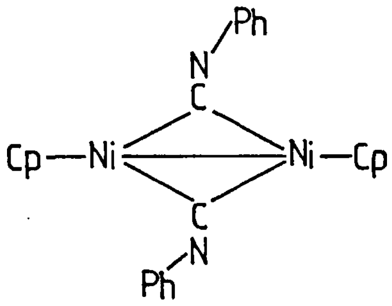


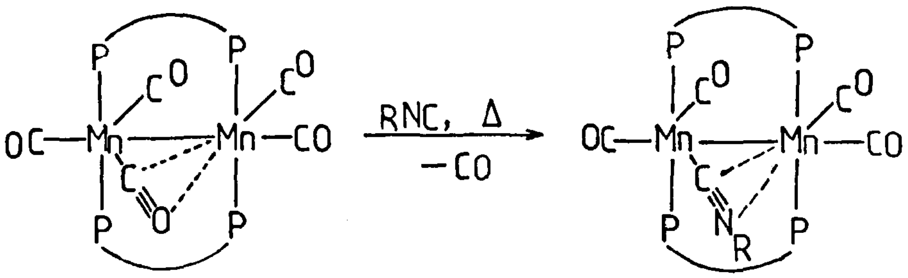
Fig. 34. [CpNi(CNPh)]$_2$.

As in the case of bridging and terminal carbonyl groups, the bridging isonitriles can be differentiated from terminal ones in having much lower C-N stretching frequencies (approximately 1700 cm^{-1} for bridging CNR and around 2100 cm^{-1} for terminal CNR).

In recent years, several complexes with at least one bridging isonitrile group have been prepared. Several complexes of the type $Cp_2Fe_2(CO)_{4-n}(CNR)_n$, with different R groups, have been prepared, the nature of the R group determining the site that the isonitrile adopts[77]. Thus, in the monosubstituted complexes when R = Ph, the isonitrile preferentially adopts the bridging site, as mentioned above, whereas when R = Bu^t, the isonitrile is found exclusively in the terminal position. Between the two extremes, a mixture of isomers in which the isonitrile is exchanged between the bridging and terminal sites is obtained[78]. The interconversion equilibrium shifts in favour of the isomers with the isonitrile in the bridging site along the series $R = Bu^t < cyclo\text{-}C_6H_{11} < Bu^{\underline{s}} < Bu^{\underline{i}} < Bu^n < Pr^{\underline{i}} < Et < Me$. The destabilisation of the bridging isonitrile isomers can be attributed to two factors: (i) the C-N-R in the bridging position is significantly nonlinear[76,80] and so the steric interaction between the R group and the CpFe(CO) moiety towards which the R group is directed implies that the larger the R group, the less favourable it is for the isonotrile to take the bridging position, (ii) the increasing overall electron withdrawing ability of R along the series above should favour bridging isonitrile isomers. In the case of phenylisocyanide, the electronic factor is very important because the electronic charge can be delocalised over the aromatic ring.

The mechanism by which the isomers of $Cp_2Fe_2(CO)_3(CNR)$ interconvert[79] is the same by which cis-trans interconversion takes place for the parent iron dimer, $[CpFe(CO)_2]_2$[15]. The process involves symmetric bridge opening, followed if necessary by internal rotation about the M-M bond of the non-bridged intermediate, and simultaneous bridge closing to generate a doubly bridged isomer which has undergone bridge-terminal ligand exchange and/or cis-trans interconversion.

Isonitrile, being isoelectronic with carbon monoxide, is expected to display a similar variety of bonding modes. In addition to acting as a terminal and doubly bridging ligand, CNR may also function as a doubly bridging four electron donor. Thus, treatment of $Mn_2(CO)_5[Ph_2PCH_2PPh_2]_2$, which contains a doubly bridging four electron CO group, with CNR (R = CH_3, $C_6H_5CH_2$, p-$CH_3C_6H_4$) gives the mono-substituted complex $Mn_2(CO)_4(CNR)[Ph_2PCH_2PPh_2]$ (Scheme 8)[93].



Scheme 8.

In $Os_6(CO)_{18-n}(CNR)_n$,[97] one or more of the isonitrile ligands act as four electron donors.

Although carbon monoxide has in general dominated the chemistry of low valent transition metal chemistry, it is being increasingly recognised that the high π acceptor characteristics of the carbonyl group imposes certain restrictions on the chemical behaviour of the metal in a metal carbonyl complex. For instance, the high degree of backbonding reduces the nucleophilicity of the metal centre. The phosphines, although being able to increase the metal centre nucleophilicity, impose steric constraints and block the co-ordination sites. Isonitriles are less sterically hindering, are weaker π acceptors than carbonyls but exhibit a range of bonding modes. On this basis metal isonitrile complexes should have a rich chemistry, both in terms of structure and reactions, and yet until recently, very few low valent metal complexes had been reported with isonitriles as the only ligands[81]. One such complex is $Fe(CNR)_5$. It is prepared by the reduction of $FeBr_2$ with sodium amalgam in the presence of excess CNR, and has a trigonal bipyramidal arrangement of the CNR around the central metal atom, with the radial isonitrile groups being significantly bent[83]. This has been attributed to extensive backbonding from the metal into the antibonding orbitals of the isonitrile ligand. Thus, the infrared spectra of these compounds show, in addition to the normal terminally bonded isonitrile stretching frequencies, strong bands in the 1930-1870 cm^{-1} range, which are assigned to the bent isonitrile ligands. A less pronounced bending of a terminally bound isonitrile has been observed in the complex $[Mo(PCH_2CH_2PPh_2)_2(CNMe)_2]$[84]. The discovery of $[Co_2(CNBu^t)_8]$[85] and $[Fe_2(CNR)_9]$[86] has allowed comparisons of these binary metal-isonitrile complexes to be made with the analogous metal carbonyl complexes.

The remainder of the thesis gives an account of the work carried out involving the reactions of several metal carbonyl complexes and their derivatives with isonitriles. The effect of substitution of one or more carbonyl groups by isonitrile has been studied using infrared and n.m.r. techniques.

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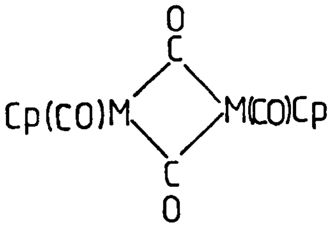
CHAPTER 2

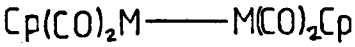
SYNTHESIS AND FLUXIONAL CHARACTER OF ISONITRILE SUBSTITUTED THIOCARBONYL ANALOGUES OF $Cp_2Fe_2(CO)_4$

I. Introduction

Complexes of composition $Cp_2M_2(CO)_4$ (M = Fe,Ru,Os) are of special interest because they exist in solution in two isomeric molecular forms (I) and (II).



I



$Cp(CO)_2M—M(CO)_2Cp$

II

In the case of (M = Fe), the bridged form predominates while approximately equal proportions of both forms occur in solution when M = Ru[1]. The osmium complex exists in both solid and solution as the non-bridged form. The structure adopted by the complexes is sensitive to substitution of one or more carbonyl groups by other donor ligands such as those discussed in Chapter 1. Thus, complexes of the type $Cp_2M_2(CO)_{4-n}(L)_n$ (n = 1-3) have been shown to exist solely in the bridged form[2]. Spectroscopic data for $Cp_2M_2(CO)_3(CNR)$ show that, in solution, mixtures of isomers containing bridging and terminal isonitrile ligands exist (Fig. 1).

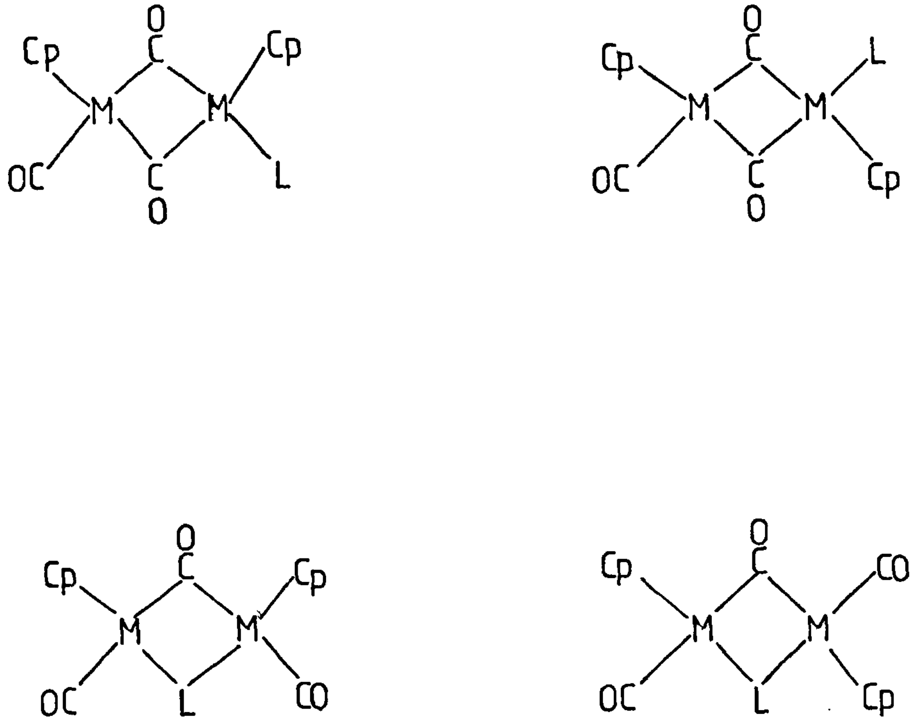


Fig. 1. M = Fe, Ru.

The isomers interconvert by the Adams-Cotton mechanism, which involves symmetric bridge opening, followed if necessary by rotation about the M-M bond, and simultaneous bridge closing to yield a new isomer. The equilibria shift toward the isomers with the isonitrile in the terminal position along the series

$R = Me < Et < Bu^n < Bu^i < Bu^s < cyclo\text{-}C_6H_{11} < Bu^t$, which can be attributed to increasing steric interactions between R and the $CpM(CO)_t$ moieties and to the decreasing electron withdrawing ability of R. The complexes $Cp_2M_2(CO)_3PX_3$ [X = R, (OR)]^3, $Cp_2M_2(CO)_2(CS)_2$ and $Cp_2M_2(CO)_3(CS)^4$ all adopt a totally bridged structure in solution. The thiocarbonyl exists solely as a bridging ligand in the latter two examples.

Fig. 2 shows a detailed molecular orbital diagram for $Cp_2Fe_2(CO)_4$, the orbitals being built up from those of one $(CpFe)_2$ (left), two terminal carbonyl, and two bridging carbonyl (right) fragments^5.

The formal oxidation state of Fe in $(CpFe)_2$ is +1 so that only one orbital of the 'valence' group of a_g symmetry is occupied. Adding two terminal carbonyls does not modify the occupancy of the 'valence' orbitals, but the a_u orbital involved in backbonding with the carbonyls is significantly stabilised. Thus, the two lowest orbitals, a_u and a_g, are the metal-metal π interaction and the metal-metal σ interaction respectively, while the remaining two orbitals, b_g and b_u are the metal-metal π^* interaction and the metal-metal σ^* interaction. The right hand side of Fig. 2 shows the combinations of the ligands' (μ-CO) σ and π^* orbitals to form the symmetric a_g and b_g orbitals, and the antisymmetric a_u and b_u orbitals. These ligand combinations interact with the $(CpFe(CO)_2)$ orbitals of the same symmetry. The a_u and a_g interactions form two low lying orbitals which are localised mainly along the Fe-C axes with little Fe-Fe bonding character, and the b_u and b_g interactions form the HOMO and LUMO for the molecule respectively. It cna be inferred that there is no substantial metal-metal interaction, with the HOMO formed by interaction

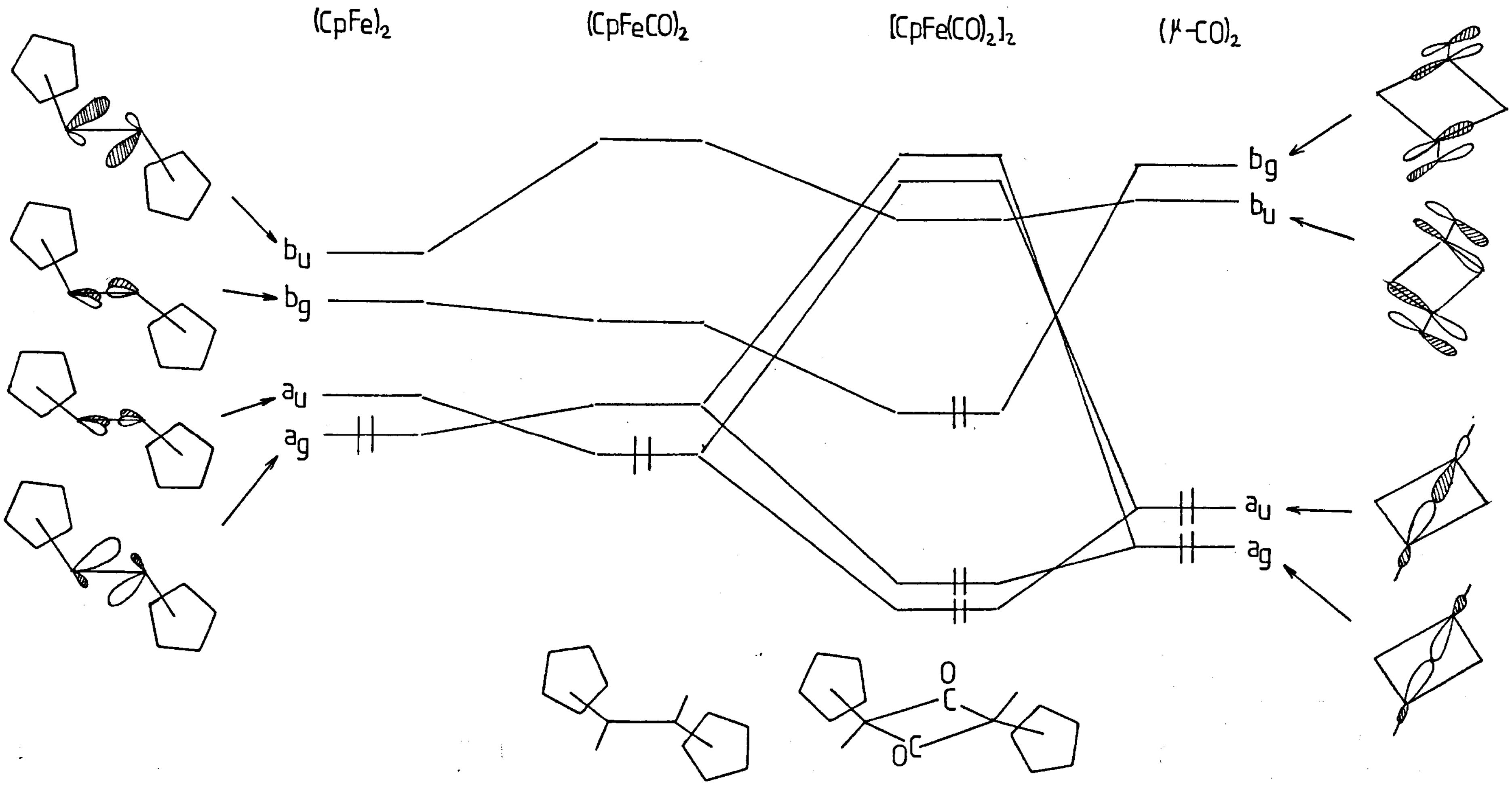


Fig. 2 . Molecular orbital diagram of $Cp_2Fe_2(CO)_4$.

of π* CO orbitals with a metal valence orbital which is antibonding with respect to metal-metal bonding. The calculations are consistent with experimentally obtained electron density maps which show very little electron density along the metal-metal axes. The bonding model is also supported by the geometry of the Fe(μ-CO)$_2$Fe system. To maximise overlap, the CO ligands in the cis isomer would have to move out of the Fe(μ-CO)$_2$Fe plane, puckering the ring, while in the trans isomer, the ring would be planar. This has been observed in the two isomers of $Cp_2Fe_2(CO)_4$[6-9]. Calculations[10] also suggest that whereas σ donation from CO to metal is approximately the same in bridging and terminal positions, metal to CO π back donation is much more significant with bridging carbonyl. This is reflected in the C-O bond lengths of terminal and bridging carbonyls (1.152 Å and 1.180 Å respectively).

Energies of the σ HOMO and π LUMO orbitals of several two electron ligands are given in table 1[11].

Table 1.

	Energy (a.u.)	
Ligand	σ-HOMO	π-LUMO
CO	-0.547	+0.158
CNMe	-0.459	+0.212
CS	-0.460	+0.077
PMe_3	-0.322	+0.212
PF_3	-0.454	+0.175
PH_3	-0.385	+0.188
CH_2	-0.477	-0.403

In terms of σ donor ability, the order observed is $PMe_3 > PH_3 > PF_3 \simeq CNMe \simeq CS > CH_2 > CO$, while in terms of π acceptor ability, the order is $CH_2 > CS > CO > PF_3 > PH_3 > CNMe \simeq PMe_3$. In table 1 all the ligands are better σ donors than CO, and so it would appear reasonable that on substitution of a $Cp_2M_2(CO)_4$ dimer, the substituting ligand will adopt a position that maximises the π back donation. Therefore, those ligands which are better π acceptors than CO will adopt bridging positions, while those which are poorer π acceptors are expected to adopt terminal positions.

Recently, $Cp_2Fe_2(CO)_3(CS)$ and $Cp_2Fe_2(CO)_2(CS)_2$, the thiocarbonyl analogues of $Cp_2Fe_2(CO)_4$ have been prepared[4,12-14]. In both these compounds, the CS group has been found to occupy the bridging position due to its much greater π-acceptor ability than CO. Infrared and n.m.r. data indicate that both compounds exist in solution in interconverting cis and trans forms.

The reaction of $CpFe(CO)_2^-$ with $(PhO)_2CS$ results in the formation of the complex $Cp_2Fe_2(CO)_3(CS)$ (I), whereas the reaction of $CpFe(CO)_2^-$ successively with CS_2, CH_3I and CF_3SO_3H yields the cationic thiocarbonyl complex $[CpFe(CO)_2CS]^+$, which on reduction with NaH gives the dithio complex $Cp_2Fe_2(CO)_2(CS)_2$ (II). In view of the interesting isomerism shown by isonitrile derivatives of $Cp_2M_2(CO)_4$ (M = Fe, Ru), it was decided to prepare isonitrile derivatives of these thiocarbonyl analogues to investigate the effect of ligand substitution on the structures adopted by the isonitrile substituted complexes. During the course of this work, $Cp_2Fe_2(CO)_3(CS)$ was shown to react with PEt_3, PMe_2Ph, $PMePh_2$ and $P(OMe)_3$ to give the monosubstituted derivatives $Cp_2Fe_2(CO)_2(PR_3)(CS)$, in which the CS group remains in the bridging position[15]. Infrared spectra of the PEt_3 and PMe_2Ph complexes in the carbonyl region display a terminal ν(CO) and a bridging ν(CO) absorption, the bands appearing at lower frequencies than in the parent compound, as would be expected on substitution of CO by a better donor ligand. However, the spectra of the $PMePh_2$ and $P(OMe)_3$ derivatives show additional $\nu(CO)$ bands, which suggests the presence of cis and trans isomers of $Cp_2Fe_2(CO)_2(PR_3)(CS)$, with one isomer being predominant in polar solvents. Since the cis isomer of $Cp_2Fe_2(CO)_3(CS)$ predominates in polar solvents it seems likely that it is the cis isomer of the $Cp_2Fe_2(CO)_2(PR_3)(CS)$ complexes which is more favourable in such solvents.

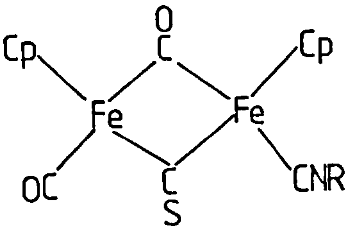
II. Discussion

a) Synthesis:

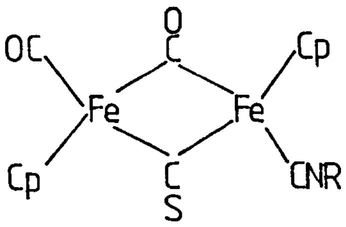
We have prepared the isonitrile substituted derivatives $Cp_2Fe_2(CO)_2(CS)(CNR)$ (III a-d; R = Me, Et, Pr^i, Bu^t), and $Cp_2Fe_2(CO)(CS)_2(CNMe)$ (V) by thermal substitution of the thiocarbonyl compounds (I) and (II) respectively. Prolonged reactions of the monosubstituted compounds did not yield the disubstituted complexes; the compound $Cp_2Fe_2(CO)(CS)(CNMe)_2$(IV) was prepared by the photochemical substitution of (IIIa). Prolonged thermal reaction of (I) with $CNBu^t$ resulted in substitution of the CS group to yield the complex $Cp_2Fe_2(CO)_2(CNBu^t)_2$ (VI). The complexes were purified by chromatography and recrystallisation, and the green crystalline solids were characterised by microanalysis, infrared and ^1H and ^{13}C n.m.r. spectroscopy (Tables 3-5).

b) Structure:

Infrared and n.m.r. spectra of complexes (III a-d) indicate the presence of the four isomers A-D in solution, there being no evidence for the presence of isomers containing terminal CS ligands.



(A)



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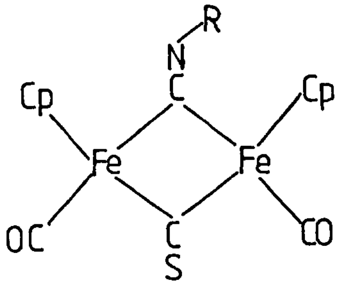

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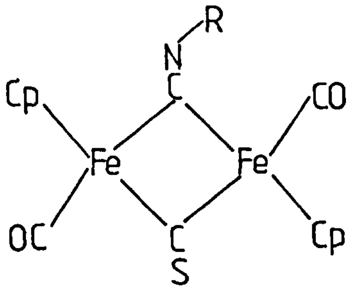
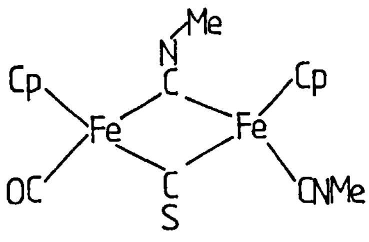


(D)

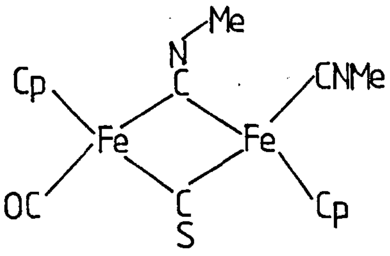
The bands at approximately 2100-2150, 1963, 1794 and 1110-1120 cm^{-1} are attributed to terminal isonitrile, terminal carbonyl, bridging carbonyl and bridging thiocarbonyl vibrations respectively of isomers (A)/(B). The doubling of the bridging thiocarbonyl and terminal isonitrile vibrations (for III b, d) may be taken as an indication of the presence of both cis (A) and trans (B) isomers. Weaker bands at 2013, 1975 and 1747 cm^{-1} may be assigned to the terminal CO and bridging CN vibrations of isomers (C)/(D) for complexes (III a-c). There is no detectable concentration of isonitrile bridged isomer (C) or (D) for the Bu^t derivative (III d).

The ratio of the isomers (C):(D) has been calculated from the relative intensities of the terminal CO bands and yields a value of 57:43[16]. The cis:trans ratios for the parent thiocarbonyl (I), $Cp_2Fe_2(CO)_4$ and the dithiocarbonyl (II) are 46:54, 36:64 and 57:43 respectively in the same solvent. The increasing proportion of cis isomer on substitution of a bridging ligand of (I) is a feature common also to isonitrile substituted derivatives of $Cp_2Fe_2(CO)_4$.

The infrared spectrum of the disubstituted complex IV does not show a bridging carbonyl vibration, thus indicating that this complex exists solely as isomers (E)/(F).

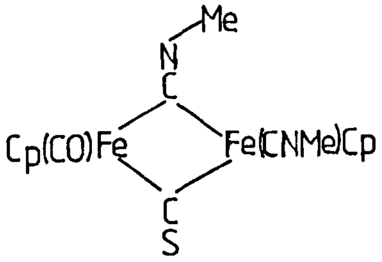


(E)

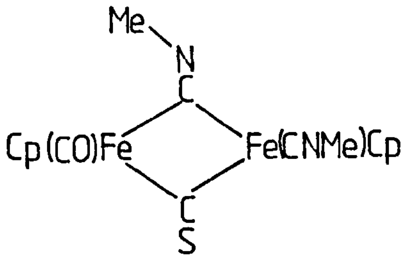


(F)

The doubling of the terminal carbonyl and bridging CS vibrations may be due either to a) resolution of the $\nu(CO_t)$ band of (E) from that of (F), b) resolution of the $\nu(CO_t)$ bands of syn and anti forms of either (E) or (F) (with one isomer being absent) or c) a mixture of syn and anti isomers of (E) and (F) in which the bands are coincident.



syn

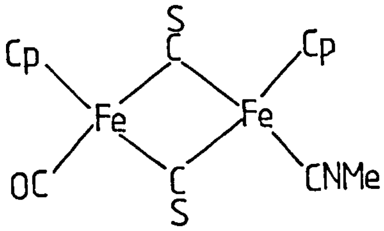


anti

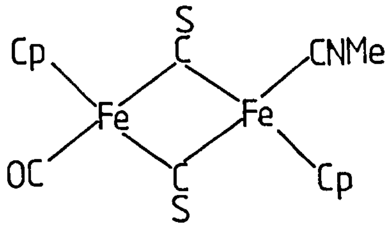
The complexes $Cp_2Fe_2(CO)_2(CNR)_2$ exhibit similar spectra in the $\nu(CO_t)$ region. In the photochemical preparation of IV, there is no evidence for the formation of the isomer of structure

Cp(CNMe)Fe(μ-CO)(μCS)Fe(CNMe)Cp which has been reported to be formed in small yield from thermal reaction of $Cp_2Fe_2(CO)_3(CS)$ and CNMe[15].

Complex (V) exists in solution only as the terminally bound structures (G)/(H), infrared spectrum showing no bridging isonitrile vibration. Although only one terminal CO vibration is observed, coincidence of bands may mask the presence of both isomers.



(G)



(H)

The spectroscopic properties associated with the ligands in bridging positions [particularly ν(CO), ν(CS) and ν(CNR) and $\delta(^{13}C)$ values] provide a useful guide to relative π back donation in these complexes. Table 2 lists the infrared stretching frequencies and chemical shifts for several complexes in which the bridging and/or terminal carbonyls have been substituted by other ligands.

In both $Cp_2Fe_2(CO)_3(CS)$ (6) and $Cp_2Fe_2(CO)_2(CS)_2$ (7), the CS ligands occupy bridging positions. The greater π acceptor character of CS, which results in a decrease in electron density for π-back donation to the bridging carbonyl in (6), is apparent in the increase in $\nu_{CO}{}^b$ as compared to $Cp_2Fe_2(CO)_4$, coupled with a decrease in the chemical shift of the bridging carbonyl resonance. Similarly a decrease in the chemical shift

TABLE 2.

	$\nu_{CO}{}^{b}$	$\delta_{CO}{}^{b}$	$\nu_{CS}{}^{b}$	$\delta_{CS}{}^{b}$	$\nu_{CN}{}^{b}$	$\delta_{CN}{}^{b}$
1) $Cp_2Fe_2(CO)_4$	1797	272.9	-	-	-	-
Replacement of terminal CO						
2) $Cp_2Fe_2(CO)_3$(t-CNMe)	1774	278.8	-	-	-	-
3) $Cp_2Fe_2(CO)_3$(t-$CNBu^t$)	1773	278.1	-	-	-	-
4) $Cp_2Fe_2(CO)_2$(t-$CNBu^t$)$_2$	1750	286.5*	-	-	-	-
5) $Cp_2Fe_2(CO)_3[P(OEt)_3]$	1750	282.2	-	-	-	-
Replacement of bridging CO						
6) $Cp_2Fe_2(CO)_3(CS)$	1811	267.2	1130	378.3	-	-
7) $Cp_2Fe_2(CO)_2(CS)_2$	-	-	-	373.5	-	-
8) $Cp_2Fe_2(CO)_3$(μ-CNMe)	1802	272.6	-	-	1737	246.6
Replacement of bridging and/or terminal CO						
9) $Cp_2Fe_2(CO)_2(CS)(PEt_3)$	1760	278.3	1102	396.2	-	-
10) $Cp_2Fe_2(CO)_2(CS)$(t-CNMe)	1794	274.4	1116*	391.4	-	-
11) $Cp_2Fe_2(CO)_2(CS)$(μ-CNMe)	-	-	-	-	1747	-

12) $Cp_2Fe_2(CO)(CS)_2$(t-CNMe)	-	-	1108	385.3	-	-
13) $Cp_2Fe_2(CO)(CS)(\mu$-CNMe)(t-CNMe)	-	-	1115	394.1	1723	256.1
14) $Cp_2Fe_2(CO)_2(\mu$-CNMe)(t-CNMe)	1784	280.1	-	-	≠	257.5
15) $Cp_2Fe_2(CO)_2(\mu\text{-CNMe})_2$	-	-	-	-	≠	248.5
16) $Cp_2Fe_2(CO)(\mu\text{-CNMe})_2$(t-CNMe)	-	-	-	-	1702	258.8

of the CS carbon is observed on replacement of the remaining bridging CO ligand of (6) to give (7).

In contrast, phosphine or phosphite substitution of $Cp_2Fe_2(CO)_4$ always results in substitution of a terminally bound CO. This is a consequence of these ligands being weaker π acceptors but better σ donors than CO. As a result, in $Cp_2Fe_2(CO)_3P(OEt)_3$ (5), for example, the terminal coordination of the phosphite gives rise to a decrease in $\nu_{CO}b$ and an increase in chemical shift for the bridging CO and CS ligands of (6) on substitution with PEt_3 to give $Cp_2Fe_2(CO)_2(CS)(PEt_3)$ (9). The much greater downfield shift of the CS resonance implies a greater π back donation of the increased electron density to this ligand.

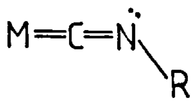
Isonitrile substitution presents a different situation. In terms of overall bonding characteristics, it can be seen from Table 1 that CNR most resembles carbon monoxide, and on isonitrile substitution of $Cp_2Fe_2(CO)_4$, equilibrium mixtures of $Cp(CO)Fe(\mu\text{-}CO)_2Fe(CNR)Cp$ (R = Me, Bu^t) and $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CNR)Fe(CO)Cp$ (R = Me) structures are obtained. The decrease in $\nu_{CO}b$ and increase in the chemical shift of the bridging carbonyl in the terminally bound isomer are consistent with the greater σ donor but poorer π acceptor properties of CNR (see Table 1). The shifts in stretching frequencies and chemical shifts are smaller than for phosphite substitution. Similarly, isonitrile substitution of $Cp_2Fe_2(CO)_3(CS)$ and $Cp_2Fe_2(CO)_2(CS)_2$ to give $Cp_2Fe_2(CO)_2(CS)(t\text{-}CNR)$ and $Cp_2Fe_2(CO)(CS)_2(t\text{-}CNR)$ respectively results in a decrease in $\nu_{CO}b$ and $\nu_{CS}b$ and an increase in the CO^b and CS^b chemical shifts. Disubstitution of $Cp_2Fe_2(CO)_4$ with $CNBu^t$ to give

$Cp(CNBu^t)Fe(\mu\text{-}CO)_2Fe(CNBu^t)Cp$ results in a further shift in the same direction.

In contrast to the terminally substituted molecule, the $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CNR)Fe(CO)Cp$ isomer exhibits a small increase in $\nu_{CO}{}^b$ and a small decrease in the chemical shift of the bridging carbonyl resonance. The results thus imply that isonitrile in a bridging position is as good as or slightly better than CO in terms of π acceptor capacity. Similar conclusions can be reached from a study of di- and trisubstituted isonitrile derivatives of $Cp_2Fe_2(CO)_4$ and $Cp_2Ru_2(CO)_4$.

The geometry of the isonitrile ligand is substantially altered on adoption of a bridging position. In derivatives of $Cp_2Fe_2(CO)_4$, terminal isonitriles are nearly linear ($<C\text{-}N\text{-}C = 171°$) while bridging isonitriles are substantially bent ($<C\text{-}N\text{-}C = 128°$). Table 3 shows the extent of CNR bending in various complexes[17-21]. The substantial bending of the axial isonitrile ligands in $Fe(CNBu^t)_5$ can be attributed to extensive back bonding from metal into the antibonding orbitals of the isonitrile ligand. This results in an increase in the sp^2 character of the N atoms of radial CNR ligands, which is reflected by not only the much smaller C-N-C angle but also in the increase in C-N separation, and a shortening of Fe-C bond, implying multiple bond character. In valence bond terms, the canonical form (ii) makes a significant contribution to the electronic structure.

(i)



(ii)

TABLE 3.

C-N-C ANGLES OF COORDINATED ISONITRILES

Complex	Bridging CNR	Terminal CNR
$Cp_2Fe_2(CO)_3(CNPh)$	131°	-
$Cp_2Fe_2(CO)_2(CNCH_3)_2$	128°	171°
$Co_2(CNBu^t)_8$	131°	154-164°
$Pt_3(CNBu^t)_6$	133°	175°
$\{Pd_2(CNCH_3)_3[(C_6H_5)_2PCH_2P(C_6H_5)_2]_2\}[PF_6]_2$	131°	178-180°
$Mo(CNMe)_2(dppe)_2$	-	156°
$Fe(CNBu^t)_5$	-	135° (radial) 152° (axial)
$Fe_2(\mu\text{-}CNEt)_3(CNEt)_6$	123°	165-179°

The reduced C-N bond order can be seen by much lower C-N stretching frequency (ν_{CN} = 1830 cm^{-1}) for the radial isonitriles. The axial isonitriles, with a smaller deviation from linearity, have C-N stretching frequencies in the range 2000 - 2100 cm^{-1}. Similarly, in $[Fe_2(\mu\text{-}CNEt)_3(CNEt)_6]$, ν_{CN} for bridging isonitriles fall in the range 1700 - 1650 cm^{-1} and for terminal isonitriles, 2060 - 1920 cm^{-1}.

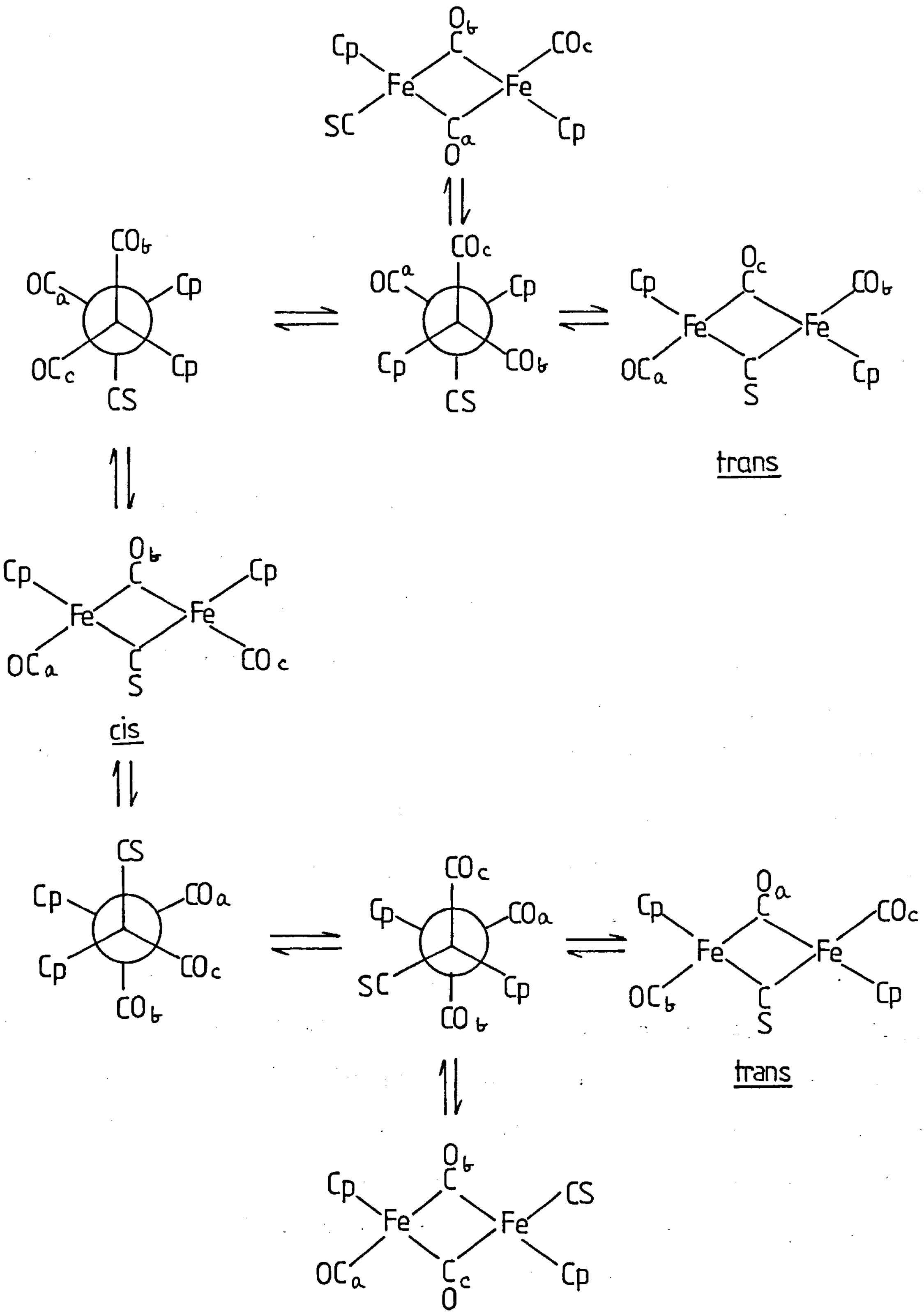
In conjunction with Dr. J.Y. Saillard (University of Rennes), we are currently investigating by ab initio molecular orbital calcuations, the variation in electronic structure of the CNR ligand on variation of the CNR angle. It is observed that as the C-N-C angle in $CNCH_3$ is decreased, the donor ability of the isonitrile is slightly decreased, although it still remains a better donor ligand than CO, and the π-acceptor ability is greatly increased, the isonitrile in fact becoming a better π-acceptor than CO.

Through the series (III a-d) the terminal:bridged ratio (A + B):(C + D) increases in the order Me < Et < Pr^i < Bu^t. The same order is found for the $Cp_2Fe_2(CO)_3(CNR)$ series, and is consistent both with the increase in steric interaction of the R group with the cyclopentadienyl ligands in a bridging position, and with the poorer π acceptor (but better σ donor) character of the isonitrile with increasing methyl substitution of the α-carbon. For (III a), the (A + B):(C + D) ratio (as determined by n.m.r. spectroscopy) is approximately 24:1. The analogous ratio for the isomers $Cp(CO)Fe(\mu\text{-}CO)_2Fe(CNMe)Cp$ and $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CNMe)Fe(CO)Cp$ is 4:1 in toluene[2a]. The change in isomer distribution is again consistent with the increased π acceptor character of CS as compared to CO. For the same reason (V) exhibits only the isomers (G) and (H) containing terminally bound isonitrile, as any other isomeric form would involve terminal thiocarbonyl. The complex $Cp_2Fe_2(CO)_2(CNMe)_2$ exists as a 1 : 0.35 mixture of the isomers $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CNMe)Fe(CNMe)Cp$ and $Cp(CO)Fe(\mu\text{-}CNMe)_2Fe(CO)Cp$, whereas IV exhibits only the isomer of structure (E)/(F). Adoption of a bis-$(\mu\text{-}CNMe)_2$ structure would again involve a structure containing terminal thiocarbonyl.

c) Fluxional behaviour:

The thiocarbonyl complex $[Cp_2Fe_2(CO)_3(CS)]$ exists in solution as a mixture of cis and trans forms and just as for the isostructural $[Cp_2Fe_2(CO)_4]$, interconversion between the isomers can occur by the Adams-Cotton mechanism. Thus, the ^1H n.m.r. spectrum of the monothio complex in d^8-toluene (Fig. I) down to -80°C shows two resonances at $\delta 4.11$ and $\delta 4.22$ ppm due to the Cp ligands of cis and trans isomers[14]. The lower field peak becomes more intense as the solvent polarity increases, and thus may be assigned to the cis isomer. Scheme 1 shows the mechanism by which the isomerisation, plus exchange between bridging and terminal carbonyl ligands can take place.

On warming the solution of $[Cp_2Fe_2(CO)_3(CS)]$, broadening and coalescence occur to yield a single broadened Cp resonance at 61°C, the coalescence temperature being over 100°C higher than that found for $Cp_2Fe_2(CO)_4$. This retarding effect of the bridging CS ligand on the rate of cis-trans isomerisation has also been observed for $Cp_2Ru_2(CO)_3(CS)$, and it can be attributed to the CS bridged structure being able to dissociate less readily to the non-bridged form required by the Adams-Cotton mechanism. Consideration of the mechanism (Scheme 1) clearly



Scheme 1.

shows that although isomers with terminal CS groups are available, it is not necessary for the isomerisation to pass through these isomers. This is supported by the fact that isomers with terminal CS groups are not detected spectroscopically. Also, it is interesting to note from Scheme 1 that the cis-trans isomerisation is accompanied by exchange of carbonyl groups between bridging and terminal sites.

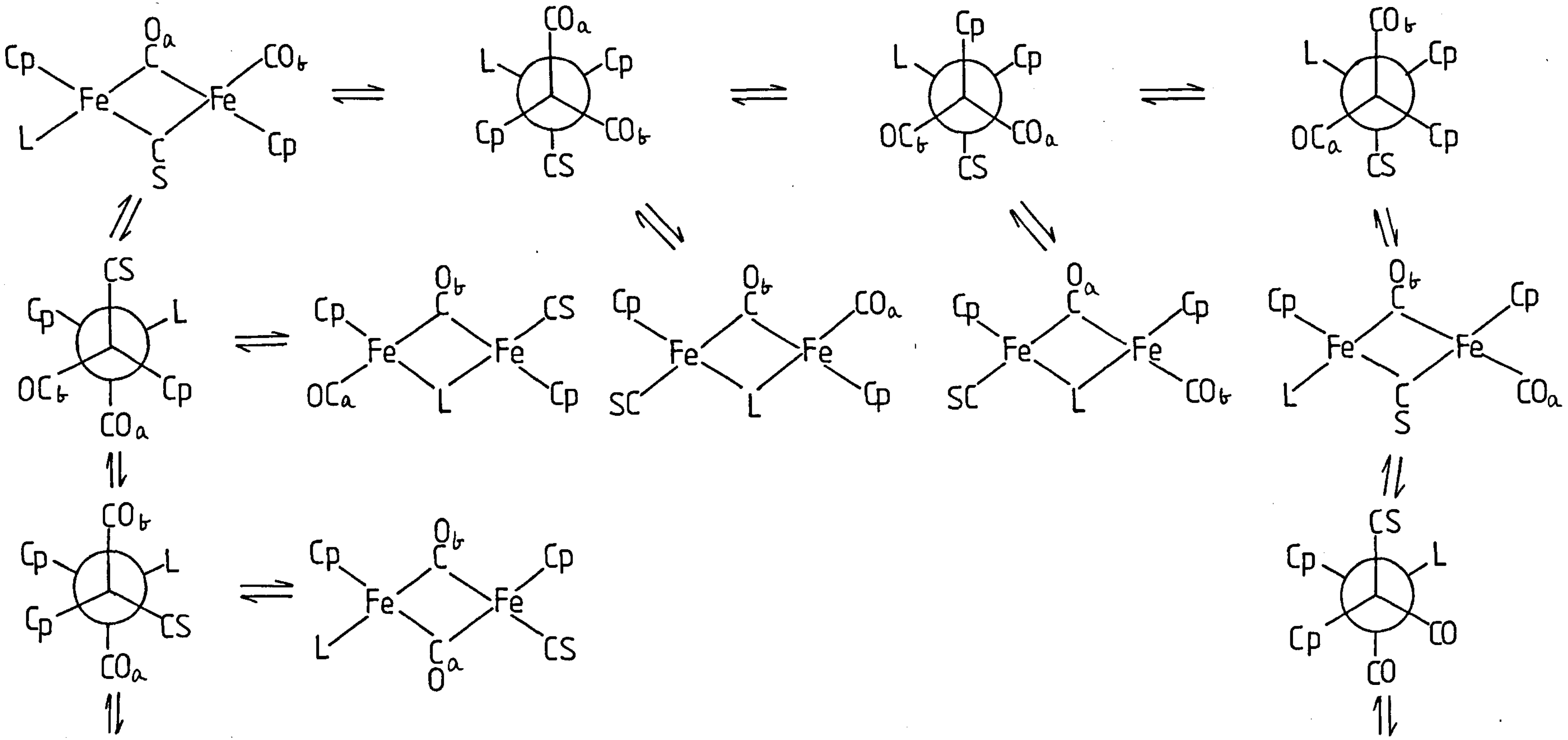
The ^{13}C spectrum (Fig.II) of complex (I) at room temperature shows two Cp resonances (90.3 and 92.2 ppm), terminal and bridging CO resonances (209.0 and 267.2 ppm respectively), and a CS resonance at 378.3 ppm. On warming a solution of $Cp_2Fe_2(CO)_3(CS)$, the complex eventually decomposes without showing any averaging of either the carbonyl resonances or the Cp resonances, which would be expected for the isomerisation. The assignment of the resonances is in agreement with those made by Angelici for $Cp_2Fe_2(CO)_3(CS)$[14]. In contrast, whereas Angelici has assigned the resonance at 287.6 ppm to the bridging CS of $Cp_2Fe_2(CO)_2(CS)_2$, we find that the CS group in this complex has a chemical shift of 373.5 ppm, (Fig.III).

^1H n.m.r. spectra (Fig.IV) of (III a-c) in d^8-toluene down to -80°C typically show two resonances at δ4.30 and δ4.28 ppm assignable to the inequivalent Cp ligands of (A) and/or (B), together with a much smaller singlet resonance at δ4.12 ppm due to isomers (C) and/or (D). The ^1H n.m.r. spectrum in $CD_2C\ell_2$ (Fig.V) at -80°C shows the singlet resonance at a greater chemical shift relative to the two larger resonances. This type of behaviour has also been observed in complexes of the type $Cp_2Fe_2(CO)_3(CNR)$. Spectra in $CD_2C\ell_2$ are essentially invariant with temperature from -80° to +20°C. In d^8-toluene, two Cp resonances assignable to (A) and/or (B) in the temperature range -80° to +20°C are observed. At -40°C there is a merging of the two resonances which eventually separate out again to give two peaks at +20°C (Fig.IV). There is however no broadening of the peaks associated with these changes, which are the result not of a fluxional process, but of a temperature dependent chemical shift of the resonance at δ4.36.

The results thus imply that (i) the resonances due to (A)/(B) and (C)/(D) are coincident, (ii) only one isomer of each pair is present or (iii) that the pairs of isomers are exchanging rapidly with each other even at low temperature.

The possibilities of exchange between the different isomers of $Cp_2Fe_2(CO)_2(CS)(L)$ can be visualised in terms of the Adams-Cotton mechanism, and are outlined in Scheme 2. The scheme is simplified in that pathways leading to isomers having terminal CS groups have been regarded as 'dead ends'. For instance, interconversion between (B) and (C) may proceed by two pathways, as shown in Scheme 3, with one of the pathways proceeding through an isomer with a terminally bonded CS group. The energy profile diagram (Fig. 3) for the two pathways clearly shows the higher activation energy for the pathway which passes through the isomer with a terminal CS group, for which there is no spectroscopic evidence. Therefore, the cis-trans isomerisation is likely to proceed via that pathway which does not pass through such an isomer.

Examination of Scheme 2 leads to the following predictions: (i) If exchange processes are restricted to those involving only unsymmetrical $Cp(CS)(CNR)FeFe(CO)_2Cp$ rotamers, exchange only between isomers (A) and (B) is possible. This



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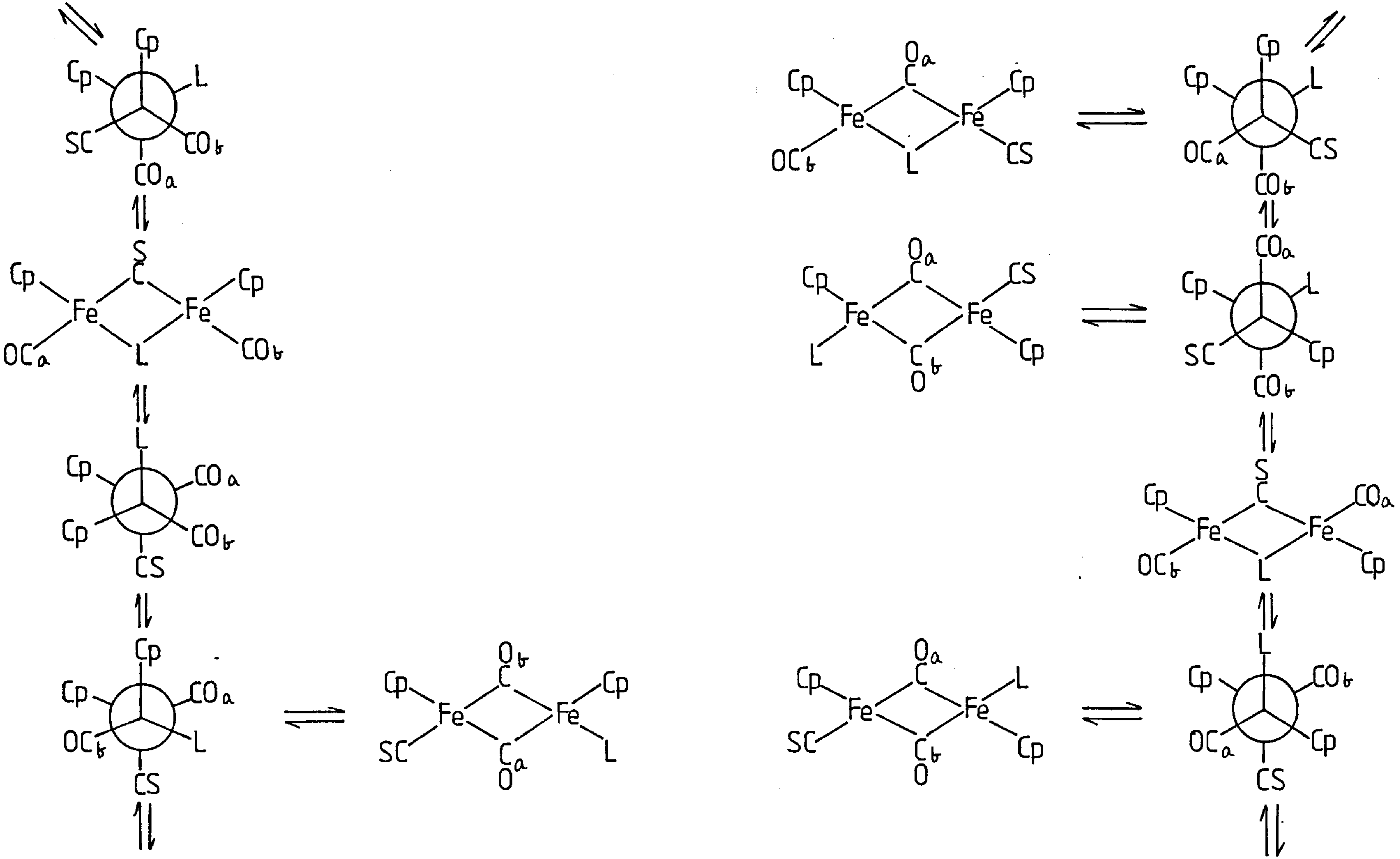
Scheme 2.



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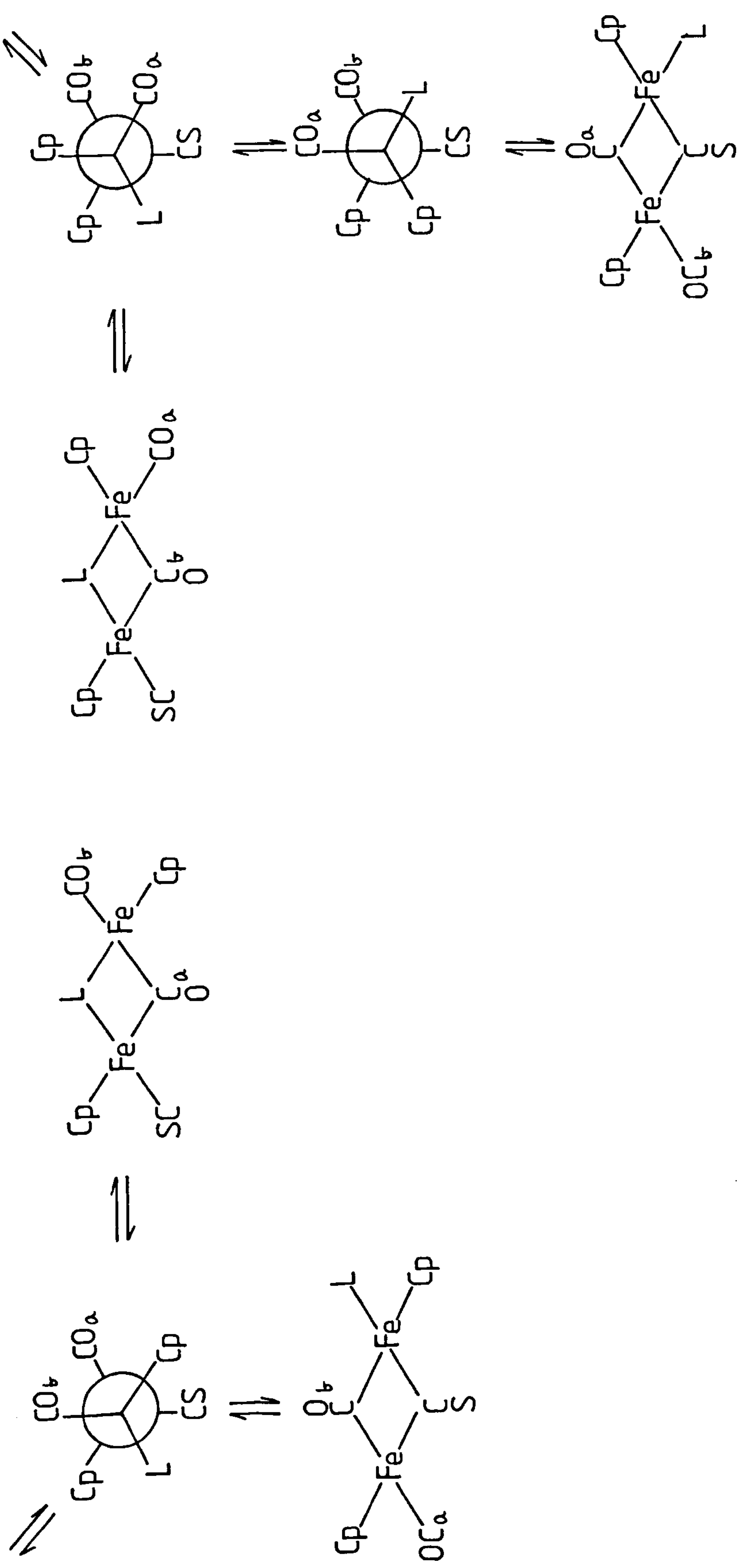
Cp
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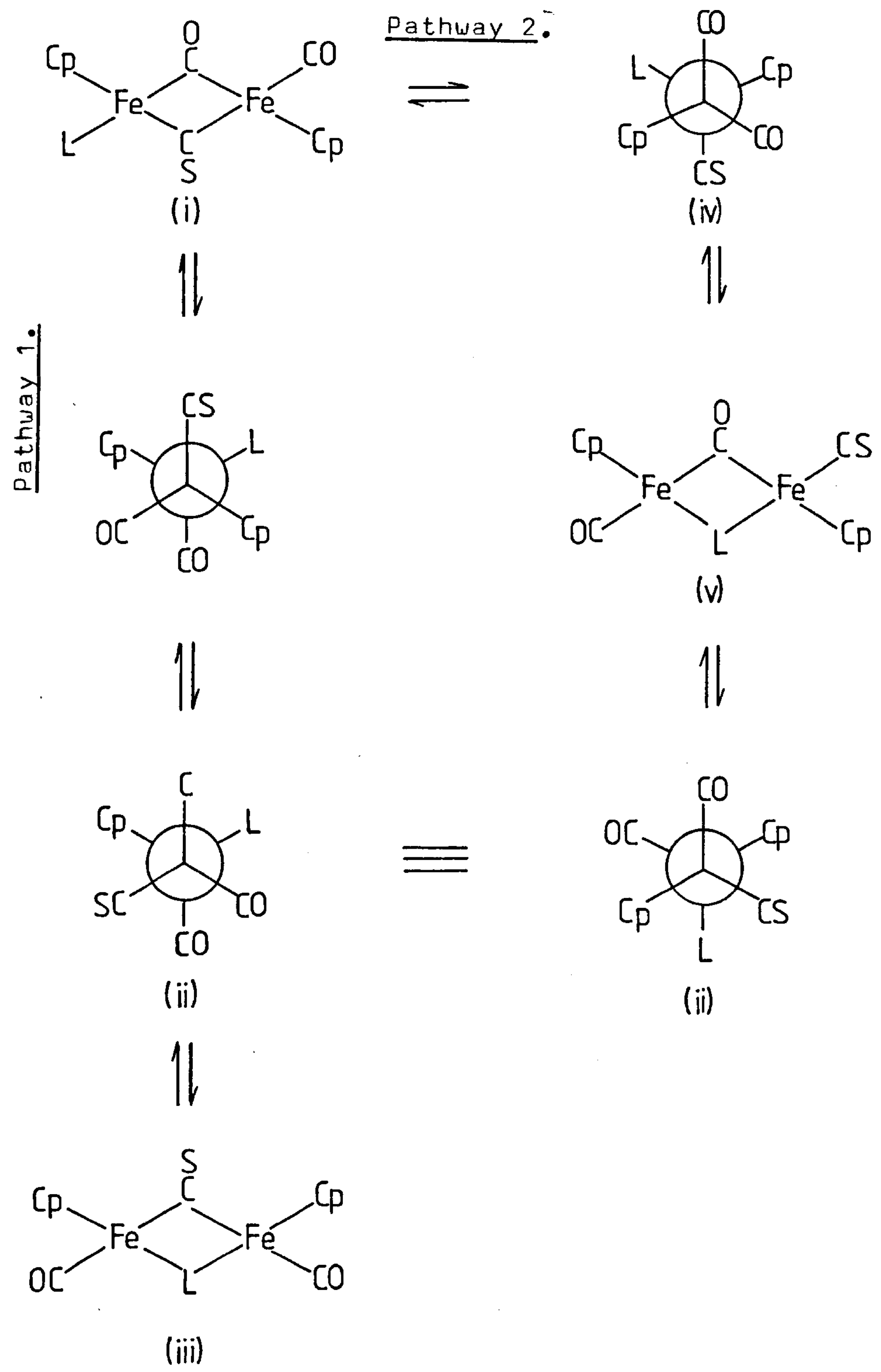


Scheme 3.

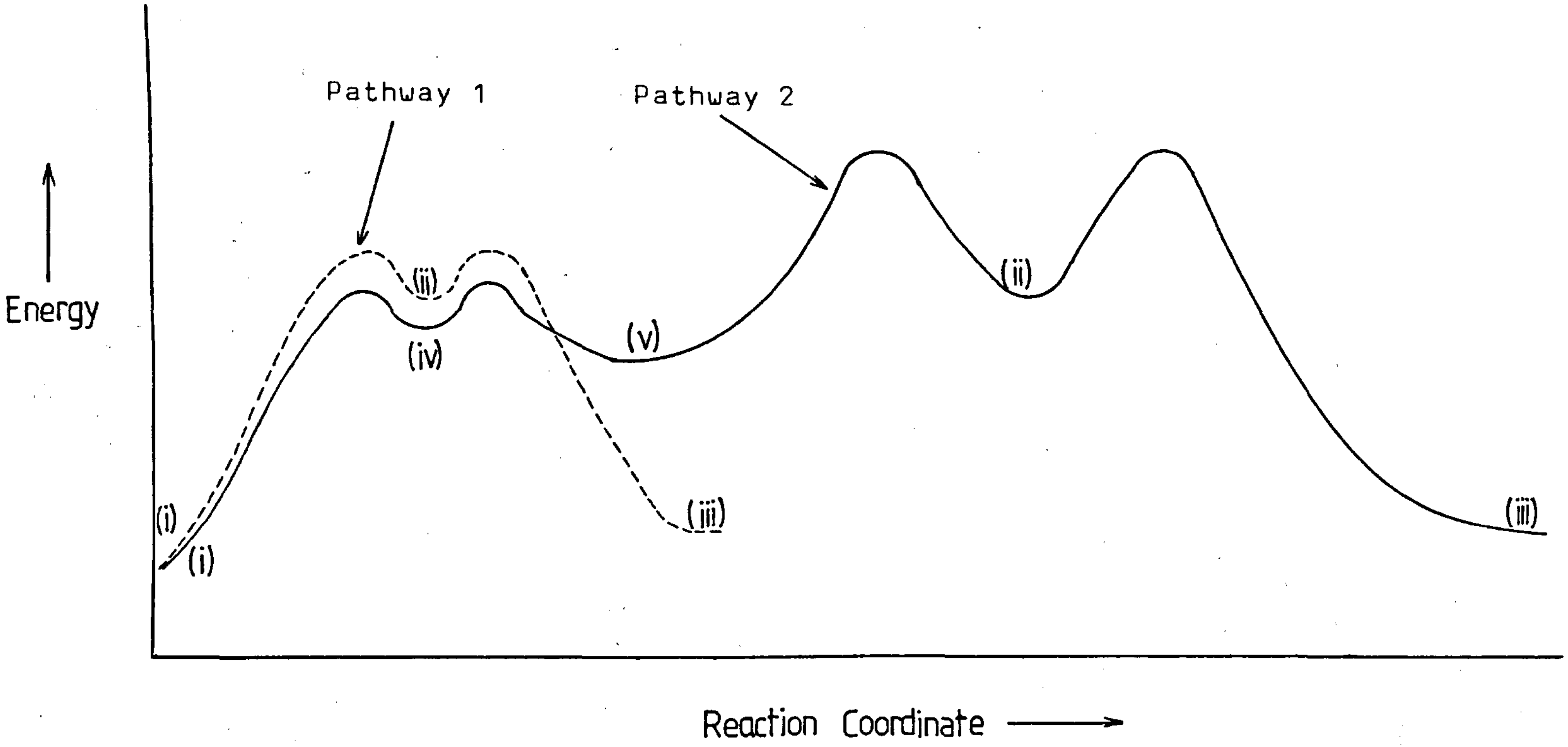
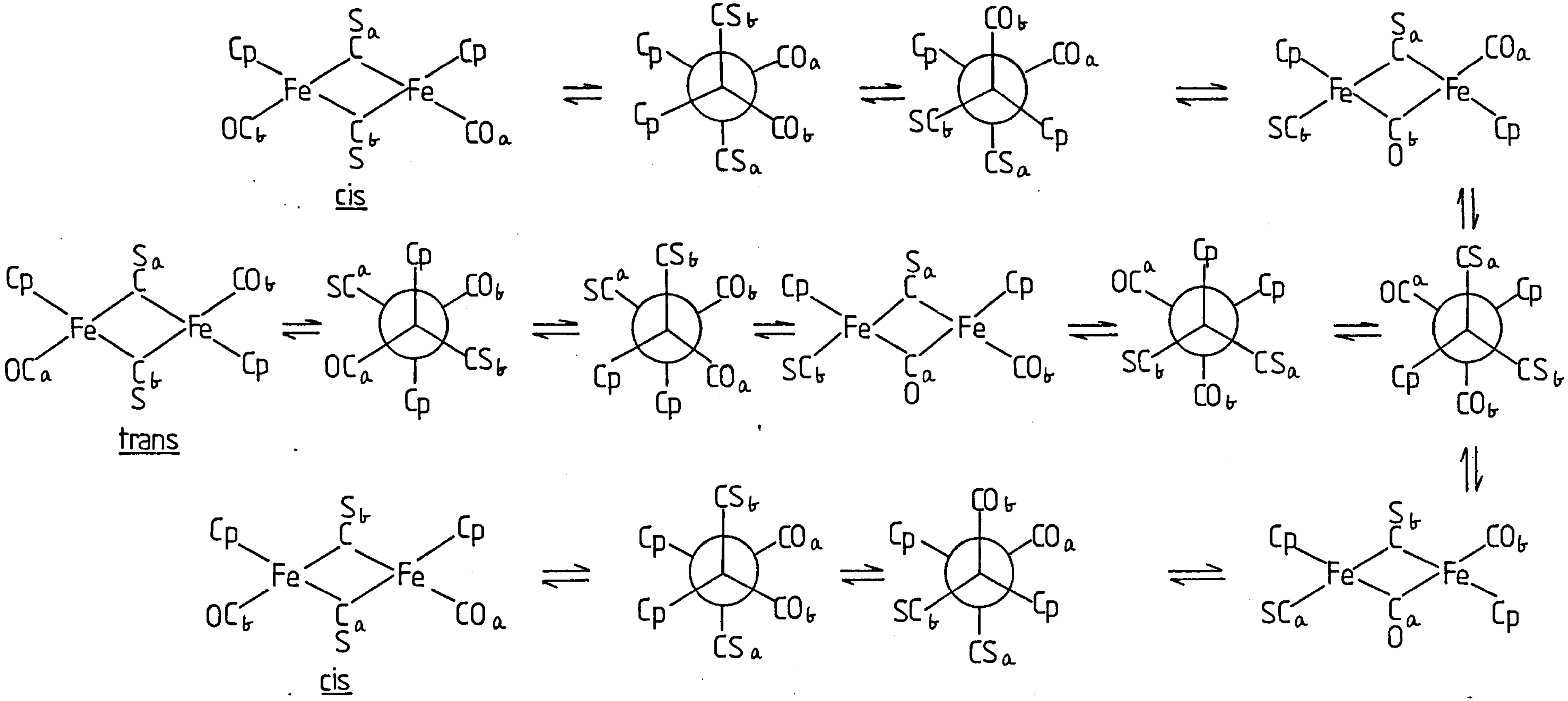

Pathway 1
Pathway 2
Energy
(i)
(i)
(ii)
(iv)
(v)
(iii)
(ii)
(iii)
Reaction Coordinate

Fig. 3.

must be accompanied by CO bridge-terminal exchange, but not by exchange of CNR between the metal atoms. (ii) If only rotamers of the type Cp(CO)(CS)FeFe(CNR)(CO)Cp are allowed, then exchange can occur between either (A) and (D) or between (B) and (C). This must be accompanied by bridge-terminal CO exchange and by scrambling between the two metal atoms. If both processes are allowed, then complete exchange between (A) and (D) is possible. It has been postulated that (i) represents a lower energy pathway, as the ligand of greatest σ donor power,(CNR), is on the same iron atom as the best π acceptor, (CS), and that the absence of separate resonances due to cis and trans isomers is due to rapid exchange even at low temperature. ^{13}C spectra, however, are static at 0°C; thus coincidence of signals in the ^{1}H spectrum seems the most likely explanation. However, as will be discussed later, in the complex $Cp_2Fe_2(CO)_2(CNBu^t)_2$, the exchange processes which involve rotamers of type $Cp(CO)_2FeFe(CNBu^t)_2Cp$ (in which both σ donor CNR ligands are on the same iron atom) do have a higher activation energy than those involving the symmetrical rotamers $Cp(CO)(CNBu^t)FeFe(CO)(CNBu^t)Cp$, although steric congestion may be important as well in this case.

On warming the solution of complex $[Cp_2Fe_2(CO)_2(CS)(CNR)]$, broadening and coalescence occur to yield a single broadened Cp resonance at +100°C, consistent with the operation of both (i) and (ii).

On the basis of the Adams-Cotton mechanism, it is possible to predict the possible pathways involved in the interconversion of different isomers of complexes II, IV and V.



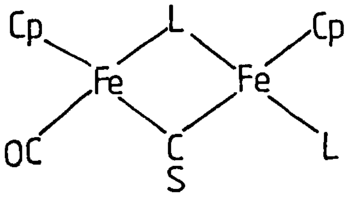
Scheme 4.

Complex (II) has been shown to exist in the cis and trans forms (Fig. 4), there being no evidence for an isomer with a non-bridging CS group.

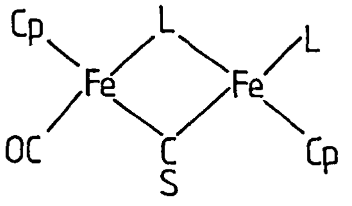
Fig. 4 . $Cp_2Fe_2(CO)_2(CS)_2$

Scheme 4 outlines the pathway by which the two isomers can interconvert by the Adams-Cotton mechanism. The interconversion, which involves dissociation of the very stable CS bridged structure to the non-bridged form and also the formation of an intermediate with terminally bonded CS groups, clearly has a higher activation energy than that for the analogues $[Cp_2Fe_2(CO)_3(CS)]$ and $[Cp_2Fe_2(CO)_4]$.

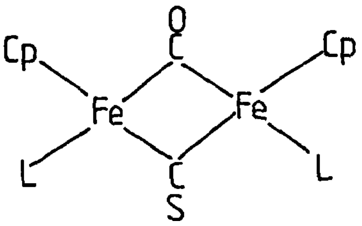
Complex IV can exist in four different isomeric forms, as shown below, in which the CS group occupies a bridging position. Spectroscopically, however, only (E) and/or (F) are observed.



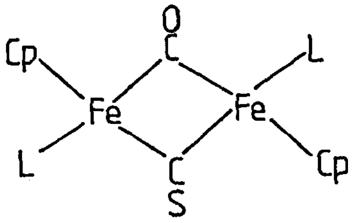
(E) cis-bt



(F) trans-bt



(J) cis-tt



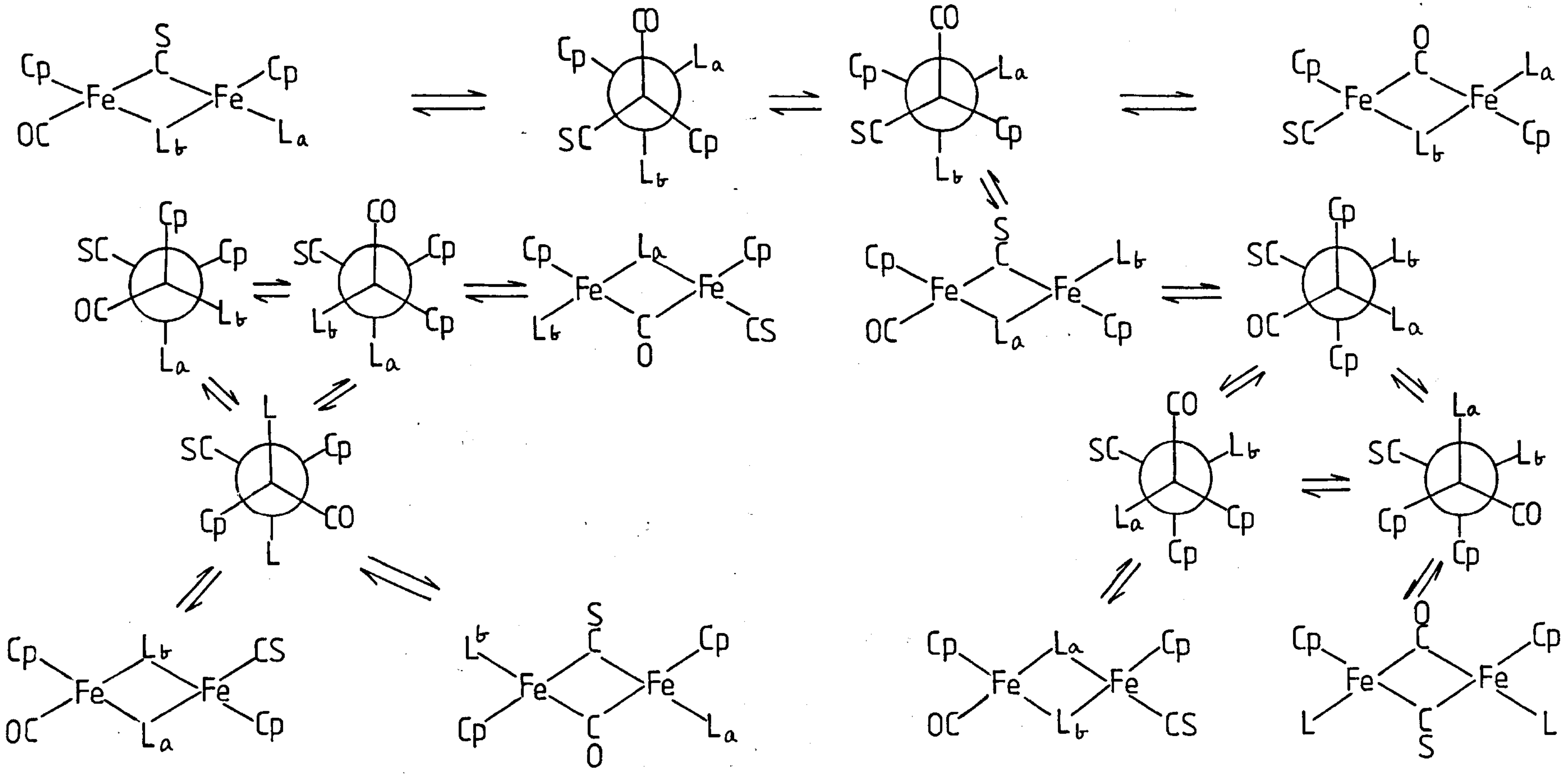
(K) trans-tt

On the basis of the Adams-Cotton mechanism, it is possible to predict the interconversion between the four isomers as:

$$\begin{tikzcd}
(E) \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, phantom, "\upharpoonright\downharpoonleft"] & (K) \\
(F) \arrow[r, phantom, "\rightleftharpoons"] & (J)
\end{tikzcd}$$

Thus, if intermediates of type Cp(CO)(L)FeFe(CS)(L)Cp are formed, then interconversion of (E) ⇌ (K) and (F) ⇌ (J) is possible. This would be accompanied by bridge-terminal isonitrile exchange and scrambling of the terminal isonitrile ligands between the iron atoms. However, if intermediates of type $\mathrm{Cp(CO)(CS)FeFe(L)_2Cp}$ are involved, then interconversion of (E) ⇌ (F), accompanied by bridge-terminal isonitrile exchange would be predicted. The second process in which both the better donor ligands are on the same metal atom probably represents a higher energy pathway , (see Scheme 5).

^{1}H n.m.r. spectrum (Fig.VI) of IV in d^8-toluene at +20 °C shows two Cp signals at δ4.47 and 4.42 ppm due to (E) and/or (F). The two signals show no broadening when a solu-



Scheme 5. Predivted pathways for interconversion of isomers of $Cp_2Fe_2(CO)(CS)CNR)_2$.

tion of IV is warmed upto +100°C; thus, in common with $[Cp_2Fe_2(CO)_{4-n}(CNR)_n]$ (n = 1-3) complexes, increasing isonitrile substitution raises substantially the barrier to exchange between the isomers.

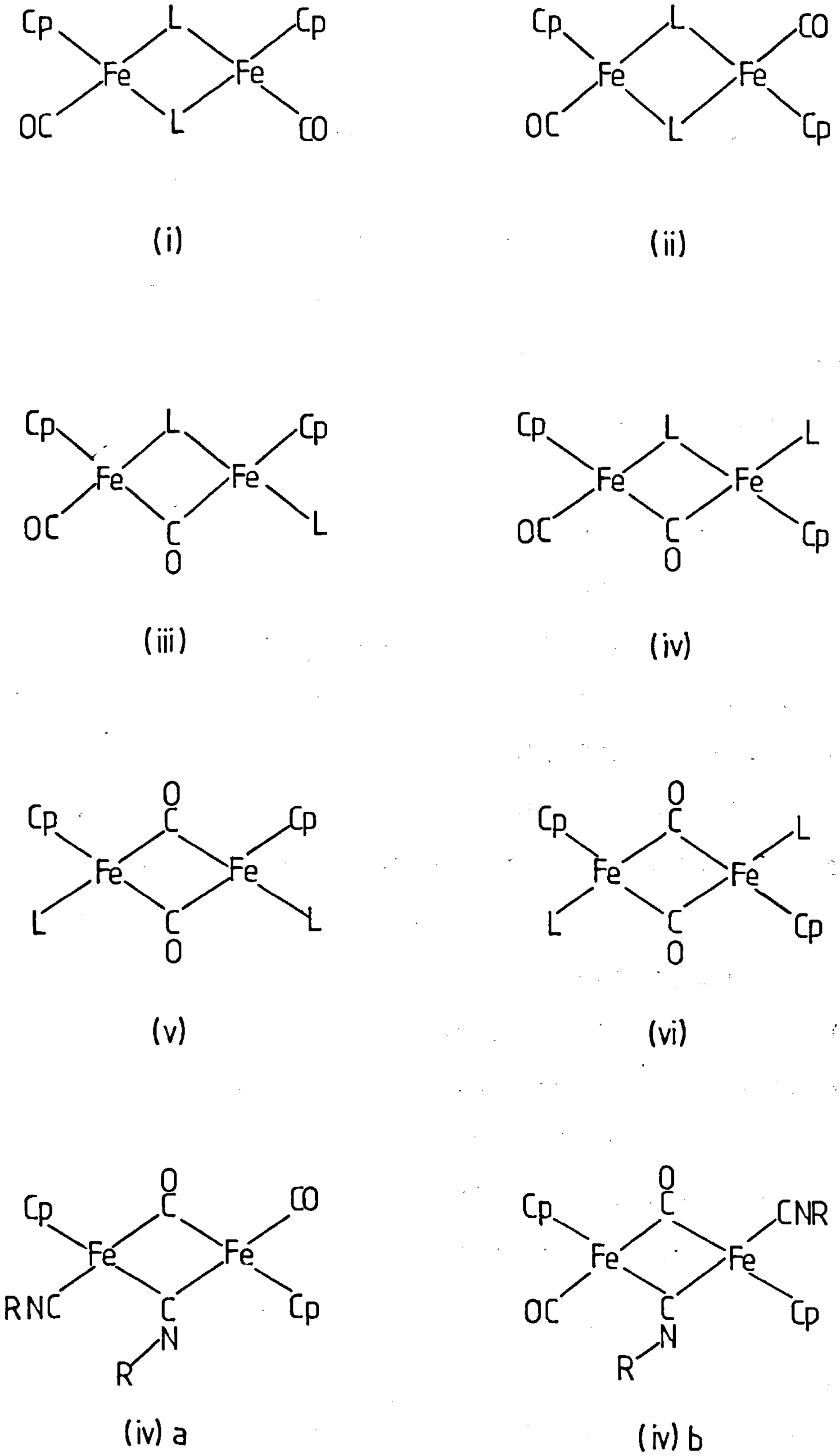
As with complexes I-IV, there is no spectroscopic evidence for any isomers of V with non-bridging CS groups. Scheme 4, in which CO_b has been replaced by L, can be used to predict the possible pathways for the interconversion of the isomers (G) and (H) of complex V. It can be seen that isomers with bridging and terminal isonitrile groups are available and the cis-trans isomerisation is accompanied by scrambling of the isonitrile between the iron atoms. The ^1H n.m.r. spectrum (Fig.VII) of complex V in d^8-toluene shows two resonances at δ4.40 and δ4.39 ppm, assignable to the inequivalent Cp groups of (G) and/or (H). On warming a solution of V upto +100°C, no change is observed in the two Cp resonances. This is consistent with the high activation energy for the interconversion of (G) and (H) as predicted in Scheme 4 which shows isomers with terminally bonded CS groups.

Although it is not possible to detect the isomerisation between different isomers of complexes II, IV and V, it may be possible to detect the interconversion between different isomers in the ruthenium analogues, in which the activation energy of interconversion is generally lower than in the corresponding iron complexes.

The disubstituted complex $Cp_2Fe_2(CO)_2(CNBu^t)_2$ VI, apart from being obtained as a product of the reaction of $CNBu^t$ with $Cp_2Fe_2(CO)_3(CS)$, can also be isolated in small yield from the reaction of a large excess of $CNBu^t$ with $Cp_2Fe_2(CO)_4$ in refluxing benzene. The reaction of [$Cp_2Fe_2(CO)_3P(OPh)_3$] with fourfold excess of Bu^tNC at room temperature gives complex VI in good yield. The complex has been fully characterised by microanalysis and infrared and n.m.r. spectra. It is unusual in being green in colour, both in the solid state and in solution, in contrast to the purple-red colour of other derivatives of the type $Cp_2Fe_2(CO)_{4-n}(CNR)_n$ (n = 1-3).

Complex VI can exist in six possible isomeric forms, as shown in Fig. 4 (i-vi). Infrared spectrum shows bands at 2099 (sh), 2050 (33), 1945 (43), 1935 (50), 1779 (30), 1755 (100) and 1715 (26) cm^{-1} (relative intensities in parentheses). The two broad bands at highest frequency may be assigned to ν(C-N) (terminal) vibrations. Bands at 1945, 1935, 1779 and 1715 cm^{-1} may be assigned to ν(C-O) (terminal), ν(C-O) (bridging) vibrations of either isomer (iii) or (iv). N.m.r. results show only (iv) to be present, and the observation of two terminal ν(C-O) absorptions may be taken to indicate the presence of the two diastereoisomers (iv)a and (iv)b. Adams and Cotton have made a similar assignment for the trisubstituted $Cp_2Fe_2(CO)(CNMe)_3$ derivative[22]. The spectra showed no detectable concentrations of isomers (i) and (ii). In comparison, the monosubstituted complex $Cp_2Fe_2(CO)_3(CNBu^t)$ shows no evidence for detectable concentrations of an isonitrile-bridged isomer, while in the case of the disubstituted molecule, $Cp_2Fe_2(CO)_2(CNMe)_2$, only the isomers of structures (i) and (iv) are found in solution, with no detectable concentrations of (v) or (vi).

Proton n.m.r. spectra in d^8-toluene at various temperatures are shown in Fig.VIII. In the spectrum obtained at the lowest temperature (-80°), the doublet at δ4.15 ppm may be



(i) (ii) (iii) (iv) (v) (vi) (iv) a (iv) b

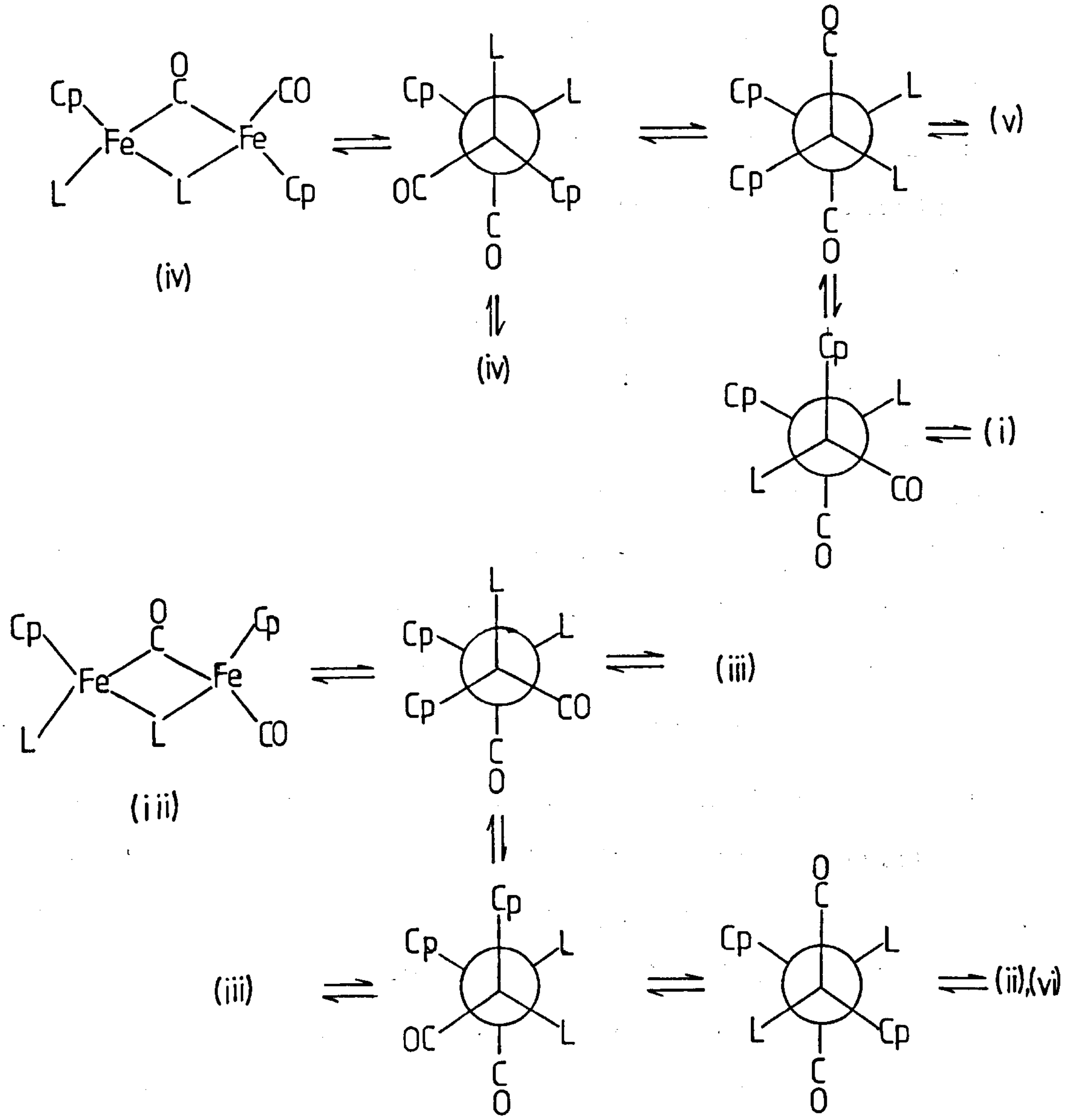
Fig. 4

assigned to the nonequivalent cyclopentadienyl ligands of either (iii) or (iv), although consideration of the mechanism is consistent with (iv) only. The resonance at δ1.69 ppm may be assigned to the bridging $CNBu^t$ group of (iv), while that due to the terminal CNBu ligand is masked by the resonances due due to (v) and (vi), although it can be seen in the spectrum obtained at -35°. By analogy with $Cp_2Fe_2(CO)_2(CNMe)_2$, cooling below -80° should result in separation of individual resonances for (iv)a and (iv)b due to the slowing of nitrogen inversion.

The cyclopentadienyl resonances at δ4.48 and 4.26 ppm (ratio 1:1.2) and the Bu^t resonances at δ1.12 and 0.78 ppm may be assigned to the cis/trans mixture of (v) and (vi). A tentative assignment of signals may be made by comparison with the spectrum in $CD_2C\ell_2$ at -80° which shows two cyclopentadienyl resonances at δ4.47 and δ4.37 ppm in the ratio of 2:1. As has been previously observed for $Cp_2Fe_2(CO)_3(CS)$ and its isonitrile derivatives, an increase in the polarity of the solvent medium increases the proportion of the more polar cis isomer. Thus, the resonance at δ4.48 ppm in the toluene spectrum can be assigned to the cis isomer, and that at δ4.26 ppm to the trans isomer. It should be noted that only one Bu^t resonance (δ1.20 ppm) is observed in $CD_2C\ell_2$, and that isomer (iv) has been depopulated below the limits of detectability. The ^{13}C spectrum in $CD_2C\ell_2$ (Fig.IX) is also consistent with a mixture of (v) and (vi), and here two Bu^t resonances are observed.

Consideration of the variable temperature spectra show that two fluxional processes are occurring: a) at lower temperature, both bridge-terminal isonitrile and most probably cyclopentadienyl site exchange in the resonances attributed to (iv), accompanied by interconversion with the cis isomer (v) only, and b) at higher temperatures, a cis-trans interconversion of (v) and (vi) which eventually yields a high temperature limiting spectrum at +60°.

The first process may be explained by the Adams-Cotton mechanism in which pairwise bridge opening yields the symmetrically substituted $Cp(CO)(CNBu^t)Fe\text{-}Fe(CO)(CNBu^t)Cp$ intermediate. By consideration of the isomers available from bridge closure of the various non-bridged rotamers, it is evident that the equilibria constitute closed sets (Scheme 7). Thus, if the lower field cyclopentadienyl resonance is assigned to (v), it follows that isomer (iv) is taking part in the fluxional process at lower temperature. The isomer (iv) can undergo bridge-terminal isonitrile exchange and cyclopentadienyl site exchange without M-M bond rotation, whereas the interconversion (iv) and (v) or (iv) and (i) require rotation. This has been verified for $Cp_2Fe_2(CO)_2(CNMe)_2$ in which the interconversion between (iv) and (i) has a higher activation energy than that found for bridge-terminal isonitrile exchange and cyclopentadienyl exchange in (iv). It is not possible to ascertain whether this is also true for the interconversion between (iv) and (v) observed here, due to the low population of (iv) and the overlap of signals. The changes observed in the doublet at δ4.15 ppm in the temperature range -80° to -35°C are not associated with a fluxional process but are due to a temperature dependent chemical shift of the resonance at higher field. Spectra in this temperature range show a coalescence of these two resonances, but with no associated broadening. Similar behaviour has been observed in the Cp resonances of $Cp_2Fe_2(CO)_2(CS)(CNR)$



Scheme 6.

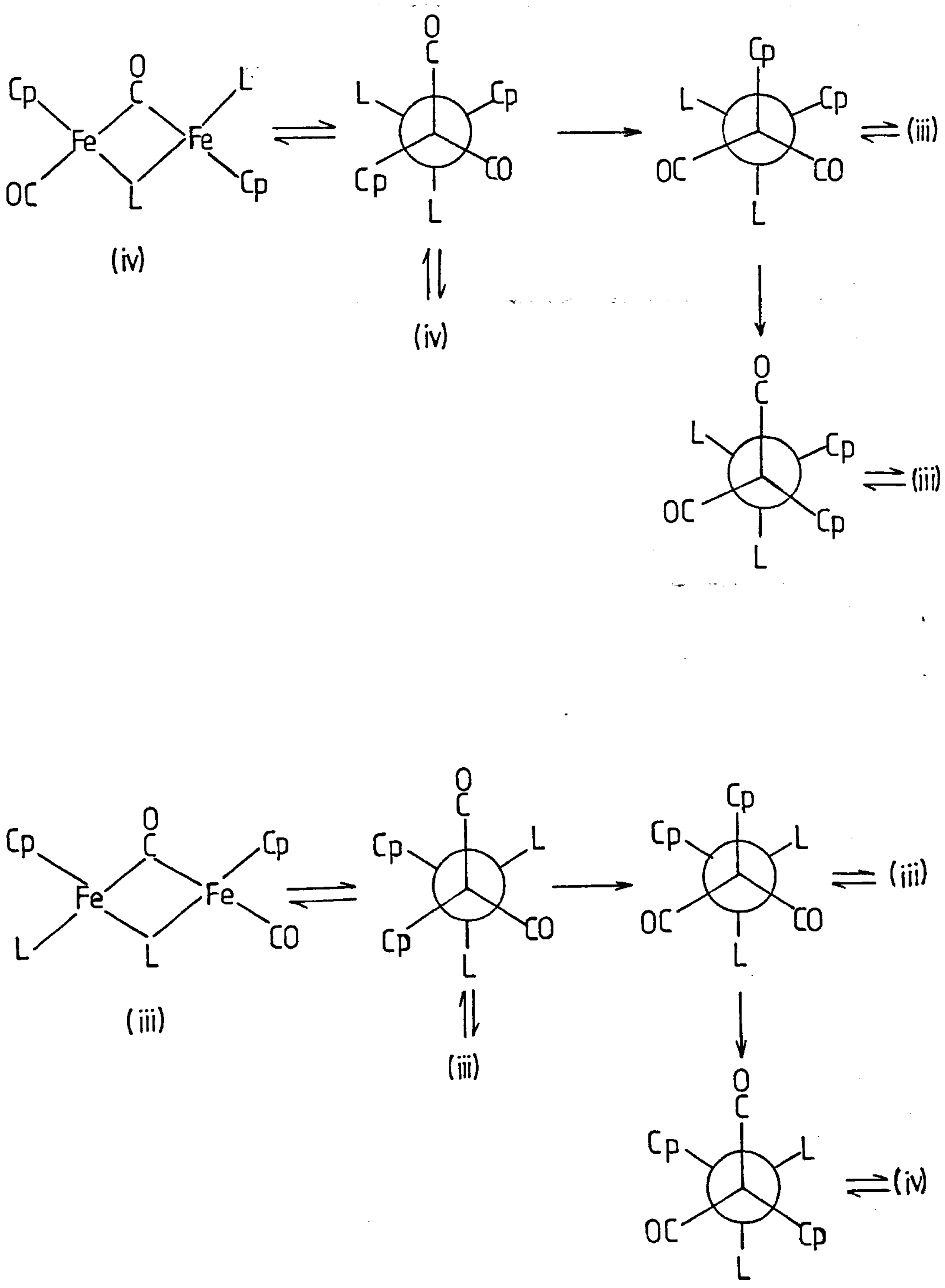
$$\begin{tikzcd}
 & (ii) \arrow[dl, shift left] \arrow[dr, shift left] & & & & (iv) \arrow[dl, shift left] \arrow[dr, shift left] & \\
(vi) \arrow[ur, shift left] \arrow[rr, shift left] & & (iii) \arrow[ul, shift left] \arrow[ll, shift left] & & (i) \arrow[ur, shift left] \arrow[rr, shift left] & & (v) \arrow[ul, shift left] \arrow[ll, shift left]
\end{tikzcd}$$

Scheme 7.

as has already been discussed.

Formation of the asymmetrically substituted $Cp(CO)_2Fe-Fe(CNBu^t)_2Cp$ intermediate on bridge opening provides a pathway for the interconversion of (v) and (vi) (Scheme 8). It can be seen 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 , it follows that interconversion of (v) and (vi) occurs, even though no concentration of (iii) may actually be detected. Thus, Scheme 8 provides a mechanism for linking the two closed sets of Scheme 6. The greater steric strain, supported by the unfavourable electronic factor of having both the better donor ligands on the same iron atom on bridge opening leads to a higher activation energy for (v) $\rightleftharpoons$ (vi) interconversion.

It should be noted that it is only in this unique situation of the interconversion (iv) $\rightleftharpoons$ (v) $\rightleftharpoons$ (vi) or (iii) $\rightleftharpoons$ (v) $\rightleftharpoons$ (vi) that a selectivity in bridge opening may be detectable. For both monosubstituted $Cp_2Fe_2(CO)_3(CNR)$ and trisubstituted $Cp_2Fe_2(CO)(CNR)_3$ complexes, pairwise bridge opening can yield only one structural isomer for the non-bridged intermediate, regardless of the isomeric form of the bridged dimer from which it was derived.


Cp
O
C
L
Fe
Fe
OC
L
Cp
(iv)
O
C
L
Cp
Cp
CO
L
(iv)
Cp
L
Cp
OC
CO
L
(iii)
O
C
L
Cp
OC
Cp
L
(iii)
Cp
O
C
Cp
Fe
Fe
L
L
CO
(iii)
O
C
Cp
L
Cp
CO
L
(iii)
Cp
Cp
L
OC
CO
L
(iii)
O
C
Cp
L
OC
Cp
L
(iv)

Scheme 8.

Fig XVIII. ^{13}C NMR spectrum of $Cp_2Fe_2(CO)(CS)_2(CNMe)$; CD_2Cl/CH_2Cl_2; proton decoupled; 0°C.

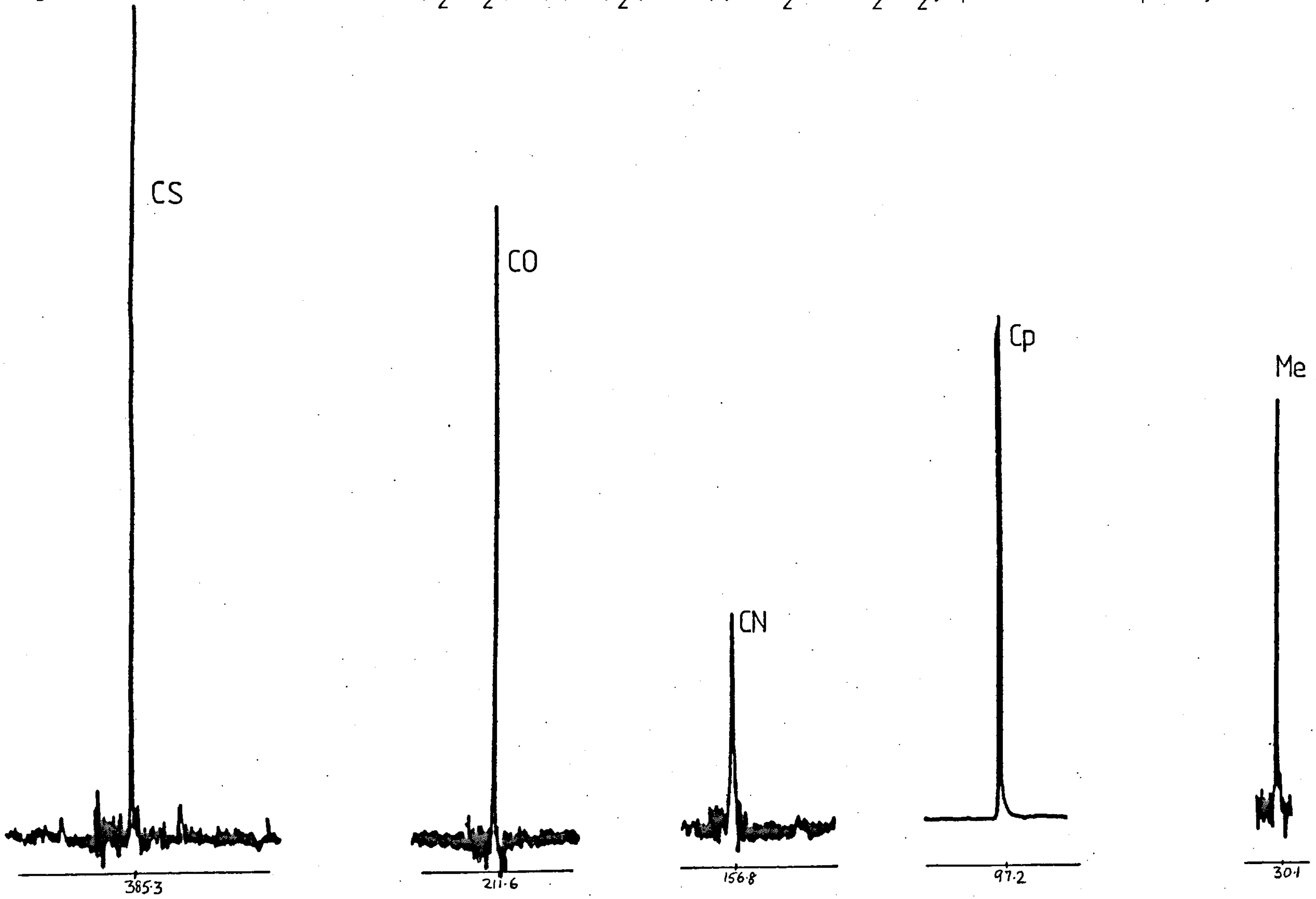


Table 4

Analytical Data

(Calculated values in parentheses)

Complex	C	H	N
$Cp_2Fe_2(CO)(CS)_2(CNMe)$	45.1 (45.1)	3.29 (3.26)	3.67 (3.51)
$Cp_2Fe_2(CO)_2(CS)(CNBu^t)$	50.4 (50.8)	4.36 (4.47)	3.55 (3.29)
$Cp_2Fe_2(CO)_2(CS)(CNPr^i)$	49.5 (49.0)	4.19 (4.14)	3.37 (3.41)
$Cp_2Fe_2(CO)_2(CS)(CNEt)$	48.2 (48.4)	3.86 (3.78)	3.64 (3.53)
$Cp_2Fe_2(CO)_2(CS)(CNMe)$	47.1 (47.0)	3.52 (3.34)	3.75 (3.65)
$Cp_2Fe_2(CO)_2(CNBu^t)_2$	56.5 (56.9)	5.96 (6.03)	6.21 (6.03)

Table 5.

Infrared Data (cm^{-1})[a]

Complex	$\nu_{CO(t)}$	$\nu_{CO(b)}$	$\nu_{CN(t)}$	$\nu_{CN(b)}$	$\nu_{CS(b)}$
$Cp_2Fe_2(CO)_4$	2007 (7.1) 1964 (10.0)	1797 (9.7)			
$Cp_2Fe_2(CO)_3(CS)$	2013 (9.2) 1975 (10.0)	1811 (9.2)			
$Cp_2Fe_2(CO)_2(CS)_2$	2012 (9.1) 1981 (10.0)				
$Cp_2Fe_2(CO)_2(CS)(CNMe)$	1999 (4.2) 1971 (sh) 1963 (10.0)	1794 (8.6)	2149 (4.4)	1747 (2.3)	1119 1113
$Cp_2Fe_2(CO)_2(CS)(CNEt)$	2000 (3.2) 1973 (2.5) 1965 (10.0)	1795 (8.8)	2139 (4.5) 2107 (sh)	1747 (0.83)	1119 1113
$Cp_2Fe_2(CO)_2(CS)(CNPr^i)$	2000 (1.6) 1973 (sh) 1965 (10.0)	1794 (9.3)	2121 (4.5)	1747 (0.37)	1121 1115
$Cp_2Fe_2(CO)_2(CS)(CNBu^t)$	1963 (10.0)	1793 (9.3)	2123 (4.0) 2080 (sh)		1119 1113
$Cp_2Fe_2(CO)(CS)(CNMe)_2$	1965 (7.2) 1955 (10.0)		2147 (5.3)	1721 (7.0)	
$Cp_2Fe_2(CO)(CS)_2(CNMe)$	1976 (10.0)		2157 (4.5)		1108
$Cp_2Fe_2(CO)_2(CNBu^t)_2$	1945 (4.3) 1935 (5.0)	1779 (3.0) 1755 (10.0)	2099 (sh) 2050 (3.3)	1715 (2.6)	

[a] Hexane solution.

Table 6.

^{1}H N.m.r. Data^a

In d^8 toluene:

Complex	Temp. (°C)	Cp	Other
$Cp_2Fe_2(CO)_2(CS)(CNR)$			
R = Me	-80	4.30 4.12 4.28	1.52 (ℓ) 3.30 (small)
R = Et	-40	4.34 4.22 4.33	CH_2 2.31 (q,J=7.4) CH_3 0.39 (t)
R = Pr^i	-40	4.34 4.21 4.32	CH_3 0.58 (d,J=6.5) 0.59 CH 2.79 (sept)
R = Bu^t	-30	4.34 4.31	CH_3 0.73 (s)
$Cp_2Fe_2(CO)(CS)_2(CNMe)$	0	4.40 4.39	CH_3 1.84
$Cp_2Fe_2(CO)(CS)(CNMe)_2$	20	4.42 4.47	CH_3-<u>b</u> 3.54 CH_3-<u>t</u> under solvent
$Cp_2Fe_2(CO)_2(CNBu^t)_2$	-80	4.48 4.18 4.26 4.11	CH_3 1.69 (s) 1.12 (s) 0.78 (s)

In $CD_2C\ell_2$:

$Cp_2Fe_2(CO)_2(CS)(CNMe)$	-80	4.75 4.88 4.63	CH_3 2.98 (ℓ) 3.65 (small)
$Cp_2Fe_2(CO)(CS)_2(CNMe)$	0	4.82 4.70	CH_3 3.03
$Cp_2Fe_2(CO)_3(CS)$	0	4.11 (ℓ) 4.22 (small)	
$Cp_2Fe_2(CO)_2(CS)_2$	20	4.19 (ℓ) 4.25 (small)	
$Cp_2Fe_2(CO)(CS)(CNMe)_2$	0	4.66 4.82	CH_3-<u>t</u> 2.96 CH_3-<u>b</u> 3.66
$Cp_2Fe_2(CO)_2(CNBu^t)_2$	-80	4.47 4.37	CH_3 1.20 (s)

[a] Chemical shifts (δ) from TMS, ℓ = large, q = quartet, t = triplet, d = doublet, s = singlet, sept = septet, <u>t</u> = terminal, <u>b</u> = bridging.

Table 7.

^{13}C N.m.r. Data[a]

Complex	Temp. (°C)	CO	CS	CN	Other
$Cp_2Fe_2(CO)_3(CS)$	0	209.0 (t) 267.2 (μ)	378.3		92.2 90.3 Cp
$Cp_2Fe_2(CO)_2(CS)_2$	0	208.6	373.5		93.2 96.0 Cp
$Cp_2Fe_2(CO)_2(CS)CNBu^t$		211.8 274.2			88.8 89.1 Cp CH_3 29.4 C not observed
2 $Cp_2Fe_2(CO)_2(CS)(CNPr^i)$	0	212.1 274.5	391.5	157.7	89.3 89.0 Cp CH 48.2 CH_3 22.6
$Cp_2Fe_2(CO)_2(CS)(CNEt)$	0	211.8 274.4	391.4	158.1	89.0 89.2 Cp CH_2 39.3 CH_3 14.6
$Cp_2Fe_2(CO)_2(CS)(CNMe)$	0	211.7 274.4	391.4	157.7	88.6 89.2 Cp CH_3 29.8

Table 7 cont'd

$Cp_2Fe_2(CO)(CS)_2(CNMe)$	0	211.6	385.3	156.8	92.8 Cp 92.5 Cp CH_3 30.1
$Cp_2Fe_2(CO)(CS)(CNMe)_2$	0	212.1	394.1	256.1 159.5 unequal 161.6 unequal	Cp 87.9 unequal Cp 91.3 unequal Me-t 29.5 Me-b 45.1
$Cp_2Fe_2(CO)_2(CNBu^t)_2$	-20	287.3 285.8		172.0 166.	86.0 Cp 84.6 Cp 30.2 CH_3 30.0 CH_3

---

[a] $CD_2C\ell_2/CH_2C\ell_2$ solution; ppm from TMS

III. Experimental

All reactions were performed in freshly distilled solvents under nitrogen. The isonitriles were prepared as described in literature[23-25]. $Cp_2Fe_2(CO)_4$ was purchased from Strem Chemicals and used without further purification. Light petroleum ether refers to that fraction boiling between 40 and 60°C. Infrared, n.m.r. and mass spectra were run on Perkin-Elmer 257, JEOL FX-100 and AEI MS12 instruments respectively. Proton decoupled ^{13}C spectra were run in the presence of $Cr(acac)_3$.

Preparation of Diphenylthionocarbonate $\{(PhO)_2CS\}$[26].

A mixture of phenol (80 g, 0.95 mol) and 500 cm^3 of 10% sodium hydronide solution (1.25 mol) were stirred for 2 hours. After diluting the mixture four fold with water, thiophosgene (22 g, 0.19 mol) was added dropwise to the stirred solution. After stirring the solution for a further 3 hours, the diphenylthionocarbonate was extracted with chloroform, and after evaporation of the solvent under reduced pressure, recrystallisation of the crude $(PhO)_2CS$ from alcohol:light petroleum ether gave yellow-brown plate-like crystals of the pure product. Yield 9.0 g (21%).

Recently, Angelici[14] has reported the preparation of $(PhO)_2CS$ in 80% yield from reaction of phenol with sodium hydride to give sodium phenolate, which on reaction with thiophosgene gives the diphenylthionocarbonate.

Preparation of $[Cp_2Fe_2(CO)_2(CS)_2]$[4b].

$Cp_2Fe_2(CO)_4$ (5.0 g, 14.2 mmol) dissolved in 125 cm^3 of tetrahydrofuran was added to freshly prepared 1% Na amalgam (1.0 g Na, 43 mmol) 8 cm^3 Hg), and the mixture was stirred for 1 hour. After removal of the excess Na amalgam, carbon disulfide (2.5 cm^3, 36 mmol) was added to the stirred solution. Methyl iodide (2.0 cm^3, 34 mmol) was added and the mixture was stirred for a further 5 minutes. The solvent was removed under reduced pressure and the residue was extracted with benzene and filtered through celite. The benzene was evaporated off under reduced pressure and to the residue dissolved in 100 cm^3 of diethyl ether was added dropwise 3.2 cm^3 of trifluoromethanesulfonic acid in 25 cm^3 of diethyl ether. After stirring for 30 minutes, the brown coloured $[CpFe(CO)_2(CS)][CF_3SO_3]$, which precipitated out, was collected by filtration and washed several times with diethyl ether. The crude $[CpFe(CO)_2(CS)][CF_3SO_3]$ (5.1 g, 13.8 mmol) was suspended in dry tetrahydrofuran (100 cm^3) and sodium hydride (3.3 g, 0.13 mol) was added. The mixture was stirred for 1 hour, whereupon a green coloured solution was obtained. The solvent was removed under reduced pressure and the residue was dried in vacuo. Chromatography of the residue on a Florisil column using benzene as eluant gave pure $[CpFe(CO)(CS)]_2$ as a green-black solid after the solvent was evaporated off. Yield 2.1 g (39%).

Preparation of $[Cp_2Fe_2(CO)_3(CS)]^{14}$.

$Cp_2Fe_2(CO)_4$ (10.5 g, 30 mmol) dissolved in 150 cm^3 of tetrahydrofuran was added to freshly prepared 1% Na amalgam (2.0 g Na, 86 mmol); 16 cm^3 Hg), and the mixture was stirred at room temperature for 1 hour. The excess Na amalgam was removed, and a solution of $(PhO)_2CS$ (6.9 g, 30 mmol) in 30

cm^3 of tetrahydrofuran was added to the stirred reaction mixture. A mildly exothermic reaction with vigorous CO evolution occurred giving a dark brown solution. After stirring for a further 15 minutes, the solvent was evaporated off under reduced pressure. The residue was extracted with 50 cm^3 of carbon disulfide and filtered through celite. The volume of the solution was reduced to c.a. 10 cm^3 and it was chromatographed on a Florisil column. Elution with 5:1 CS_2:$CH_2C\ell_2$ mixture separated a broad black band of [$Cp_2Fe_2(CO)_3(CS)$] from a broad dark red band of [$Cp_2Fe_2(CO)_4$]. Evaporation of the solvent from the thiocarbonyl fractions gave shiny black crystals of [$Cp_2Fe_2(CO)_3(CS)$]. The product was washed several times with ice-cold hexane, and dried in vacuo. Yield 5.5 g (48%).

Preparation of $Cp_2Fe_2(CO)_2(CS)(CNMe)$

In a typical preparation, [$Cp_2Fe_2(CO)_3(CS)$] (0.6 g, 1.7 mmol) dissolved in 30 cm^3 of benzene, and MeNC (0.2 cm^3, 3.5 mmol) were refluxed for 1 hour, i.e. till infrared spectrum of the reaction mixture indicated that all of the starting material had reacted. The benzene and excess MeNC were removed in vacuo, and the dark green mass was chromatographed on an alumina column (Grade IV). Elution with dichloromethane-light petroleum ether (5:95) yielded the green [$Cp_2Fe_2(CO)_2(CS)(CNMe)$].

Complexes III b-d were prepared in an analogous manner. The derivatives III a-d were purified by recrystallisation from dichloromethane and light petroleum-ether to give yields of c.a. 65%.

Preparation of [$Cp_2Fe_2(CO)(CS)_2(CNMe)$].

$Cp_2Fe_2(CO)_2(CS)_2$ (0.4 g, 1.0 mmol) and methylisonitrile (0.55 cm^3, 10 mmol) were refluxed in 50 cm of benzene for 70 hours. The solvent and excess isonitrile were evaporated off and the dark green residue was chromatographed on an alumina column (Grade III). Elution with light petroleum ether-dichloromethane (50:50) separated a trace of the starting material, which came off the column first, from the green band of [$Cp_2Fe_2(CO)(CS)_2(CNMe)$]. After evaporating off the solvent, the crude product was recrystallised from light petroleum ether-dichloromethane to give a black crystalline solid. Yield 0.25 g (63%).

Preparation of [$Cp_2Fe_2(CO)(CS)(CNMe)_2$].

[$Cp_2Fe_2(CO)_2(CS)(CNMe)$] (0.2 g, 0.5 m mol) and MeNC (0.11 cm^3, 2 mmol) were photolysed in benzene until infrared spectra indicated that most of the starting material had reacted. A typical reaction was complete in 10 hours. After evaporating off the solvent, the residue was chromatographed on an alumina column (Grade III). Elution with carbon disulfide eluted a green band which proved to be a small amount of $Cp_2Fe_2(CO)_2(CS)CNMe$. Elution with CS_2-Et_2O (9:1) gave a second green band containing the major product, [$Cp_2Fe_2(CO)(CS)(CNMe)_2$]. The product was recrystallised from diethyl ether and hexane to to give black crystals of the product. Yield 0.06g (32%).

Preparation of [$Cp_2Fe_2(CO)_2(CNBu^t)_2$]

Complex VI may be prepared by any one of the following three methods.

(i) Thermolysis of $Cp_2Fe_2(CO)_4$ and Bu^tNC.

A mixture of $Cp_2Fe_2(CO)_4$ and twentyfold excess of the isonitrile were refluxed in benzene for two days. After evaporating off the solvent, the residue was chromatographed on an alumina column (Grade IV). Elution with light petroleum ether-dichloromethane (70:30) separated the red band of $Cp_2Fe_2(CO)_3(CNBu^t)$, which was collected first, from the green band of the disubstituted complex $Cp_2Fe_2(CO)_2(CNBu^t)_2$. The crude products were recrystallised from light petroleum ether and dichloromethane to give yields of c.a. 30% for the monosubstituted complex and c.a. 10% for the disubstituted complex.

(ii) Thermolysis of $Cp_2Fe_2(CO)_3(CS)$ and Bu^tNC.

The thermolysis reaction, using tenfold excess of the isonitrile, was carried out as above. After refluxing for 24 hours the work-up of the mixture was carried out as in (i). A trace of the complex $[Cp_2Fe_2(CO)_2(CS)(CNBu^t)]$ was collected off the column first; this was followed by the major product of the reaction, complex VI. Recrystallisation was carried out as in (i).

(iii) Reaction of $Cp_2Fe_2(CO)_3P(OPh)_3$ and Bu^tNC.

In a typical preparation, a mixture of the $Cp_2Fe_2(CO)_3P(OPh)_3$ and sixfold excess of Bu^tNC were stirred in benzene at room temperature for 6 hours. After evaporating off the solvent, the residue was chromatographed to give complex VI as the only product with a yield of c.a. 45%.

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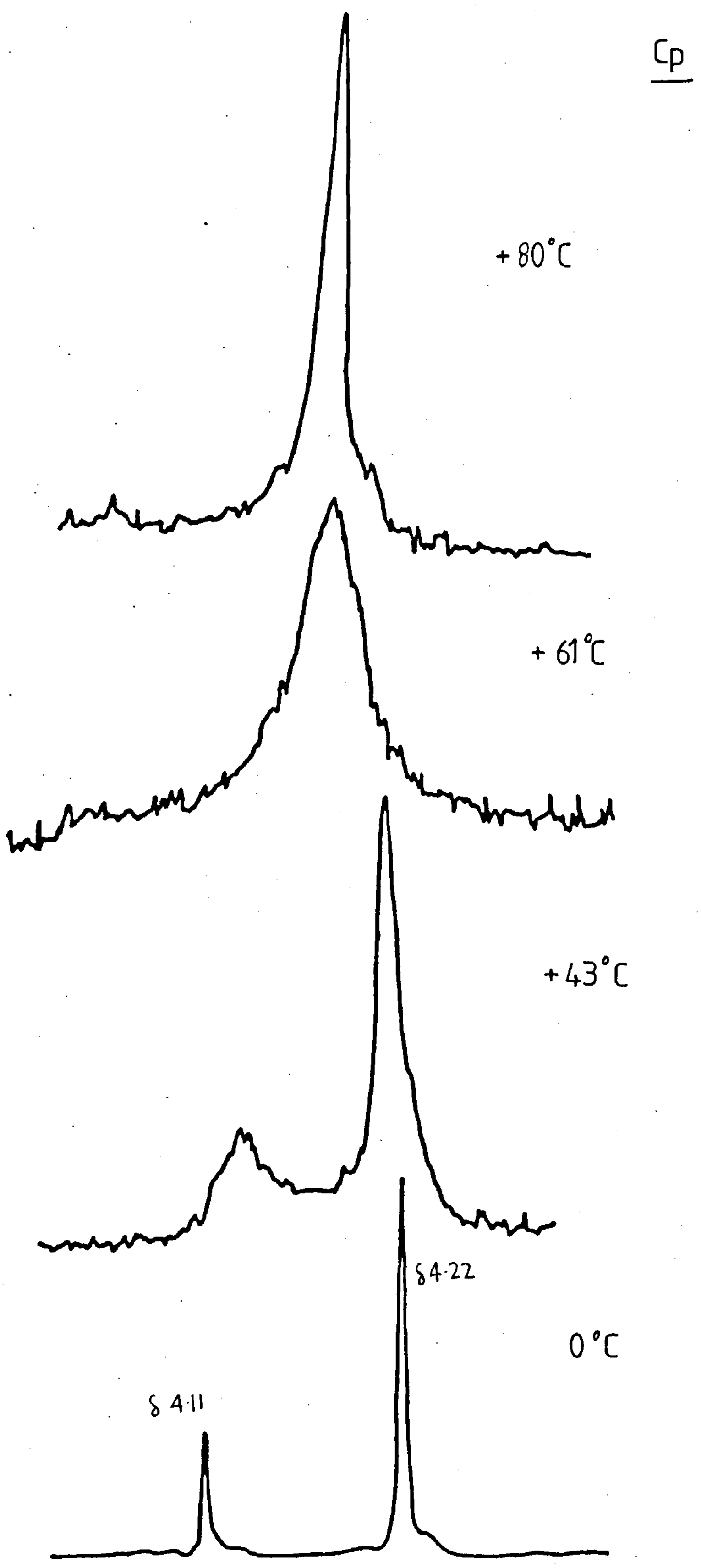


Fig I. ^{1}H NMR spectrum of $Cp_2Fe_2(CO)(CS)$; toluene - d^8; C_p region.

Fig II. ^{13}C NMR spectrum of $Cp_2Fe_2(CO)_3(CS)$; CD_2Cl_2/CH_2Cl_2; proton decoupled; $0^{\circ}C$.

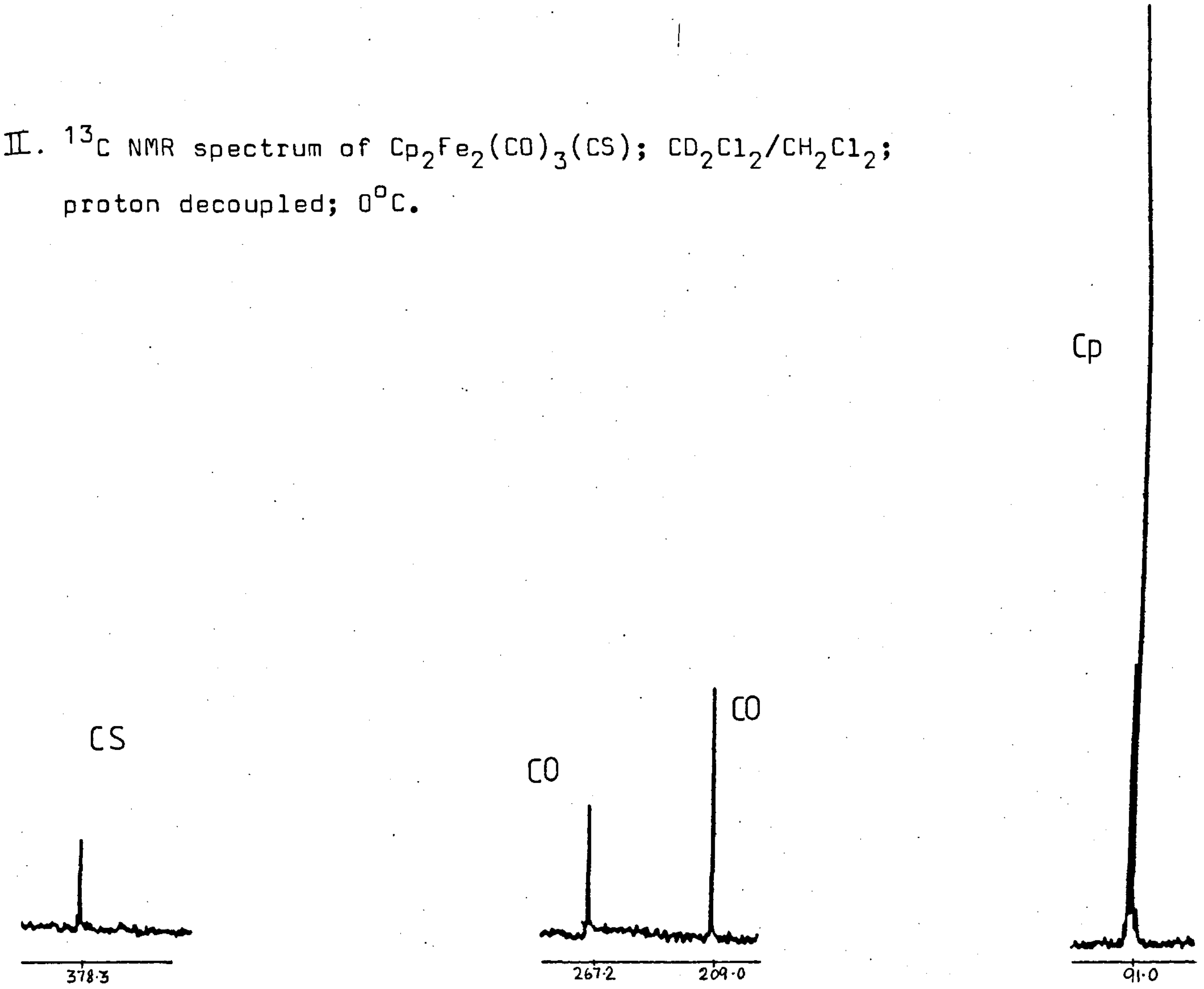


Fig III. ^{13}C NMR spectrum of $Cp_2Fe_2(CO)_2(CS)_2$; CD_2Cl_2/CH_2Cl_2; proton decoupled; $0^{o}C$.

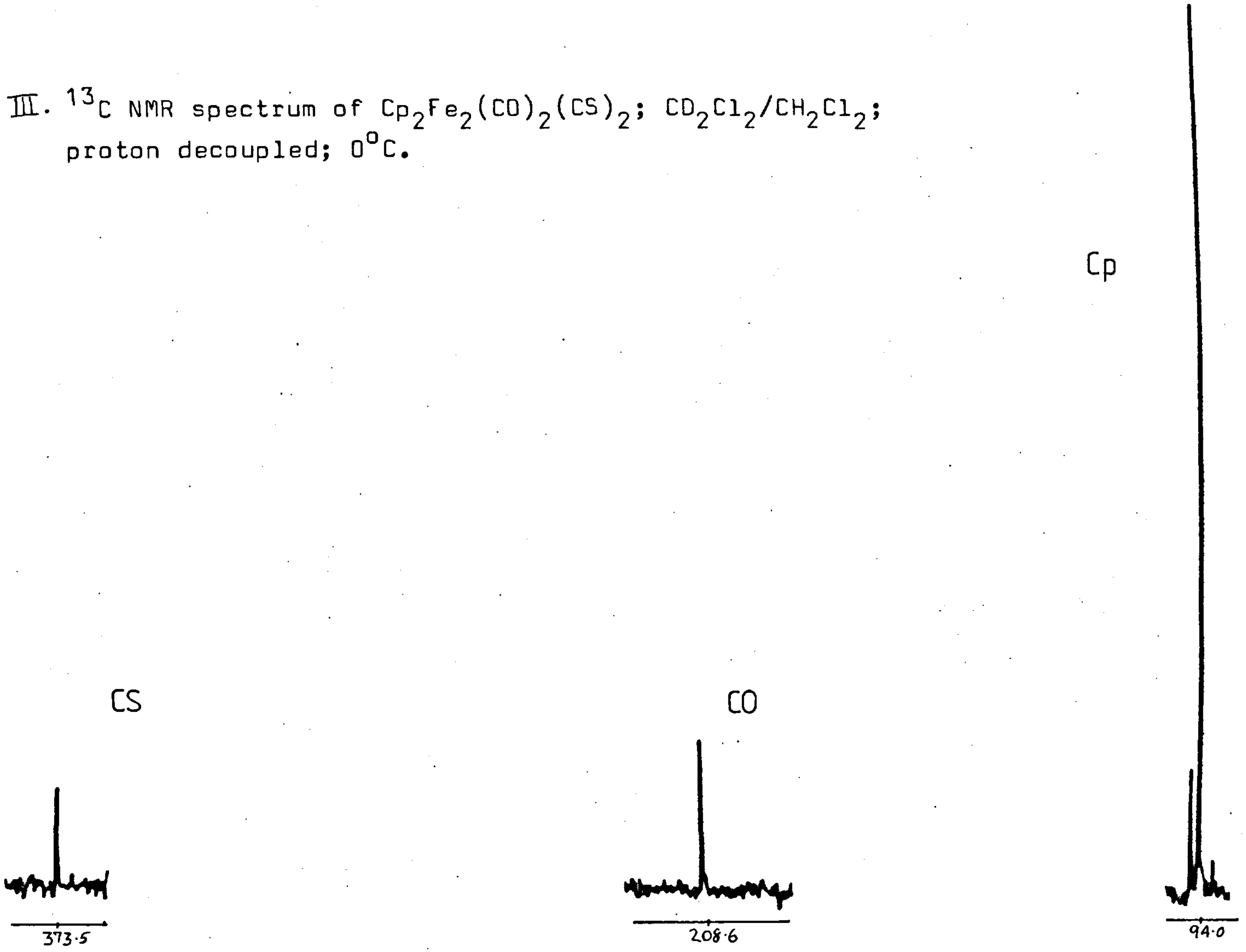
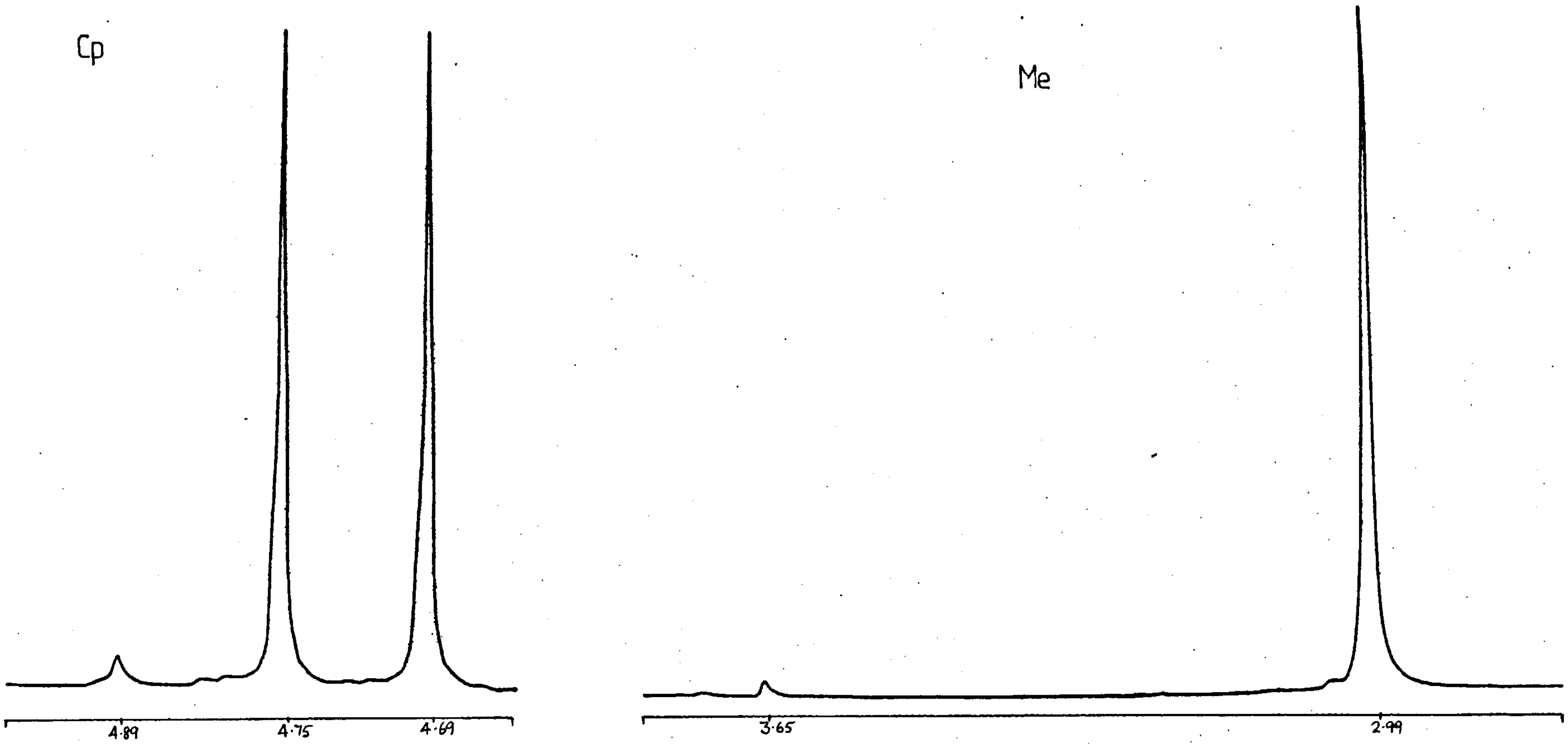


Fig V. ^{1}H NMR spectrum of $Cp_2Fe_2(CO)_2(CS)(CNMe)$; CD_2Cl_2 , 0°C.



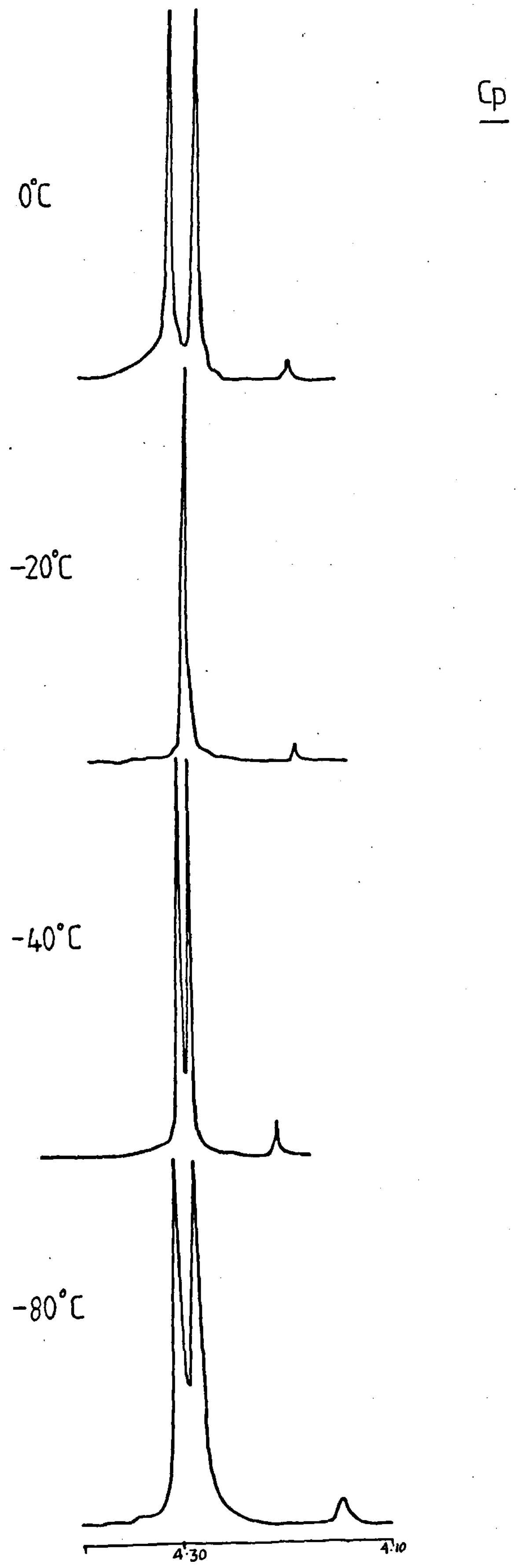


Fig IV. ^{1}H NMR spectrum of $Cp_2Fe_2(CO)_2(CS)(CNMe)$; C_p region; toluene -d^8.

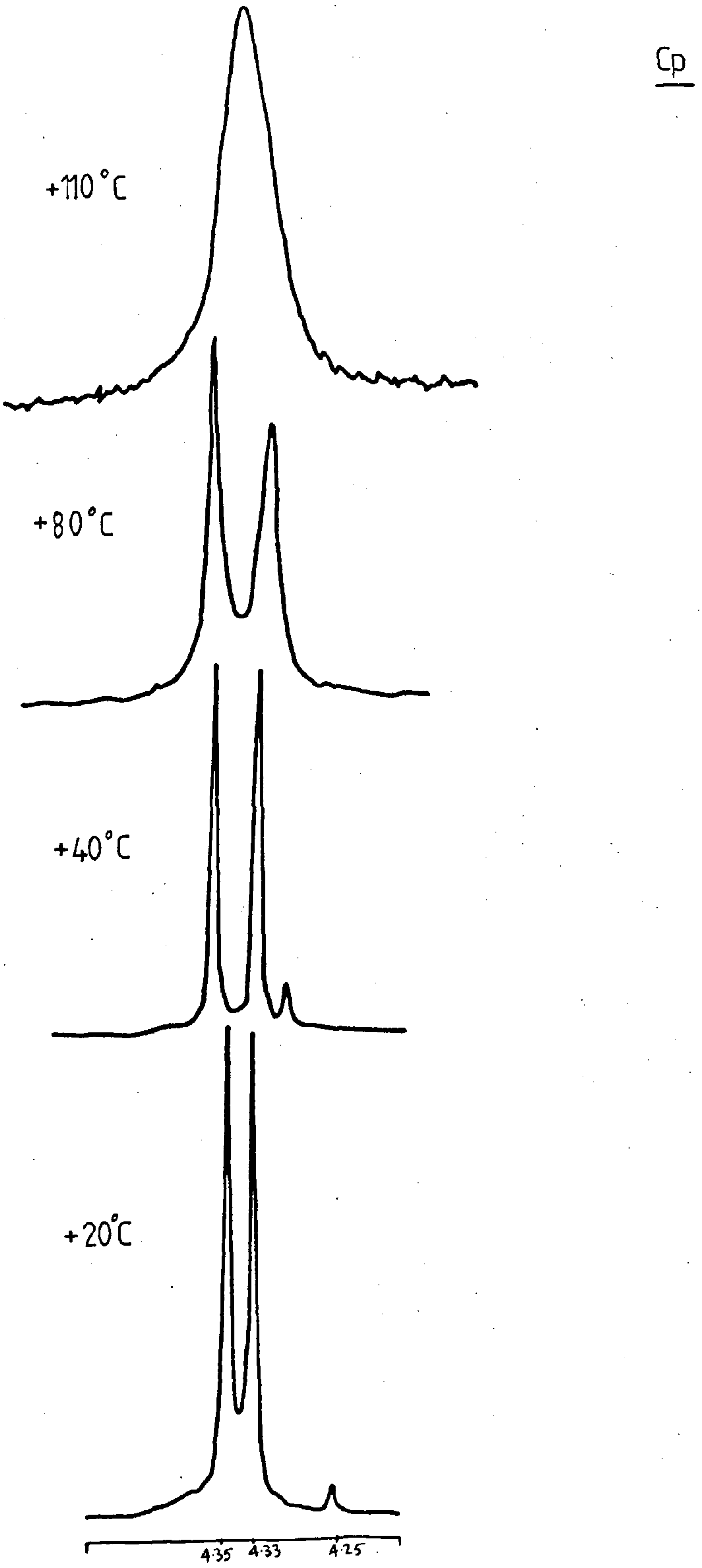


Fig VI. cont'd.

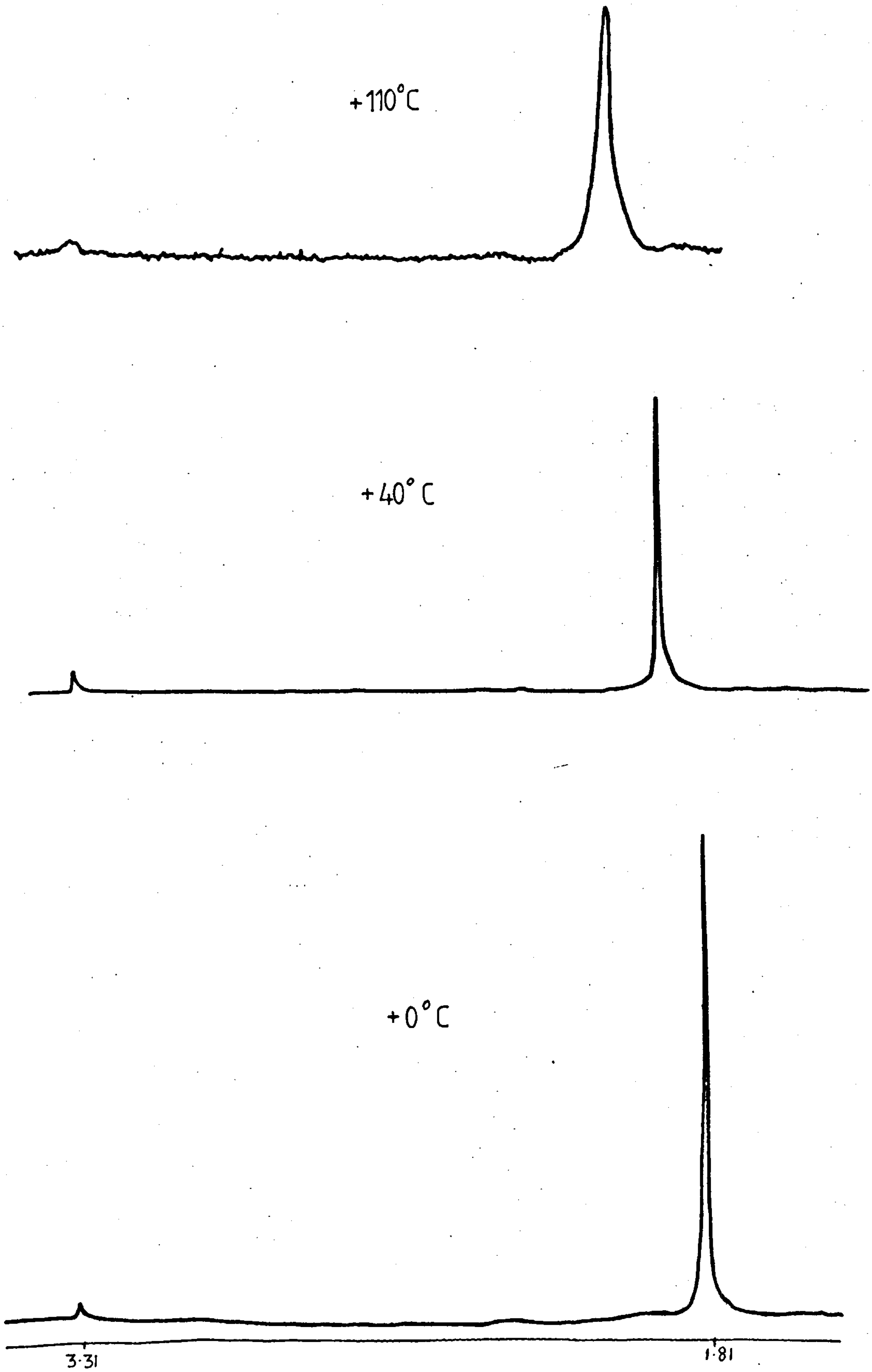


Fig V. ^{1}H NMR spectrum of $Cp_2Fe_2(CO_2(CS)(CNMe)$; toluene - d^8; Me region only.

Fig VI. ^{1}H NMR spectrum of $Cp_2Fe_2(CO)(CS)(CNMe)_2$; toluene - d^8; +20°C.

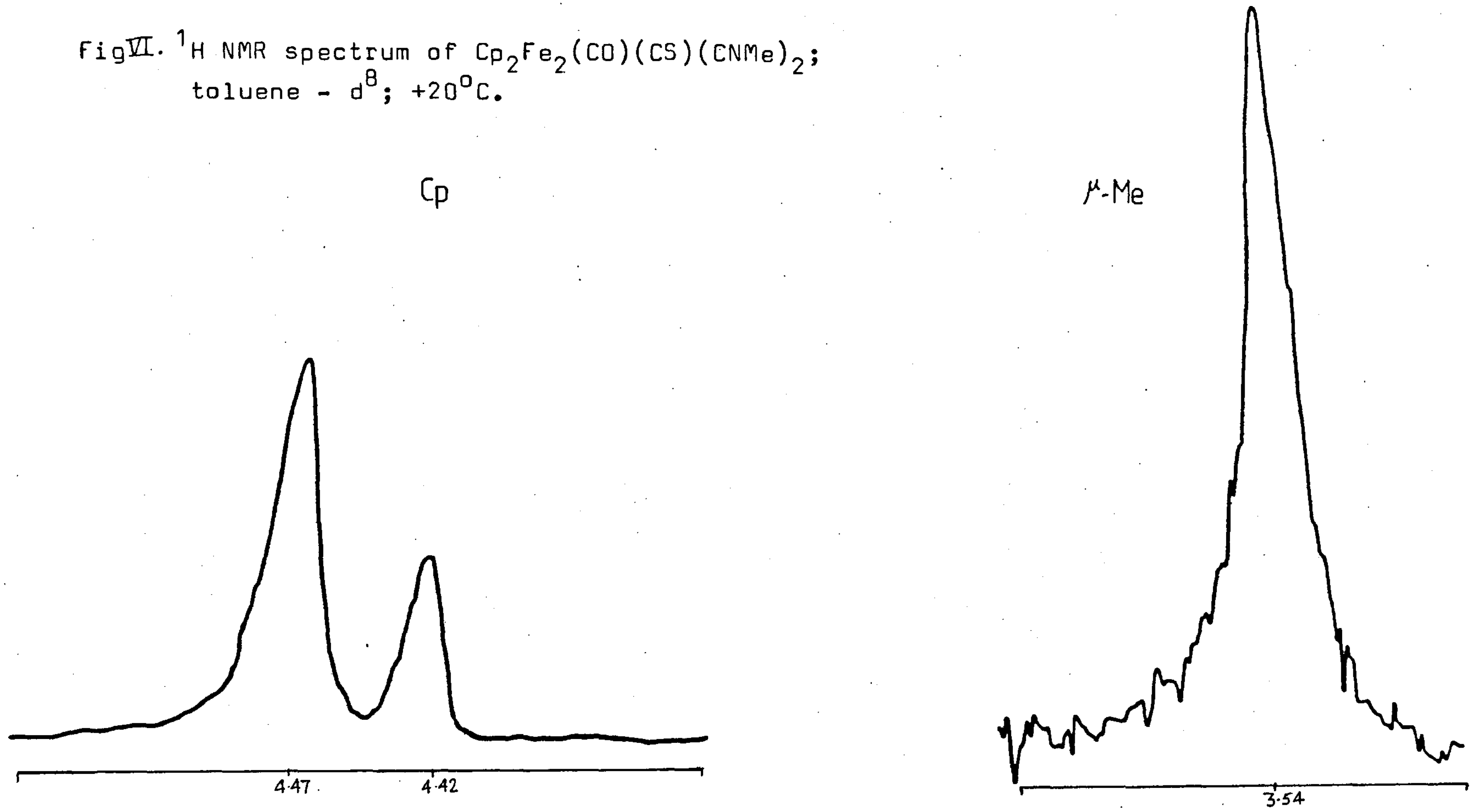
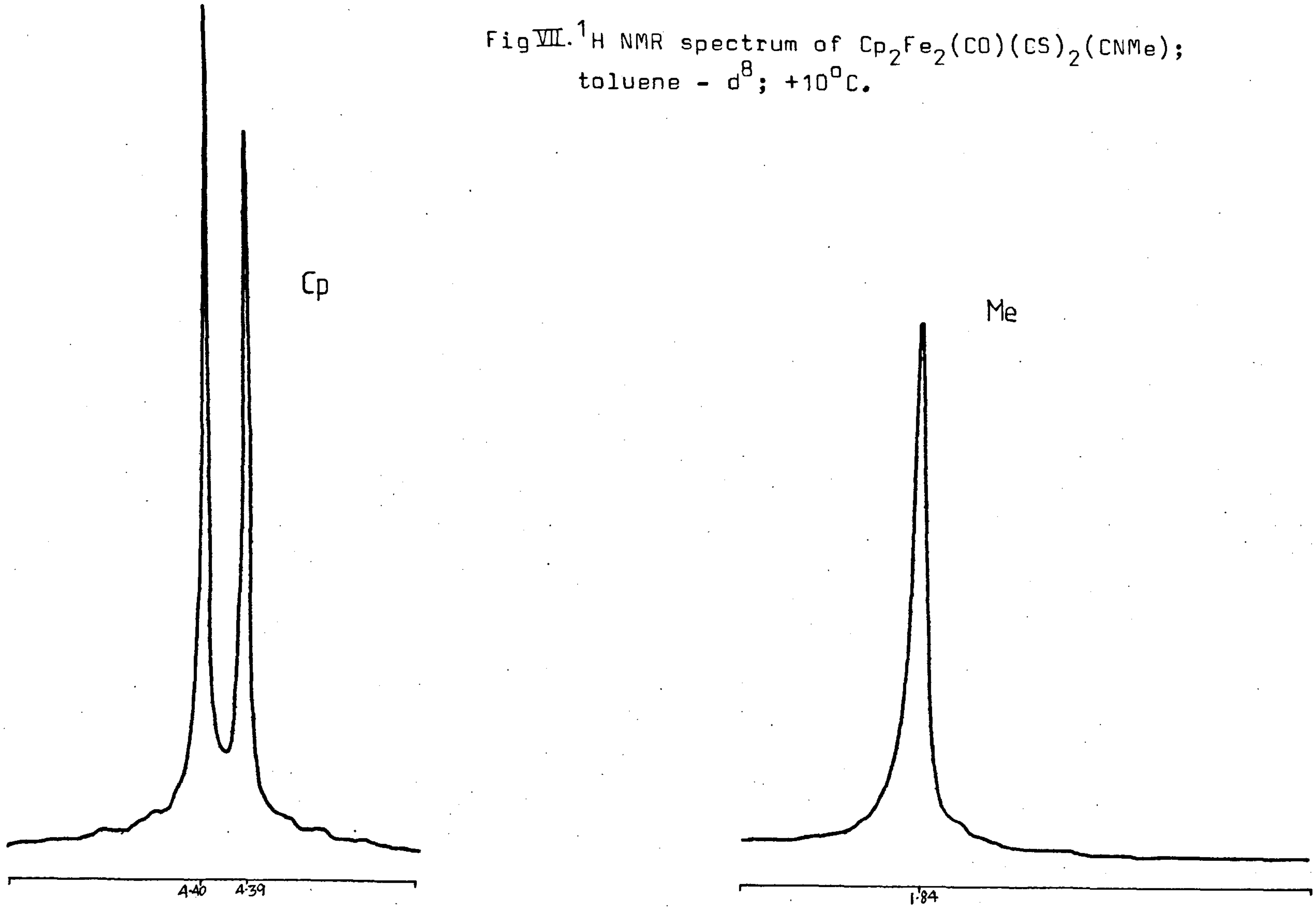


Fig VII. ^{1}H NMR spectrum of $Cp_2Fe_2(CO)(CS)_2(CNMe)$; toluene - d^8; +10°C.



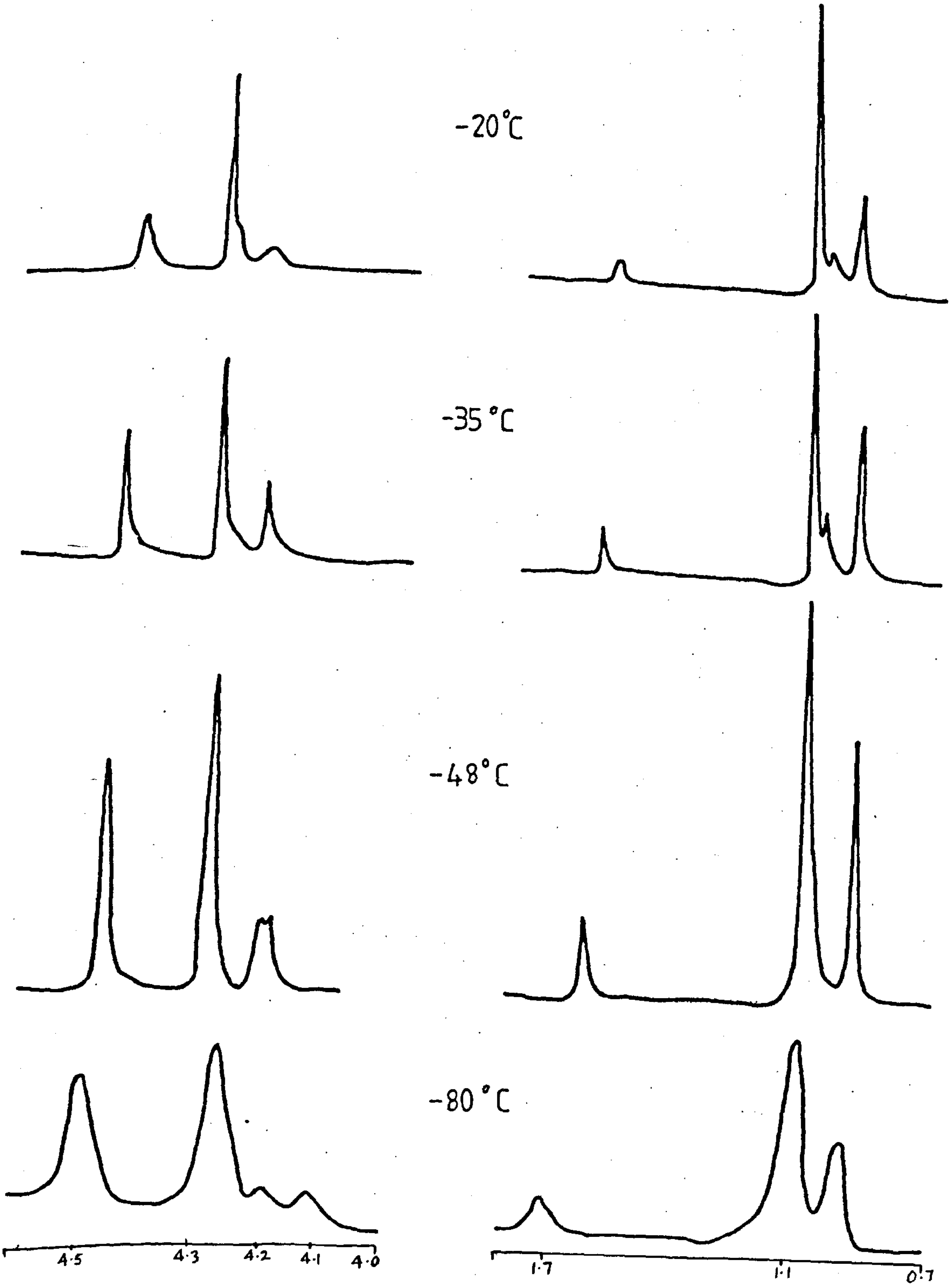


Fig VIII. ^{1}H NMR spectra of $Cp_2Fe_2(CO)_2(CNBu^t)_2$; toluene -d^8; Solvent peaks omitted.

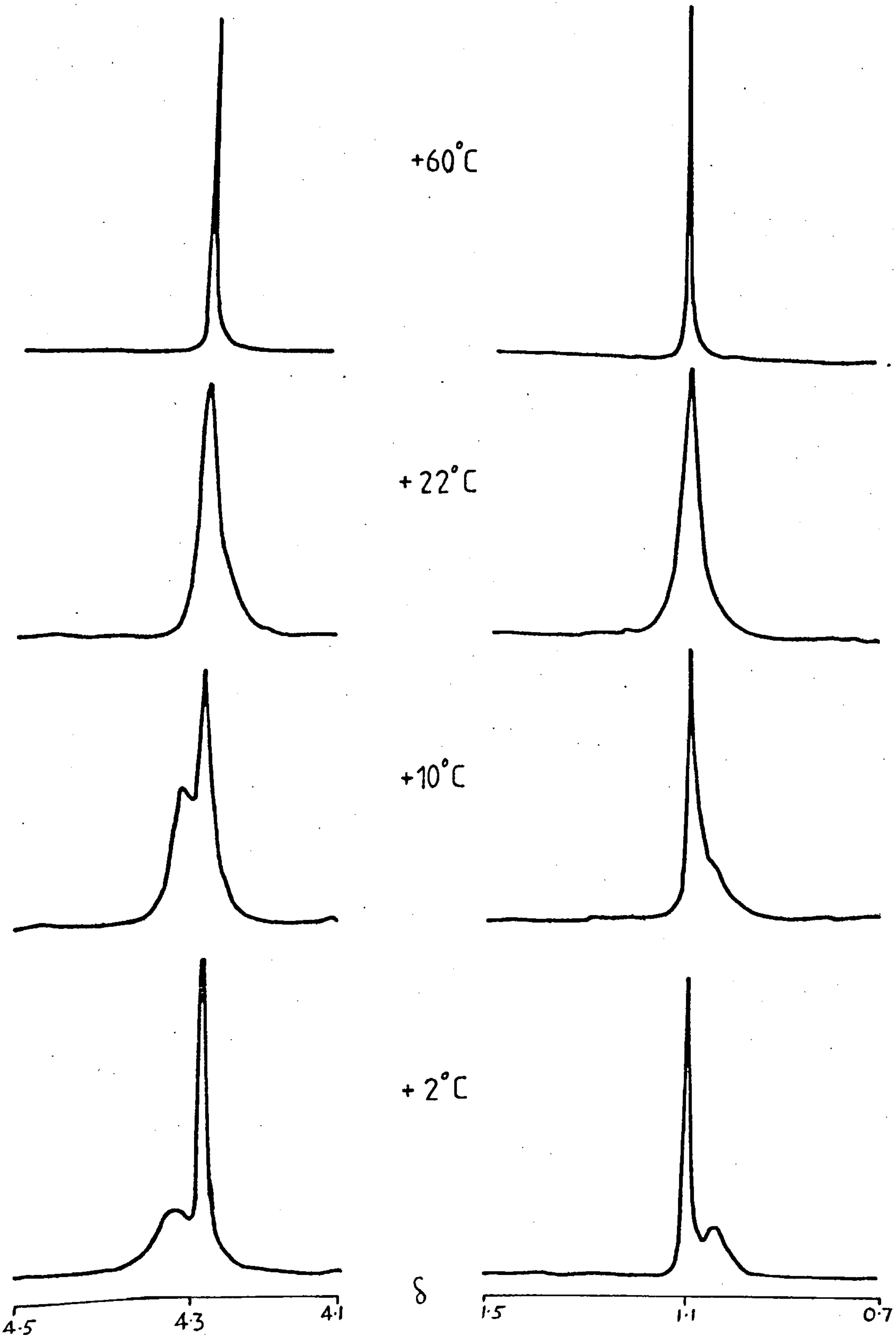


Fig VIII. cont'd.

FigIX. ^{13}C NMR spectrum of $Cp_2Fe_2(CO)_2(CNBu^t)_2$; CD_2Cl_2/CH_2Cl_2 , -20°C; proton decoupled.

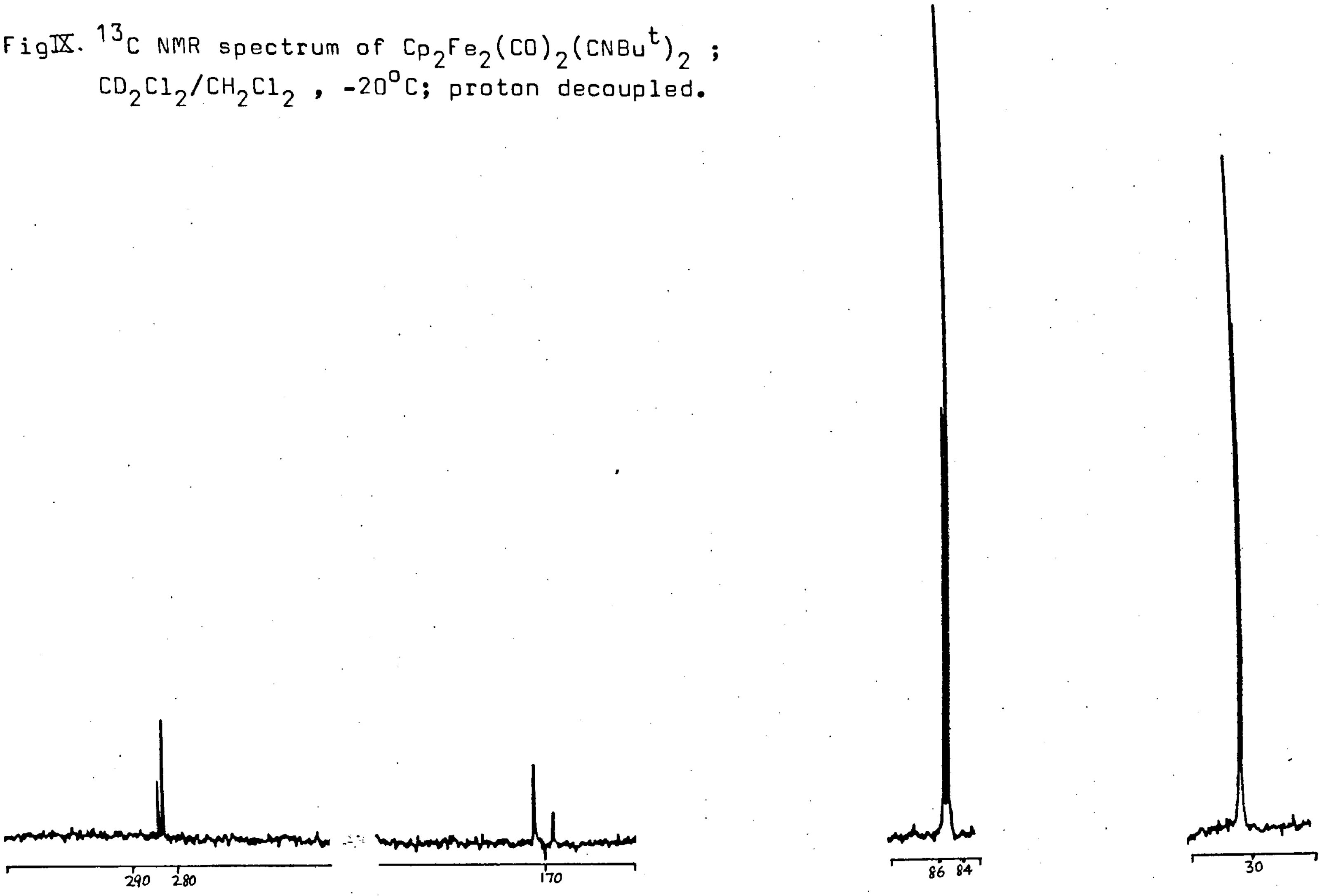
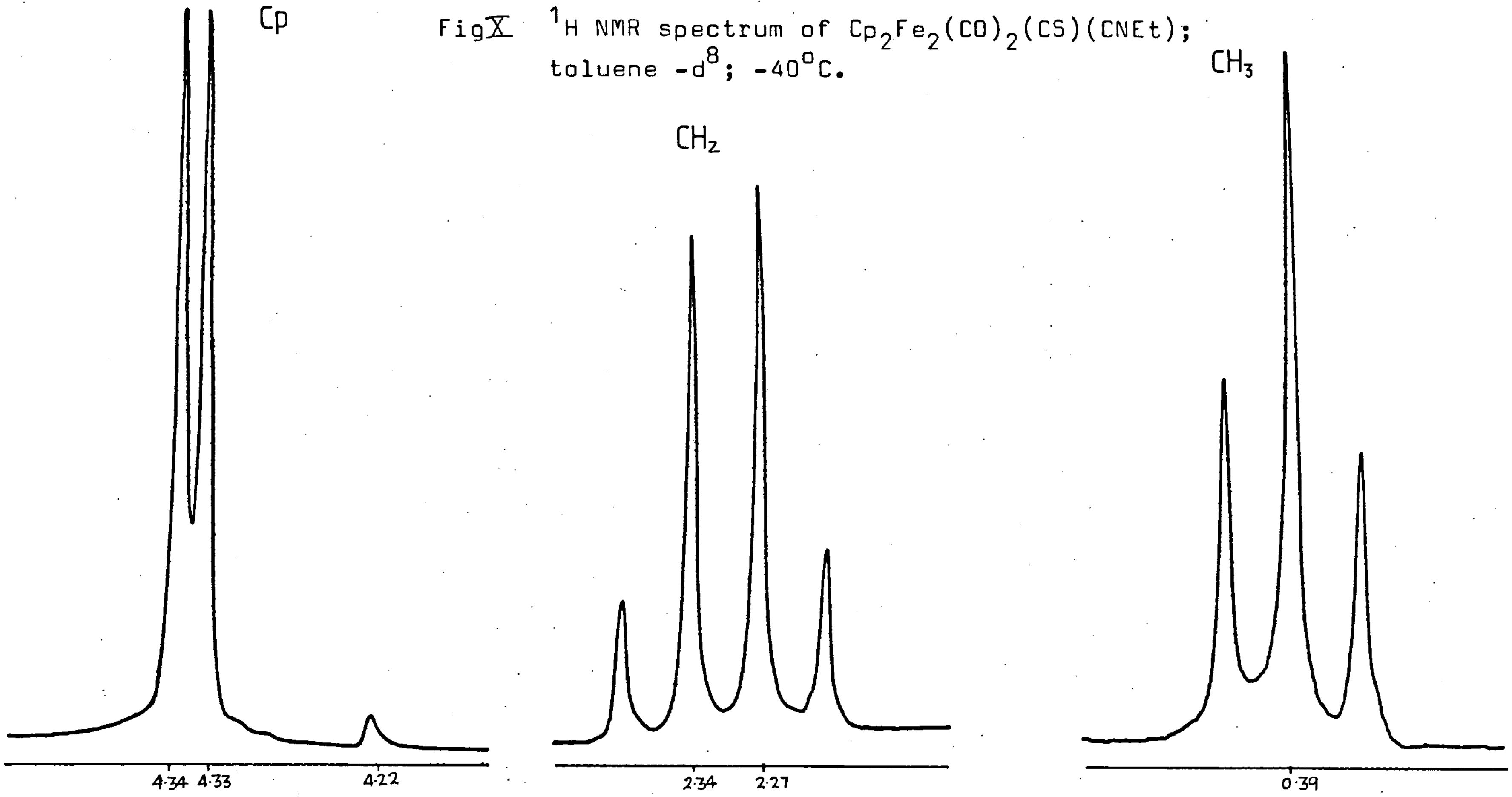


Fig X ^1H NMR spectrum of $Cp_2Fe_2(CO)_2(CS)(CNEt)$; toluene -d^8; -40°C.



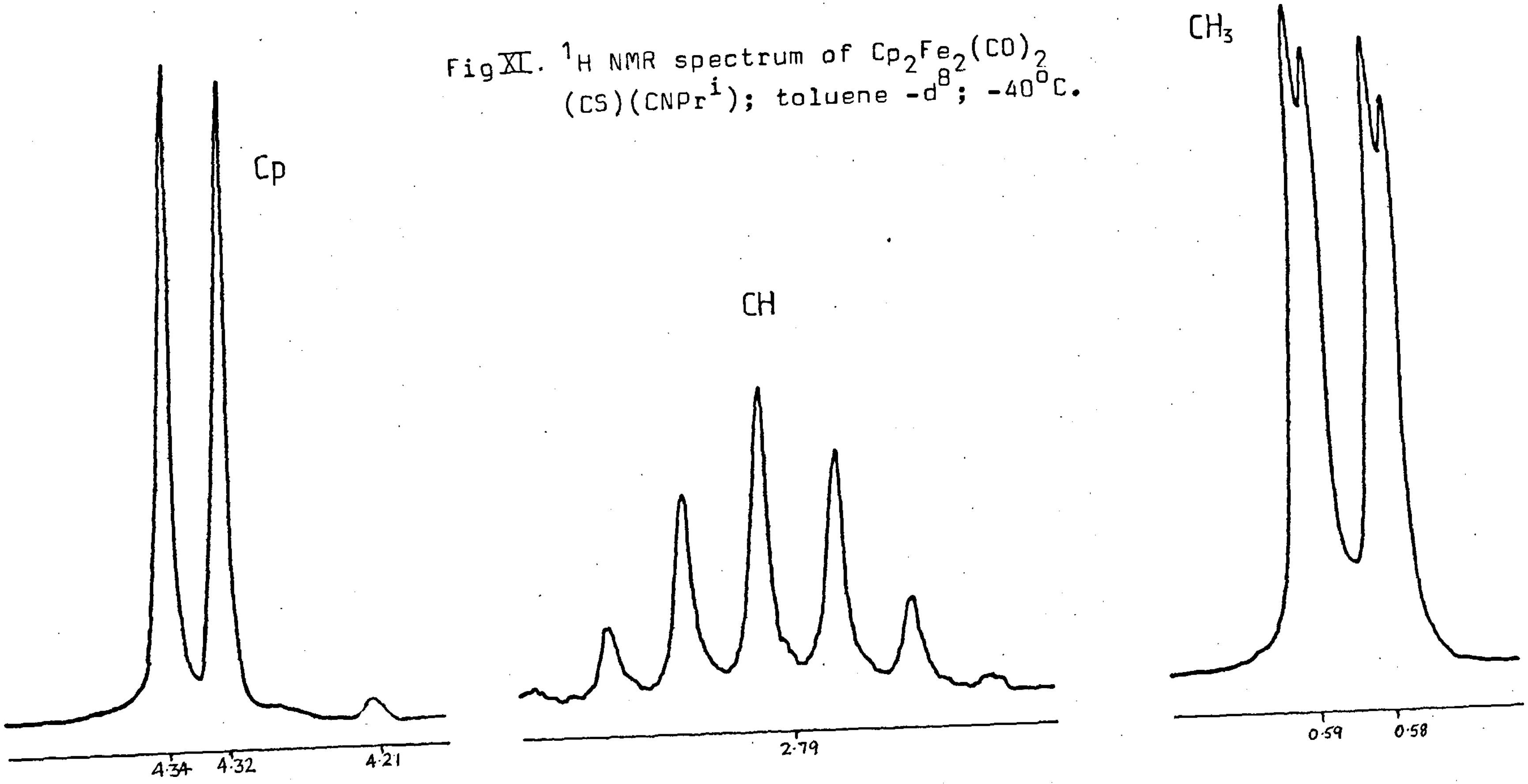


Fig XI. ^{1}H NMR spectrum of $Cp_2Fe_2(CO)_2(CS)(CNPr^i)$; toluene -d^8; -40°C.

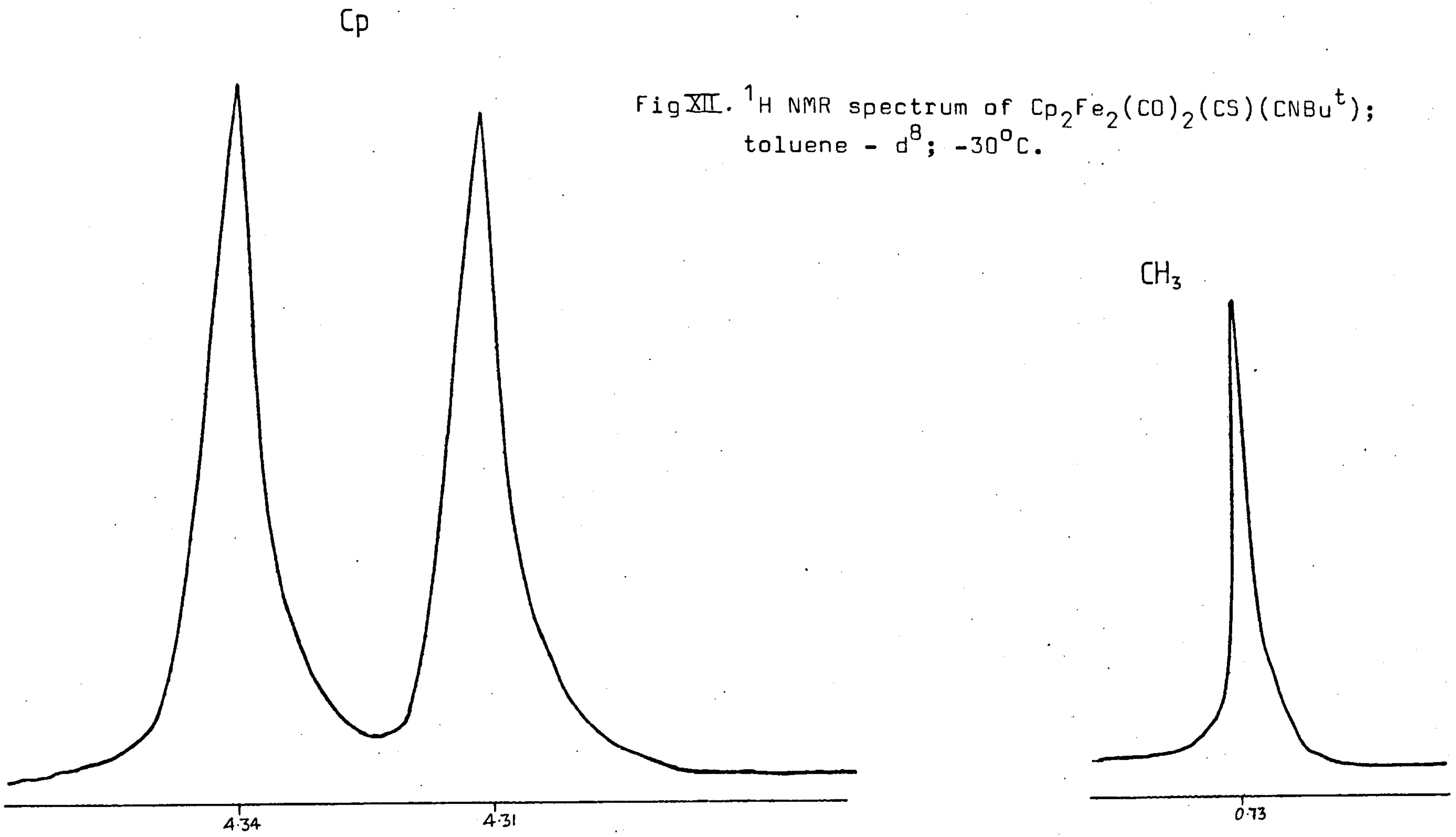


Fig XII. ^{1}H NMR spectrum of $Cp_2Fe_2(CO)_2(CS)(CNBu^t)$; toluene - d^8; -30°C.

Fig XIII. ^{13}C NMR spectrum of $Cp_2Fe_2(CO)_2(CS)(CNMe)$;
CD_2Cl_2/CH_2Cl_2, proton decoupled; 0°C.

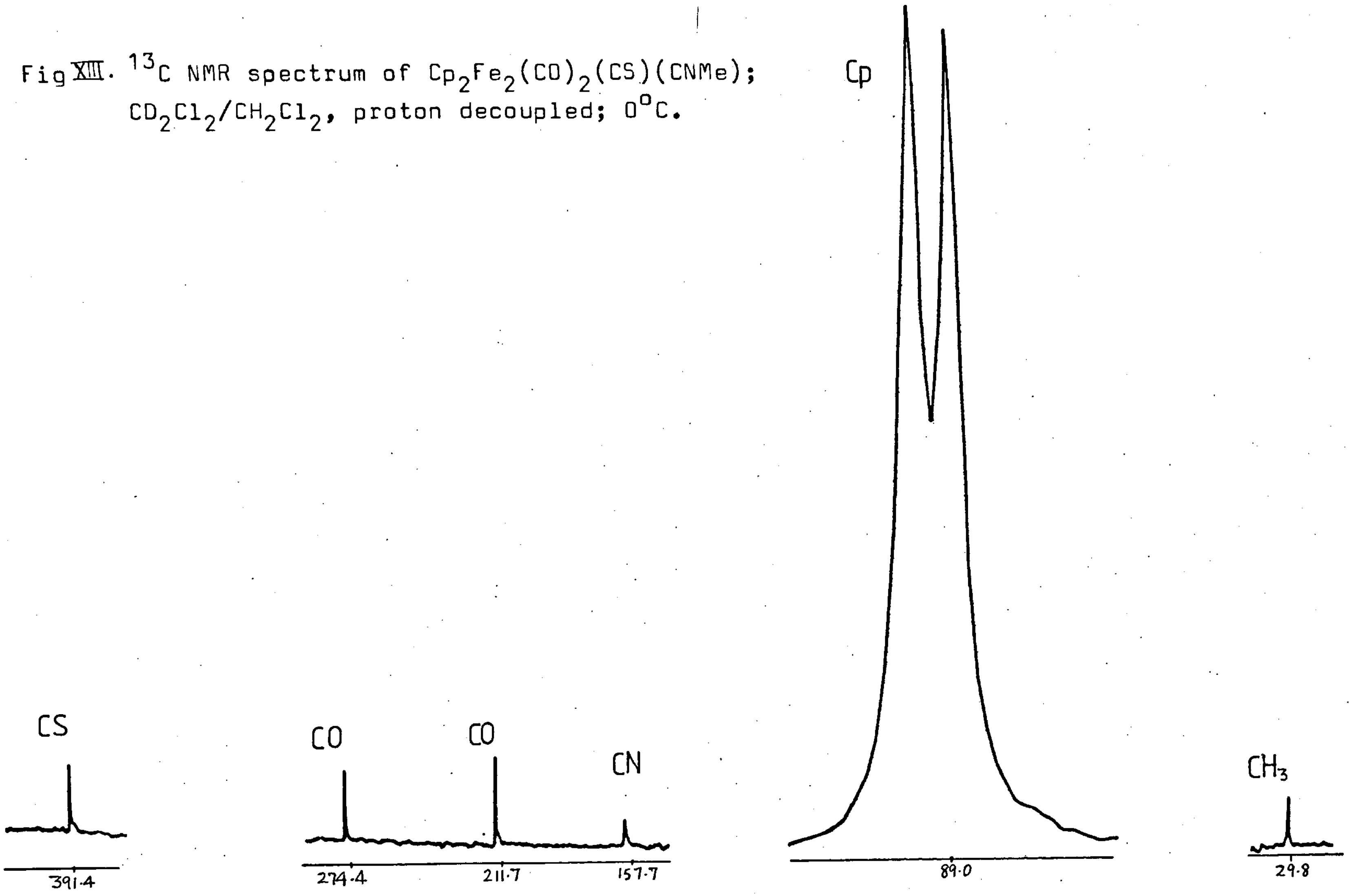


Fig XIV ^{13}C NMR spectrum of $Cp_2Fe_2(CO)_2(CS)(CNEt)$; CD_2Cl_2/CH_2Cl_2; proton decoupled; 0^oC.

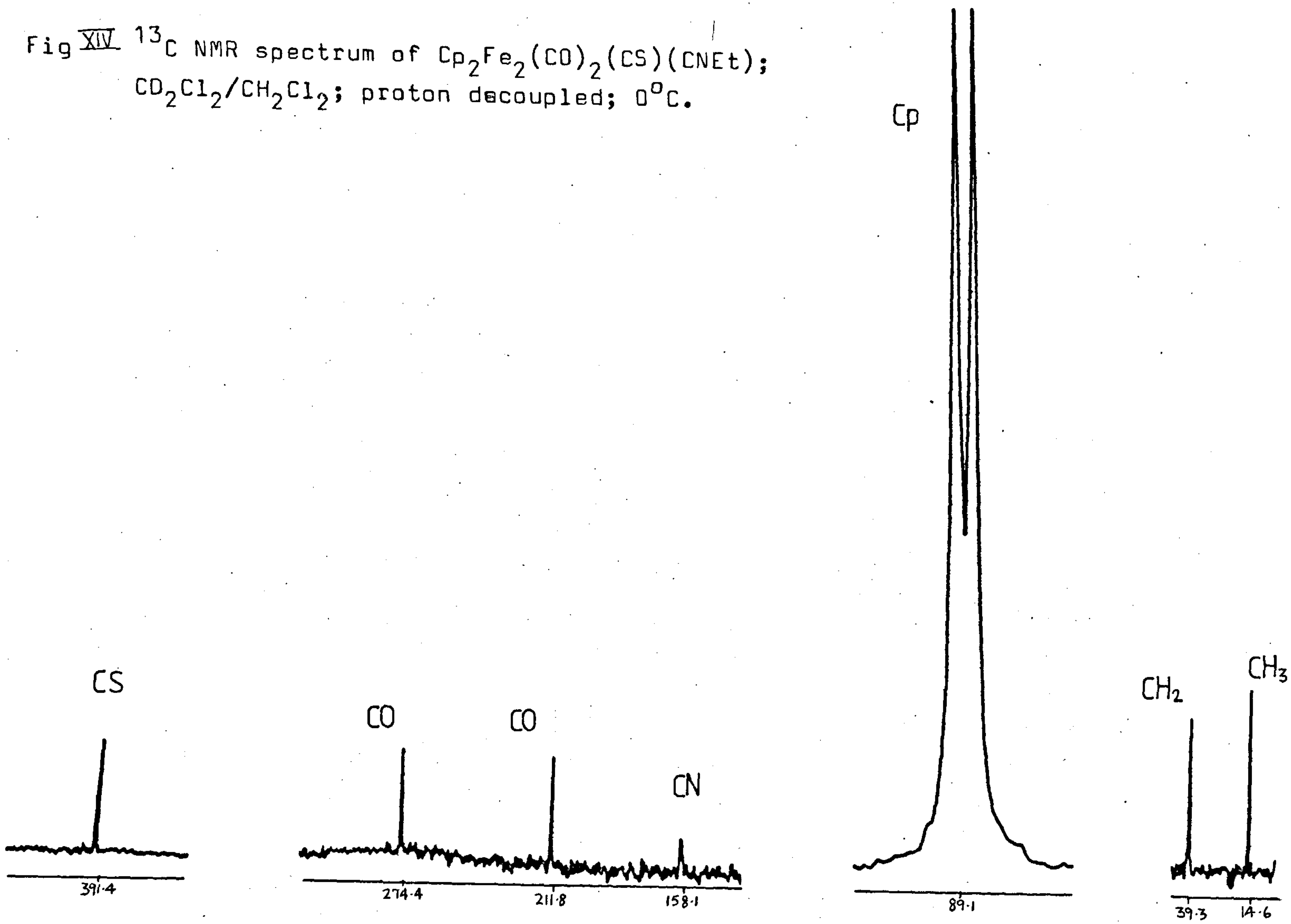


Fig XV. ^{13}C NMR spectrum of $Cp_2Fe_2(CO)_2(CS)(CNPr^i)$; CD_2Cl_2; proton decoupled; 0°C.

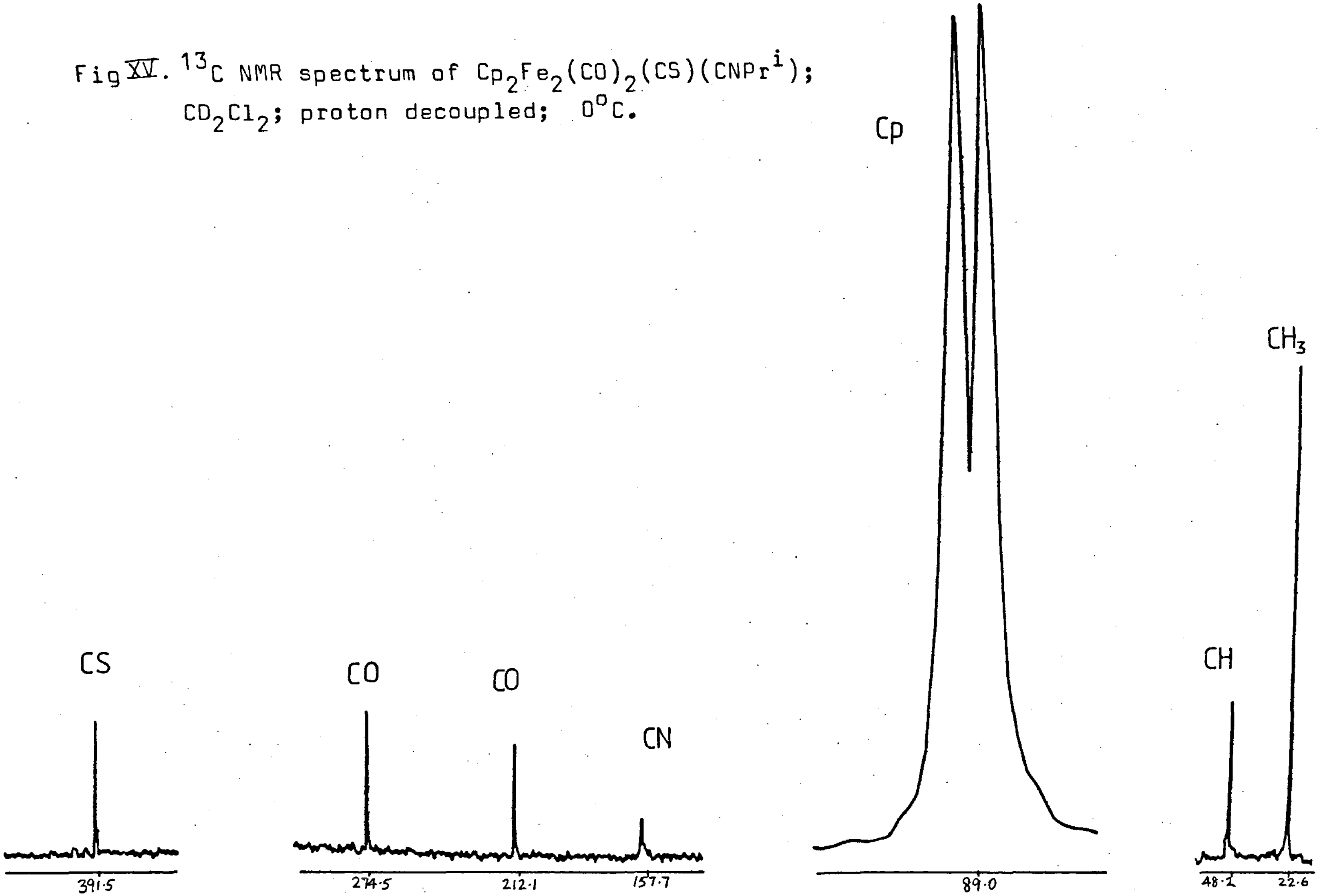


Fig XVI. ^{13}C NMR spectrum of $Cp_2Fe_2(CO)_2(CNBu^t)(CS)$; CD_2Cl_2/CH_2Cl_2; proton decoupled; 0°C.

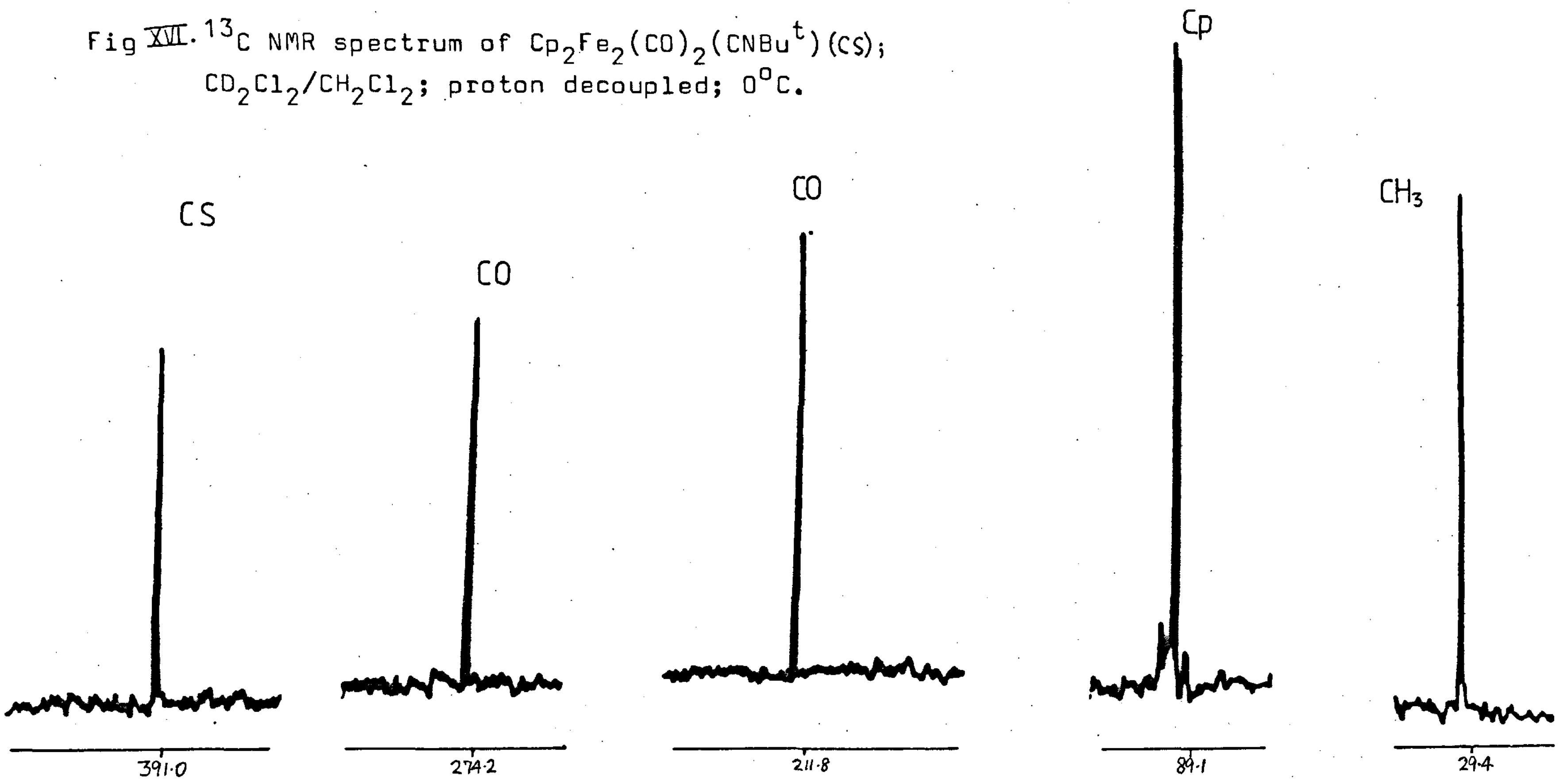
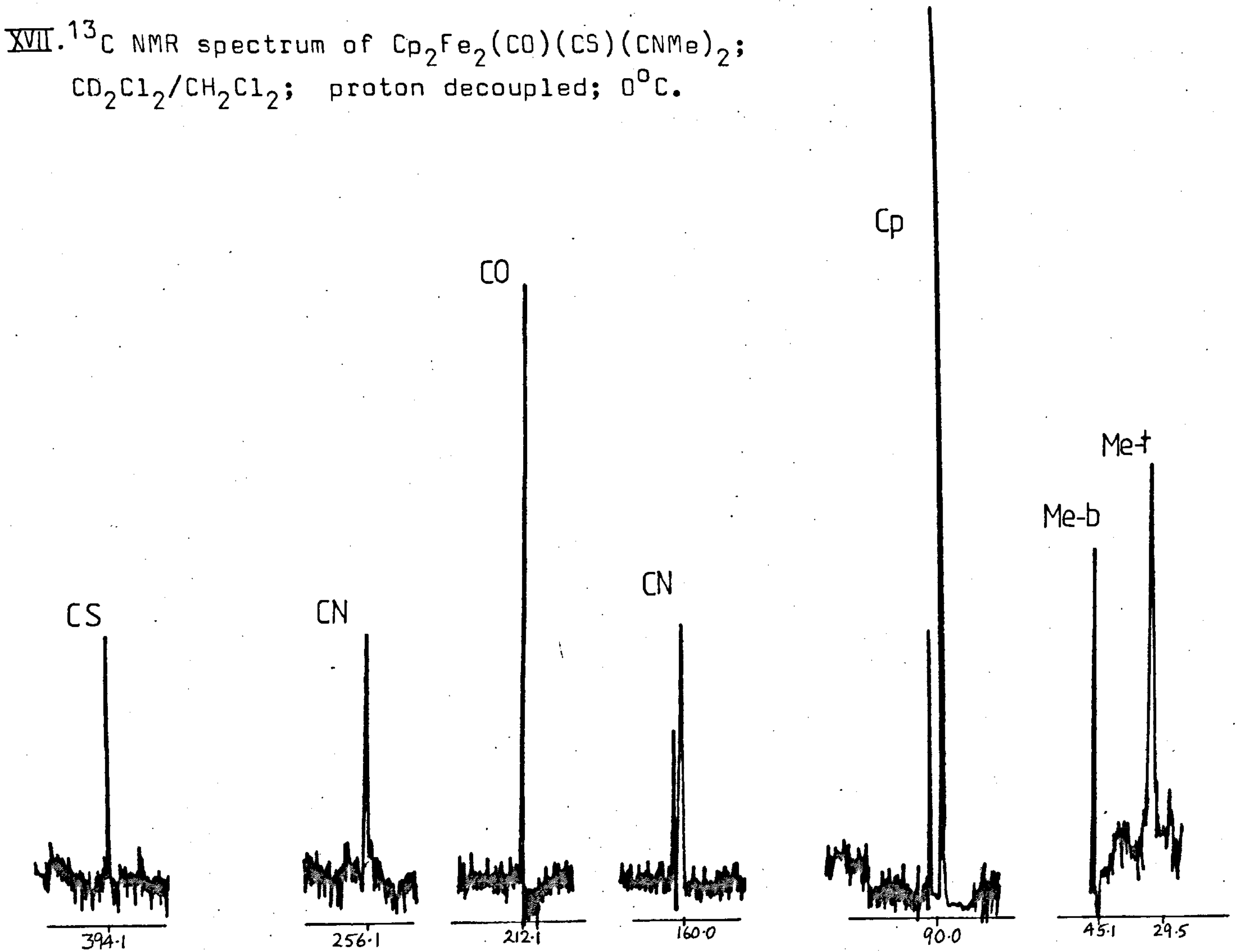


Fig XVII. ^{13}C NMR spectrum of $Cp_2Fe_2(CO)(CS)(CNMe)_2$; CD_2Cl_2/CH_2Cl_2; proton decoupled; 0^oC.

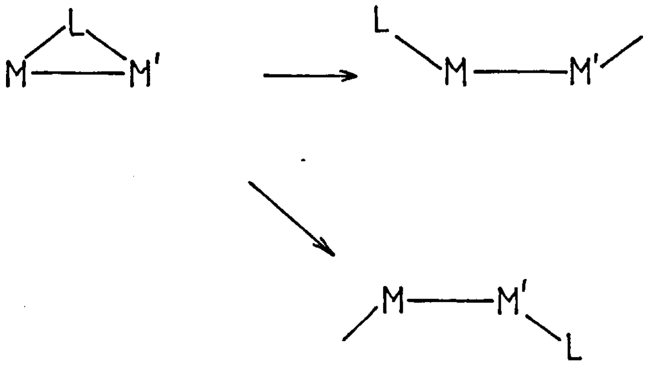


CHAPTER 3

ATTEMPTED PREPARATION OF ISONITRILE SUBSTITUTED HETEROMETALLIC COMPLEXES

I Introduction

As a continuing programme of our work on isonitrile derivatives of metal carbonyls, we have attempted the preparation of heterodimetallic carbonyl complexes in which at least one carbonyl group has been replaced by an isonitrile group. Isonitrile substitution is known to influence the structure that is adopted by a complex. For instance, whereas $Cp_2Ru_2(CO)_4$ exists in solution as a mixture of bridged and non-bridged isomers, the substituted derivative $Cp_2Ru_2(CO)_3(CNR)$ exists solely in the bridged form[1]. Thus, there exists a possibility that upon isonitrile substitution, the structure of heterodimetallic complexes may also be modified. The study of the fluxional behaviour of the isonitrile derivatives of such complexes is also of interest. Scheme I shows how for a mixed metal complex with a bridging isonitrile ligand, there exists a possibility for the formation of two different intermediates on bridge opening, depending on which pair of bonds are cleaved.



Scheme 1 .

It is of interest to study the position of isonitrile substitution. When the isonitrile is terminally bonded it may bond to either of the two different metals and thus, there arises a possibility to obtain information between exchange processes which may not be available from homometallic systems.

The first binuclear carbonyl complex with two different transition metals, $Cp(CO)_3MoW(CO)_3Cp$, was prepared by the reaction of sodium salt of tricarbonylcyclopentadienylmolybdenum with tricarbonylcyclopentadienyltungsten iodide[10]. In this case the two $CpM(CO)_3$ moieties are held together solely by a metal metal bond. The heteronuclear complex, $CpNi(CO)_2Fe(CO)Cp$, which has been prepared by reacting ironpentacarbonyl with nickelocene has two bridging and one terminal carbonyls (Fig. 1)[2-4].

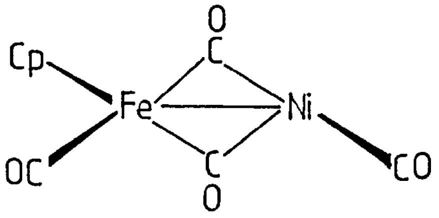


Fig. 1 . $Cp(CO)Fe(CO)_2NiCp$.

The heteronuclear complexes $Cp(CO)_2MCo(CO)_4$ (M = Fe, Ru) have been prepared from the reaction of $CpM(CO)_2I$ with $Co(CO)_4^-$ anion.

It has been reported that while $CpFeCo(CO)_6$ possesses bridging carbonyls, $CpRuCo(CO)_6$ does not[5,6]. In the solid state, infrared spectral studies have shown that only carbonyl-bridged isomers of $CpFeCo(CO)_6$ exist whereas two bridged and one non-bridged isomers probably coexist in solution (Fig. 2). Only a single non-bridged isomer of $CpRuCo(CO)_6$ has been detected.

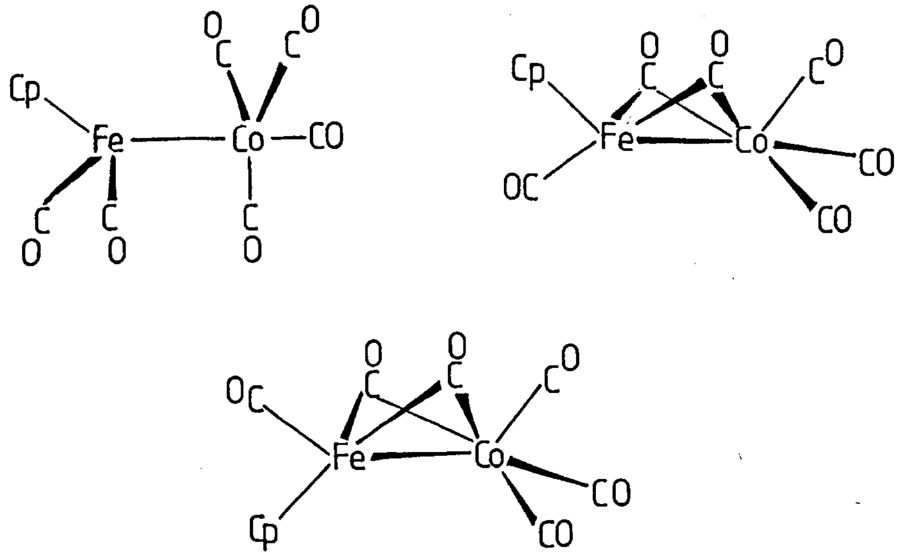


Fig. 2. Possible isomers of $CpFeCo(CO)_6$

An analogous method has been used for the synthesis of $Cp(CO)_3MFe(CO)_2Cp$ (M = Mo, W)[7,8]. Thus, the reaction of $CpFe(CO)_2I$ with $CpM(CO)_3^-$ yields the heterodinuclear complex, the infrared spectrum of which does not show any bridging carbonyl bands. It is interesting to note that a much lower yield of $Cp(CO)_3WFe(CO)_2Cp$ is obtained from the reaction of $CpFe(CO)_2^-$ with $CpW(CO)_3I$. Recently, $Cp(CO)_3MoFe(CO)_2Cp$ has been obtained from the photolysis of a mixture of $Cp_2Mo_2(CO)_6$ and $Cp_2Fe_2(CO)_4$ [9a].

Very recently, it has been reported that several heterometallic complexes are formed in solution from mixtures of the corresponding homometallic dimers. The reactions lead to equilibrium mixtures of the homometallic dimers and the heterometallic complexes[9b].

II Discussion

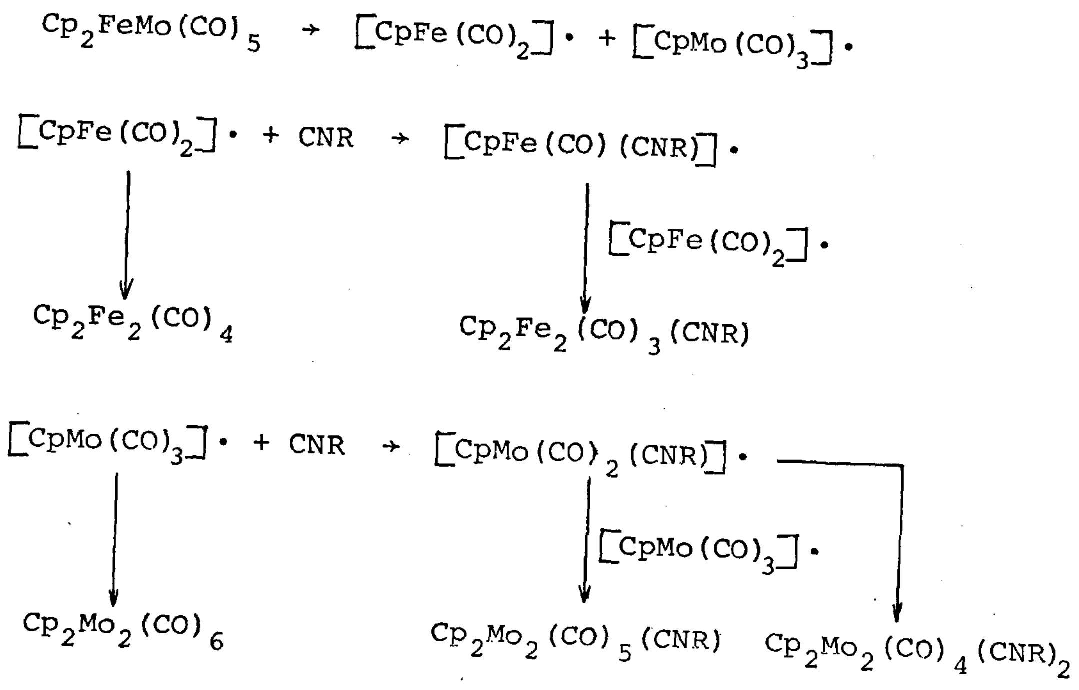
a) Direct Substitution of MM^1 dimers.

The heterodimetallic complexes, $Cp_2FeMo(CO)_5$ (1), $Cp_2FeNi(CO)_3$ (2) and $CpFeCo(CO)_6$ (3) were prepared by methods described in the literature[5,6,7]. Their reactions with isonitriles were carried out by stirring the complexes with 3 - 4-fold excess of the appropriate isonitrile at room temperature. The reactions were monitored by infrared spectroscopy and in general most of the starting material had reacted after 2-4 hours. Thus, the reaction of (1) with an excess of Pr^iNC yielded $Cp_2Fe_2(CO)_4$ (23%) and $Cp_2Fe_2(CO)_3(CNPr^i)$ (33%), the percentage yields being calculated on the basis of iron present in (1). A trace of $Cp_2Mo_2(CO)_6$ was also identified. However, during chromatography of the reaction mixture, a distinct red band decomposed prior to its collection. On the basis of the colour and the retention time, the red band most probably corresponds to a complex of the type $Cp_2Mo_2(CO)_{6-n}(CNPr^i)_n$. The reaction of (2) with an excess of Pr^iNC yielded, after chromatography of the reaction mixture, $Cp_2Ni_2(CO)_2$ (31%), $Cp_2Fe_2(CO)_4$ (33%) and $Cp_2Fe_2(CO)_3(CNPr^i)$ (23%). The reaction of (3) with an excess of Bu^tNC gave, after chromatography, $Cp_2Fe_2(CO)_4$ (27%), $Cp_2Fe_2(CO)_3(CNBu^t)$ (14%) and a trace of $Co_2(CO)_8$, most of which decomposed on the chromatography column. In addition, there was a fourth, red band which also decomposed before it could be identified.

The identifications of the complexes obtained from the above mentioned reactions are based on comparison of the infrared spectra of the products obtained with those of authentic samples prepared by literature methods (see Table 2).

All three reactions described above were accompanied by some decomposition and no heterometallic complexes could be isolated at the end of the reaction. It may also be noted that on standing in solution, unsubstituted heterodimetallic complexes undergo decomposition over a period of hours to form the homometallic dimers. Of the three complexes (1) to (3), the most unstable is complex (3), which starts to decompose in solution over a period of 1-2 hours to form $Co_2(CO)_8$ and $Cp_2Fe_2(CO)_4$.

The most probable mechanism which may account for the formation of the complexes obtained is that involving the generation of free radicals. Homolytic fission of metal-metal bonds in dimetallic species is not an unknown phenomenon. For instance, the photolytic substitution reaction of $Cp_2Fe_2(CO)_4$ with $P(OMe)_3$ to give $Cp_2Fe_2(CO)_2\{P(OMe)_3\}_2$ is reported to involve the formation of $[CpFe(CO)_2]^{\cdot}$ radicals, which undergo CO substitution prior to recombination[11a]. However, the photolytic reactions of $Cp_2Fe_2(CO)_4$ with $P(OPr^i)_3$ gives the monosubstituted $Cp_2Fe_2(CO)_3P(OPr^i)_3$, and the reaction has been proposed to proceed via a binuclear intermediate in which one of the iron atoms is a 16-electron centre[11b]. Recently, it has been reported that heterometallic complexes of the type $Cp_2FeM(CO)_5$ and $CpMCo(CO)_7$ (M = Mo, W) may be prepared by photolysing a solution of $Cp_2Fe_2(CO)_4$ with $Cp_2M_2(CO)_6$ or $Co_2(CO)_8$ with $Cp_2M_2(CO)_6$ [9]. Here too, it has been suggested that the reaction proceeds by formation of radicals, which on non geminate combination give the heterodimetallic complexes. Thus, in the case of the reaction of (1) with Pr^iNC, the possible pathways that take place are outlined in Scheme 2 .



Scheme 2 .

It has been demonstrated that there is an enhanced lability of 17 electron species towards carbonyl substitution[20,21]. This accounts for the formation of the monosubstituted $Cp_2Fe_2(CO)_3(CNR)$ from combination of $[CpFe(CO)_2]\cdot$ and $[CpFe(CO)(CNR)]\cdot$ radicals. The room temperature reaction between $Cp_2Fe_2(CO)_4$ and isonitrile yields only a very small trace of the $Cp_2Fe_2(CO)_3(CNR)$.

b) Reactions of the type $L_xM^- + L_yM^1(CNR)X$

Very recently, Manning[22] has reported the preparation of various $CpNiCo(CO)_4L$ (L = tertiary phosphine) type of complexes from the reactions of CpNi(L)Br with $[Co(CO)_4]Na$. During these reactions, the ligand L migrates from Ni to Co, and the compounds in solution exist as an equilibrium mixture of bridged and nonbridged isomers. It has been shown that at room temperature the interconversion of isomers is slow on the n.m.r. time scale.

An attempt was made in preparing $Cp_2FeMo(CO)_4(CNBu^t)$ by stirring at room temperature a THF solution of $CpFe(CO)(CNBu^t)I$ and $[CpMo(CO)_3]Na$. $CpFe(CO)(CNBu^t)I$ was prepared by the room temperature reaction of a chloroform solution of $Cp_2Fe_2(CO)_2(CNBu^t)_2$ with iodine while the anion $[CpMo(CO)_3]Na$ was prepared in situ by reduction of $Cp_2Mo_2(CO)_6$ with Na/Hg. There was considerable decomposition which made it difficult to identify the products being formed during the reaction. However, chromatography of the reaction yielded three products. Traces of $Cp_2Fe_2(CO)_4$ and $Cp_2Mo_2(CO)_6$ were eluted first off the chromatography column, and these were followed by the major product of the reaction, identified as $CpMo(CO)_2(CNBu^t)I$ [yield 33%, based on $Cp_2Mo_2(CO)_6$]. A similar yield of products was obtained from the analogous reaction of $CpFe(CO)(CNPr^i)I$ with $[CpMo(CO)_3]Na$. $CpFe(CO)(CNPr^i)I$ was prepared in the same way as $CpFe(CO)(CNBu^t)I$. The complexes $CpMo(CO)_2(CNR)I$ may also be obtained from the photochemical reaction of $CpMo(CO)_3I$ with a slight excess of the isonitrile and the infrared spectra of the products obtained from the photolysis are identical to those of the complexes obtained from the previously mentioned reactions. Thus, in both cases, the spectrum of $CpMo(CO)_2(CNPr^i)I$ in dichloromethane shows a CN stretching band at 2139 cm^{-1} with a shoulder at 2107 cm^{-1}. CO absorptions are found at 1983, 1935 and 1920 cm^{-1}.

The infrared spectrum of $CpMo(CO)_2(CNBu^t)I$ in dichloromethane shows bands at 2122, 1987 and 1915 cm^{-1} with a shoulder at 1921 cm^{-1}. If the complex is left standing in dichloromethane over a period of a few hours, the intensity of the band at 1987 cm^{-1} progressively increases until after 16 hours all three CO absorption bands are of approximately the same intensity. The ^1H n.m.r. spectrum of freshly prepared $CpMo(CO)_2(CNBu^t)I$ in $CDC\ell_3$ at room temperature shows a Cp resonance at δ 5.29 ppm and a $C(CH_3)_3$ resonance at δ 1.51 ppm. On leaving the solution to stand at room temperature over a period of hours, additional resonances at δ 5.42 ppm and 1.50 ppm are observed. This data is similar to that reported for $CpMo(CO)_2(CNBu^t)C\ell$, which has been prepared by photolysis of $CpMo(CO)_3C\ell$ and $CNBu^t$ [23]. It has been reported that the ^1H n.m.r. of this complex shows resonances at δ 5.27 and δ 1.49 ppm for the diagonal isomer and resonances at δ 5.47 and δ 1.55 ppm for the lateral isomer (Fig. 3).

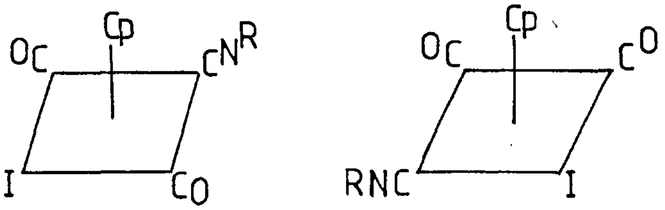
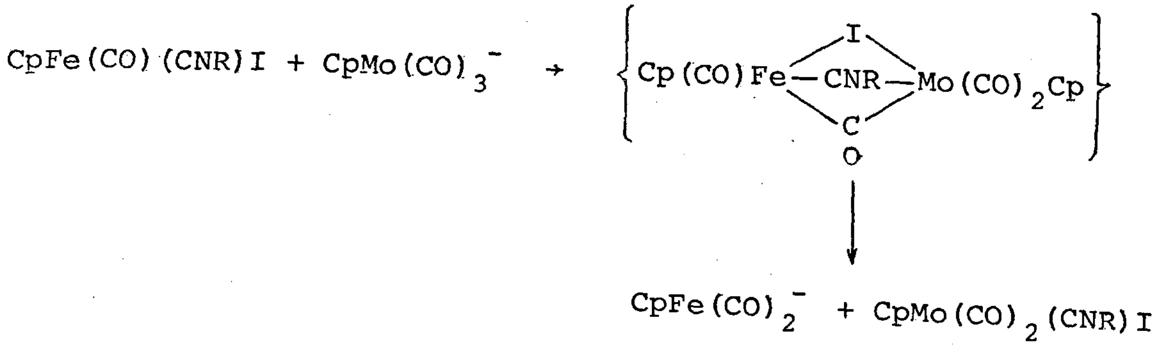


Fig. 3.

Thus, initially it is the diagonal isomer which is formed in the reaction of $CpMo(CO)_3I$ with $CNBu^t$ and after a period of a few hours in solution, an equilibrium mixture of both the diagonal and lateral isomers is obtained. From the heights of the Cp resonances after 16 hours, the ratio of lateral: diagonal isomers of $CpMo(CO)_2(CNBu^t)I$ is calculated to be 7.5:4.

The formation of $CpMo(CO)_2(CNR)I$ from the reaction of $CpFe(CO)(CNR)I$ with $CpMo(CO)_3^-$ may be explained by a mechanism involving electron transfer accompanied by CNR and I transfer as well via an intermediate of the type shown in Scheme 3.



$$\mathrm{CpFe(CO)(CNR)I} + \mathrm{CpMo(CO)_3^-} \rightarrow \left\{\mathrm{Cp(CO)Fe}\overset{\mathrm{I}}{\underset{\mathrm{CO}}{\text{—CNR—}}}\mathrm{Mo(CO)_2Cp}\right\} \rightarrow \mathrm{CpFe(CO)_2^-} + \mathrm{CpMo(CO)_2(CNR)I}$$

Scheme 3.

The reaction of $\mathrm{CpFe(CO)(CNBu^t)I}$ with $[\mathrm{Co(CO)_4}]\mathrm{Na}$ similarly did not yield any heterometallic complexes; the only products obtained after chromatography were $\mathrm{Cp_2Fe_2(CO)_4}$ (22%), $\mathrm{Cp_2Fe_2(CO)_3(CNBu^t)}$ (17%), $\mathrm{Cp_2Fe_2(CO)_2(CNBu^t)_2}$ (7%) and $\mathrm{Co_2(CO)_8}$ (18%). These were identified by comparison of their infrared spectra with those of authentic samples. There was considerable decomposition during the reaction and this may explain the non-isolation of $\mathrm{Co(CO)_3(CNBu^t)I}$, which would be expected to be formed on the basis of the mechanism outlined in Scheme 4. The formation of the substituted complexes, $\mathrm{Cp_2Fe_2(CO)_3(CNBu^t)}$ and $\mathrm{Cp_2Fe_2(CO)_2(CNBu^t)_2}$ may be explained by a mechanism involving only charge transfer without any ligand transfer between the two metals as well as that involving a transfer of ligands as shown below:

(i) With CNR, I transfer:

$$\begin{tikzcd}[column sep=small] \mathrm{CpFe(CO)(CNR)I} + \mathrm{Co(CO)_4^-} \arrow[r] & \mathrm{Co(CO)_3(CNR)I} + \mathrm{CpFe(CO)_2^-} \arrow[d, "\text{oxidation}"] \\ & \mathrm{Cp_2Fe_2(CO)_4} \end{tikzcd}$$

$$\mathrm{CpFe(CO)(CNR)I} + \mathrm{CpFe(CO)_2^-} \rightarrow \mathrm{Cp_2Fe_2(CO)_3(CNR)}$$

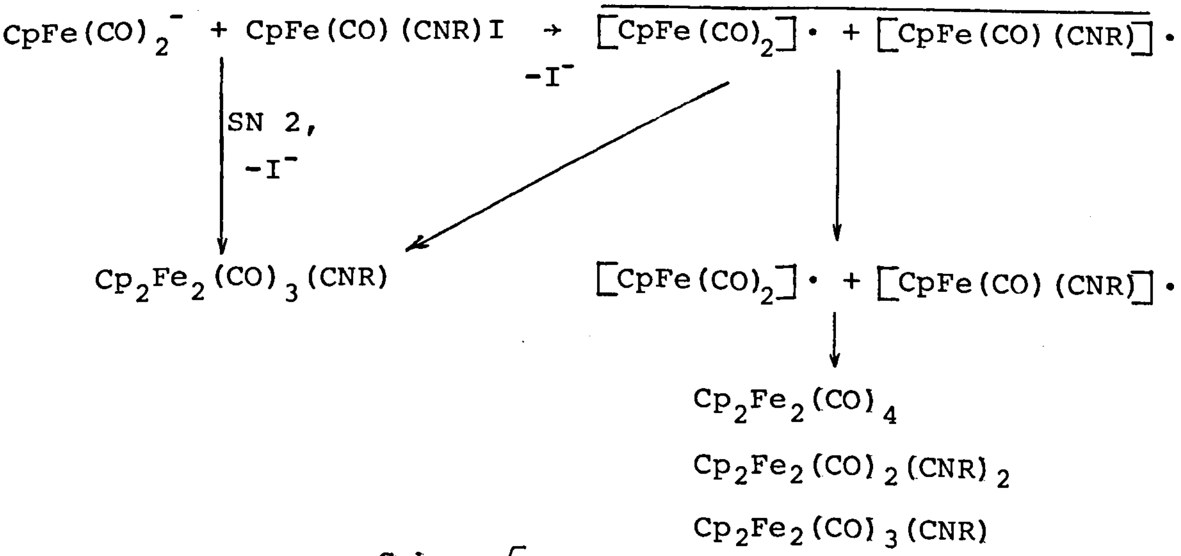
(ii) With CO, I transfer or no ligand transfer

$$CpFe(CO)(CNR)I + Co(CO)_4^- \rightarrow CpFe(CO)(CNR)^- + Co(CO)_4I$$

$$CpFe(CO)(CNR)I + CpFe(CO)(CNR)^- \rightarrow Cp_2Fe_2(CO)_2(CNR)_2 .$$

Scheme 4.

In order to further investigate the unexpected behaviour in the above reactions, $[CpFe(CO)_2]Na$ was treated with a series of $CpFe(CO)(CNR)X$ (4a-d, R = Bu^t, Pr^i, Et, X = I; R = Bu^t, X = Br) complexes. The products and yields obtained from these reactions are summarised in Table I . Although the expected dimetallic species, $Cp_2Fe_2(CO)_3(CNR)$ was obtained as the major product in each case, smaller amounts of the unsubstituted and disubstituted complexes were also isolated. In addition to the SN 2 displacement reaction to form $Cp_2Fe_2(CO)_3(CNR)$, it is evident that there must be at least one other competing pathway by which the other two complexes are formed. One such reaction is that involving an initial one electron transfer, followed by geminate and/or non-geminate radical combination steps (Scheme 5).



Scheme 5.

It is also possible that an electron and ligand transfer reaction, followed by a radical chain process, may occur as shown in Scheme 6 . The step involving CNR and I^- transfer has been omitted since that only regenerates the starting species.

(i) With CO, I transfer or no ligand transfer:

$$CpFe(CO)(CNR)I + CpFe(CO)_2^- \rightarrow CpFe(CO)(CNR)^- + CpFe(CO)_2I$$

$$Cp_2Fe_2(CO)_3(CNR)$$

(ii) Radical formation:

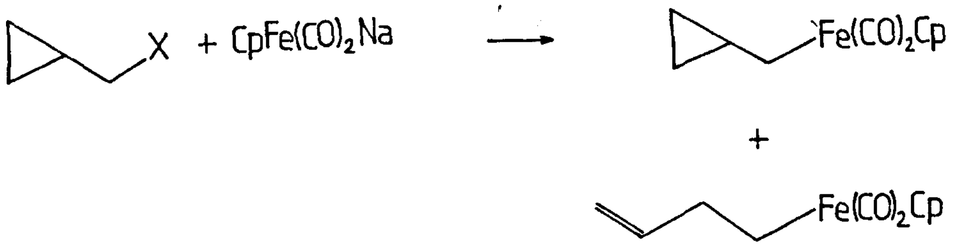
$$CpFe(CO)(CNR)^- + CpFe(CO)_2I \xrightarrow[-I^-]{} [CpFe(CO)(CNR)]\cdot + [CpFe(CO)]\cdot$$

$$Cp_2Fe_2(CO)_2(CNR)_2$$
$$Cp_2Fe_2(CO)_4$$
$$Cp_2Fe_2(CO)_3(CNR)$$

Scheme 6.

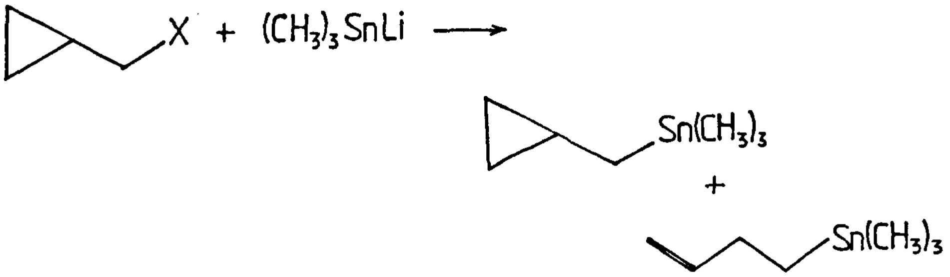
The stabilisation of the anion $CpFe(CO)(CNR)^-$ is dependent on efficient π back-bonding of the isonitrile ligands. Adams[24] has synthesised the anions $CpMo(CO)_{3-x}(CNMe)_x$ (x = 1,2) by Na/Hg reduction of the molecules $CpMo(CO)_{3-x}(CNMe)_xC\ell$ and demonstrated by infrared spectroscopy the extensive π back-bonding between the metal atom and the isonitrile ligands.

Observations similar to those mentioned have been reported on several other reactions. For instance, in the reaction of cyclopropylcarbinyl iodide with $CpFe(CO)_2^-$ to give cyclopropyl- and allylcarbinyl (cyclopentadienyl)(dicarbonyl) iron (Scheme 7), an ESR spectrum of allylcarbinyl radical is observed[12].



Scheme 7

In the reactions of lithium trimethyltin with cyclopropylcarbinyl halides, the formation of the rearranged product trimethyl (allylcarbinyl) tin is observed (Scheme 8).



Scheme 8.

It has been proposed that the two reactions cited above proceed by a pathway involving free radicals in addition to the SN 2 displacement reaction. This is supported by the report that in some of the reactions of trialkyltin anions with alkyl halides, retention of configuration has been observed, the stereochemistry of the reaction being dependent on the nature of the solvent and the alkali metal counterion in R_3SnM [13].

It is possible that redistribution reactions might occur after a dinuclear compound has been formed. Thus,

$$M^- + M\text{-}M^1 \rightarrow M\text{-}M + M^{1-}$$

In such cases, the inverse addition of anions to halides (with the halide always in excess) may lead to quite different products than normal addition, where redistribution may occur readily (anion always in excess). However, for $CpFe(CO)_2^-$ + CpFe(CO)(CNR)X reactions, the same products were obtained in the case of both normal as well as inverse additions. There are numerous examples of heterodimetallic systems in which redistribution reactions are known to occur, and it has been shown that the anion expelled is the least nucleophilic of the two possible anions derivable from the parent complex. Thus, in the following systems,

$$L_xFe^- + L_yFe\text{-}MoL_z \rightarrow L_xFe\text{-}FeL_y + MoL_z^-$$

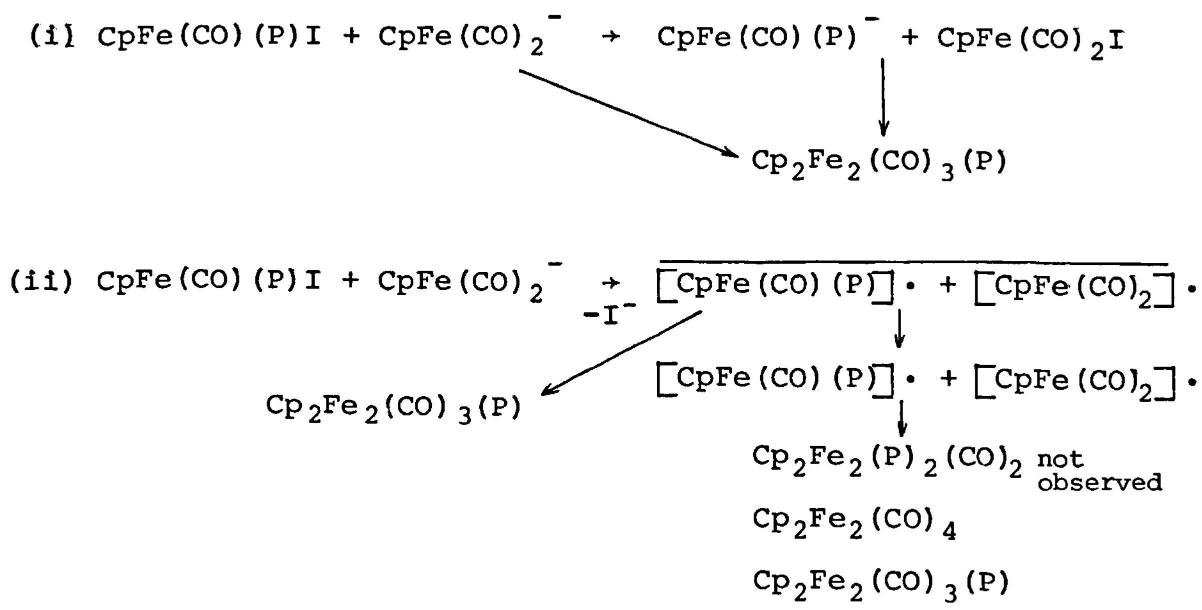
$$L_xFe^- + L_ySn\text{-}MoL_z \rightarrow L_xFe\text{-}SnL_y + MoL_z$$

the molybdenum anion has been shown to be the least nucleophilic of the three anions derivable[14].

c) Reactions of Type $L_xM^- + L_yM^1X(P)_z$ (P = phosphite)

Reactions of metallate anions with phosphite derivatives of $CpFe(CO)_2I$ were carried out to investigate whether here too there were additional pathways competing with the SN 2 displacement reaction. In a typical reaction, the phosphite derivative and the anion were stirred in THF at room temperature for 3 hours. The products formed were separated by chromatography and identified by infrared spectroscopy. As before, the identification was based on comparison of the spectra of the products obtained with those of authentic samples. Thus, the reaction of $CpFe(CO)P(OPh)_3I$ and

$[CpFe(CO)_2]Na$ gave $Cp_2Fe_2(CO)_4$ (55%) and $Cp_2Fe_2(CO)_3P(OPh)_3$ (11%). The reaction of $CpFe(CO)P(OMe)_3I$ with the anion similarly gave $Cp_2Fe_2(CO)_4$ (36%) and $Cp_2Fe_2(CO)_3P(OMe)_3$ (20%). The monosubstituted phosphite derivatives of the iron dimer have previously been isolated from the thermal reaction of $Cp_2Fe_2(CO)_4$ with a slight excess of the phosphites[15b]. In both of the reactions described above, the relatively high yields of $Cp_2Fe_2(CO)_4$ suggest that in addition to the SN 2 displacement reaction, there is at least one other competing mechanism. It should be noted that there is no spectroscopic evidence for the formation of the disubstituted complexes, $Cp_2Fe_2(CO)_2\{P(OR)_3\}_2$, in these reactions. The complex, $Cp_2Fe_2(CO)_2\{P(OMe)_3\}_2$, has previously been prepared by the photochemical reaction of $Cp_2Fe_2(CO)_4$ with $P(OMe)_3$ involving CO substitution of the $[CpFe(CO)_2]\cdot$ radicals, which are generated in the reaction[9]. Scheme 9 outlines the various routes by which the above reactions may proceed.



Scheme 9.

Combination of the caged radicals gives rise to the monosubstituted $Cp_2Fe_2(CO)_3(P)$, whereas after diffusion, geminate combination of $[CpFe(CO)_2]\cdot$ can explain the formation of $Cp_2Fe_2(CO)_4$. The $[CpFe(CO)(P)]\cdot$ radicals may be involved in a radical chain process of the type shown below:

$$[CpFe(CO)(P)]\cdot + CpFe(CO)_2^- \rightarrow CpFe(CO)(P)^- + [CpFe(CO)_2]\cdot$$

The reaction of $CpFe(CO)_2^-$ with the disubstituted, $CpFe\{P(OPh)_3\}_2I$ was carried out in the same manner as the reactions so far discussed. In addition to the $Cp_2Fe_2(CO)_4$ (18%) that was isolated, the tetrasubstituted complex, $Cp_2Fe_2\{P(OPh)_3\}_4$ (28%) was also obtained and characterised by infrared spectroscopy, which in nujol shows three intense absorptions at 1225, 1200 and 1180 cm^{-1}, characteristic of coordinated $P(OC_6H_5)_3$. Also, the spectrum shows no bands characteristic of the stretching vibration of carbonyl ligands. The spectrum is identical to that reported for the same complex which has also been prepared by the photochemical reaction of $CpFe(CO)_2Ph$ with $P(OPh)_3$ [16].

The isolation of $Cp_2Fe_2(CO)_4$ and $Cp_2Fe_2\{P(OPh)_3\}_4$ from the reaction may be explained by a charge transfer process which, if slow, may lead to the formation of the products observed, as shown in Scheme 10 .

$$CpFe(CO)_2^- + CpFe(P)_2I \rightarrow CpFe(CO)_2I + CpFe(P)_2^-$$

$$CpFe(CO)_2I + CpFe(CO)_2^- \rightarrow Cp_2Fe_2(CO)_4$$

$$CpFe(P)_2^- + CpFe(P)_2I \rightarrow Cp_2Fe_2(P)_4$$

Scheme 10.

The reaction of $CpFe\{P(OPh)_3\}_2I$ with $[CpMo(CO)_3]Na$ also yielded the tetrasubstituted $Cp_2Fe_2\{P(OPh)_3\}_4$ (57%) in addition to a trace of $Cp_2Fe_2(CO)_4$, $Cp_2Mo_2(CO)_6$ (19%) and $CpMo(CO)_3I$ (21%). There were at least two other products also formed in the reaction; these however decomposed on the chromatography column. From the red colour and retention time of the bands, they would appear to have been molybdenum derivatives of the type $Cp_2Mo_2(CO)_{6-n}(L)_n$. Scheme II describes the various pathways that may be occuring in this reaction.

$$CpFe(P)_2I + CpMo(CO)_3^- \rightarrow CpFe(P)_2^- + CpMo(CO)_3I$$

$$CpFe(P)_2^- + CpFe(P)_2I \rightarrow Cp_2Fe_2(P)_4$$

Scheme II.

The formation of a trace of $Cp_2Fe_2(CO)_4$ and complexes of the type $Cp_2Mo_2(CO)_{6-n}(P)_n$ may result from a charge transfer process accompanied by transfer of the phosphite ligands to form $CpFe(CO)_2^-$ and $CpMo(CO)(P)_2I$. Thus, the iron dimer may be formed as a result of the oxidation of $CpFe(CO)_2^-$, whereas the substituted molybdenum dimer may result from the reaction between $CpMo(CO)_3^-$ and $CpMo(CO)(P)_2I$.

The attempted preparation of a dimetallic complex containing both an isonitrile and a phosphite group was carried out by reacting $Cp_2Fe_2(CO)_3P(OPh)_3$ with an excess of Bu^tNC at room temperature. After 3 hours' stirring, infrared spectroscopy indicated that all of the starting material had reacted. The colour of the solution changed from reddish brown to a greenish brown. Chromatography of the reaction mixture gave a single green band of $Cp_2Fe_2(CO)_2(CNBu^t)_2$ (46% yield) as identified from its infrared spectrum[18]. Using a smaller excess of the isonitrile, the reaction yielded a trace of $Cp_2Fe_2(CO)_3(CNBu^t)$ in addition to the disubstituted complex. It is most probable that in these reactions the radicals $[CpFe(CO)_2]\cdot$ and $[CpFe(CO)P(OPh)_3]\cdot$ are generated. Such a process has previously been proposed for the reactions of $Cp_2Fe_2(CO)_3P(OR)_3$ (R = Me, Et) with an excess of the appropriate phosphite, which give a mixture of the phosphonate $[CpFe(CO)\{P(OR)_3\}\{P(O)(OR)_2\}]$ and acyl $[CpFe(CO)(COR)\{P(OR)_3\}]$ complexes[19].

Thus, it seems likely that once the radical species, $[CpFe(CO)_2]\cdot$ and $[CpFe(CO)P(OPh)_3]\cdot$, are formed, they undergo substitution of CO or $P(OPh)_3$ respectively in the presence of excess isonitrile to form $[CpFe(CO)(CNR)]\cdot$ species, which recombine to give the disubstituted complex.

In all of the reactions discussed in this Chapter, there is evidence for the existence of pathways other than the SN 2 displacement reactions. The tendency for the reactions to proceed via pathways involving free radicals is significant when one or more of the carbonyls of the reactants are substituted by isonitriles or phosphites.

Table 1.

Reaction of $[CpFe(CO)_2]Na$ with $CpFe(CO)(CNR)X$

		Products (Yields)[a]		
R	X	$Cp_2Fe_2(CO)_4$	$Cp_2Fe_2(CO)_3(CNR)$	$Cp_2Fe_2(CO)_2(CNR)_2$
Bu^t	I	4.3	31.9	3.5
Bu^t	Br	3.8	28.7	2.7
Pr^i	I	5.2	26.4	1.1
Et	I	2.3	28.7	2.1

Table 2.

Infrared Data (cm^{-1}). CO and CN region[a]

$Cp_2Fe_2(CO)_4$	2005 (s), 1961 (s), 1793 (s).
$Cp_2Fe_2(CO)_3(CNR)$	
R = Bu^t	2107, 2059, 1951 (s), 1771 (s).
Pr^i	2113, 2000 (s), 1955 (s), 1798 (m), 1775 (s), 1741 (w), 1711 (w).
Et	2123, 2099, 1995 (s), 1955 (s), 1797 (m), 1772 (s), 1737 (w).
$Cp_2Fe_2(CO)_2(CNR)_2$	
R = Bu^t	2099 (sh), 2055, 1955 (m), 1935 (m), 1779 (m), 1755 (s), 1715 (w).
Pr^i	2107, 2043 (br), 1985 (s), 1951 (m), 1940 (m), 1783 (s), 1730 (w), 1725 (w), 1699 (m), 1695 (m).
Et	2127 (br), 2103 (br), 1991 (s), 1955 (s), 1043 (s), 1798 (m), 1787 (s), 1728 (s), 1690 (br), 1641 (w).
$CpFe(CO)_2I$	2040 (s), 1996 (s).
$CpFe(CO)(CNR)I$	
R = Bu^t	2125, 1987 (s).
Pr^i	2031, 1987 (s).
Et	2034, 1989 (s).
$CpFe(CO)(CNBu^t)Br$	2136, 1990 (s).
$CpFe(CO)_2C\ell$	2053 (s), 2010 (s).
$Cp_2Fe_2(CO)_3P(OPh)_3$	1971 (s), 1948 (m), 1760 (vs).
$Cp_2Fe_2(CO)_3P(OMe)_3$	1964 (s), 1942 (m), 1749 (vs).

$CpFe(CO)P(OPh)_3I$	1987 (s)
$CpFe(CO)P(OMe)_3I$	1980 (m), 1969 (s).
$Co_2(CO)_8$	2071 (s), 2069 (s), 2044 (s), 2042 (s), 2031 (m), 2022 (s), 1866 (w), 1857 (w).
$CpFeCo(CO)_6$	2071 (s), 2017 (s), 2015 (sh), 2000 (m), 1982 (s), 1959 (w), 1855 (sh), 1848 (sh), 1836 (sh), 1831 (w).
$Cp_2FeNi(CO)_3$	2004 (s), 1825 (s).
$Cp_2Mo_2(CO)_6$	1963 (s), 1920 (m)
$CpMo(CO)_2(CNBu^t)I$[b]	2122, 1987 (m), 1918 (br).
$CpMo(CO)_2(CNPr^i)I$	2139 (br), 1983 (s), 1935 (s), 1920 (m).
$Cp_2FeMo(CO)_5$	2038 (w), 2000 (m), 1955 (s), 1941 (s), 1899 (w), 1883 (m).
$CpMo(CO)_2P(OPh)_3I$	1986 (s), 1916 (s).
$CpMo(CO)_2P(OMe)_3I$	1983 (s), 1912 (s).
$CpMo(CO)\{P(OPh)_3\}_2I$	1875
$CpMo(CO)_3I$	2045 (s), 1978 (s), 1962 (s).
$Cp_2Fe_2\{P(OPh)_3\}_4$[c]	3068 (m), 3045 (m), 3033 (m), 2975 (w), 2935 (w), 2870 (w), 2375 (w), 1950 (w), 1600 (s), 1560 (w), 1500 (s), 1462 (s), 1450 (s), 1437 (s), 1385 (m), 1340 (w), 1315 (w), 1295 (m), 1225 (s), 1200 (s), 1180 (s), 1120 (w), 1105 (m), 1078 (m), 1032 (s), 1020 (s), 1010 (m), 1000 (m), 985 (w), 970 (w), 890-935 (s), 880 (s), 860 (s), 830 (m), 800 (s), 765 (s), 735 (s), 722 (s), 710 (s), 697 (s).

a In hexane solution unless otherwise stated

b In $CH_2C\ell_2$ solution

c Nujol mull.

III Experimental

The same reaction conditions and instrumentation were used as specified in Chapter 2.

The mixed metal complexes, $Cp_2FeMo(CO)_5$, $Cp_2FeNi(CO)_3$ and $CpFeCo(CO)_6$ were prepared as described in the literature[5-7]. The monosubstituted phosphite derivatives were prepared by the thermal reaction of metal carbonyl complexes with an excess of the appropriate phosphite as specified in literature[15], while $CpFe\{P(OPh)_3\}_2I$ was prepared by the photochemical reaction as described by Nesmeyanov[16]. $CpFe(CO)_2I$ and $CpMo(CO)_3I$ were prepared as described in literature[17]. All other chemicals were purchased commercially.

Reaction of $Cp_2FeMo(CO)_5$ with Pr^iNC

A mixture of $Cp_2FeMo(CO)_5$ (0.41 g, 0.94 mmol) and Pr^iNC (0.20 cm^3, 1.8 mmol) in benzene (20 cm^3) were stirred at room temperature for 1 hour. The solvent was evaporated off and the reddish brown residue was chromatographed over alumina (Grade IV). Elution with 5:95 mixture of dichloromethane and petroleum ether gave $Cp_2Fe_2(CO)_4$ (0.04 g, 23%) and $Cp_2Fe_2(CO)_3(CNPr^i)$ (0.06 g, 33%). Further elution with 50:50 mixture of dichloromethane and petroleum ether gave a trace of $Cp_2Mo_2(CO)_6$ (<0.01 g). A red band stayed on the column and decomposed before it could be collected.

The reaction of $Cp_2FeMo(CO)_5$ with Bu^tNC was carried out similarly; however, only $Cp_2Fe_2(CO)_4$ could be collected off the chromatography column.

Reaction of $Cp_2NiFe(CO)_3$ with Pr^iNC

Freshly prepared $Cp_2NiFe(CO)_3$ (0.40 g, 1.5 mmol) and Pr^iNC (0.40 cm^3, 4.5 mmol) were stirred in benzene (40 cm^3) at room temperature for 3 hours. The solvent was evaporated off and the dark red residue was chromatographed over alumina (Grade III). A trace of dark green nickelocene was eluted first with petroleum ether. This was closely followed by the light green band of $Cp_2Ni_2(CO)_2$ (0.07 g, 31%). Further elution with 40:60 benzene-petroleum ether yielded $Cp_2Fe_2(CO)_4$ (0.09 g, 33%) and $Cp_2Fe_2(CO)_3(CNPr^i)$ (0.07 g, 23%). A reddish brown band decomposed on the column before it could be collected.

Reaction of $CpFeCo(CO)_6$ with Bu^tNC.

Freshly prepared $CpFeCo(CO)_6$ (1.1 g, 3.2 mmol) and Bu^tNC (1.1 cm^3, 9.6 mmol) were stirred in benzene (45 cm^3) for 1 hour. The solvent was evaporated off and the brown residue was chromatographed over alumina (Grade IV). Elution with 20:80 dichloromethane-petroleum ether separated $Cp_2Fe_2(CO)_4$ (0.16 g, 27%) from $Cp_2Fe_2(CO)_3(CNBu^t)$ (0.09 g, 14%). Most of the yellow brown third band decomposed, however a small fraction of it was collected and identified as $Co_2(CO)_8$. A fourth red band completely decomposed before it could be collected.

Preparation of $CpFe(CO)(CNBu^t)I$

A mixture of $Cp_2Fe_2(CO)_2(CNBu^t)_2$ (7.5 g, 16 mmol) and iodine (8.2 g, 34 mmol) was stirred in 200 cm^3 of chloroform for approximately 30 minutes. The excess iodine was removed by shaking the mixture with a saturated aqueous solution of sodium thiosulphate (3 × 100 cm^3). The chloroform layer was separated and left standing over $MgSO_4$ for 3-4 hours. After filtering off the $MgSO_4$, the solvent was evaporated off to give a greenish brown residue. Chromatography of this over alumina (Grade III) using a 40:60 mixture of benzene and petroleum ether gave a single brown band of $CpFe(CO)(CNBu^t)I$ with a yield of 9.7 g (86%).

Complexes $CpFe(CO)(CNR)I$ ($R = Pr^i$, Et) and $CpFe(CO)(CNBu^t)Br$ were prepared in an analogous manner. In the case of $CpFe(CO)(CNEt)I$, a trace of $CpFe(CO)_2I$ and $CpFe(CNEt)_2I$ are also formed which can be separated from the main product using the same chromatography conditions as mentioned before, $CpFe(CO)_2I$ comes off as the first band while $CpFe(CNEt)_2I$ decomposes on the column.

Preparation of $CpMo(CO)_2(CNPr^i)I$

$CpMo(CO)_3I$ (1.0 g, 2.7 mmol) and Pr^iNC (0.34 g, 3.9 mmol) in 100 cm^3 of benzene were irradiated with U.V. light for 3 hours. The benzene was evaporated off and the red residue was chromatographed over alumina (Grade IV). Elution with a 50:50 mixture of benzene and petroleum ether brought down a trace of $Cp_2Mo_2(CO)_6$, closely followed by a small amount of unreacted $CpMo(CO)_3I$. Further elution with benzene brought down the main red band of $CpMo(CO)_2(CNPr^i)I$. After evaporating off most of the solvent, $CpMo(CO)_2(CNPr^i)$ crystallised out on addition of 10 cm^3 of petroleum ether. Yield 0.63 g (58%).

Reaction of $CpFe(CO)(CNBu^t)I$ with $[CpFe(CO)_2]Na$

The anion $[CpFe(CO)_2]Na$ was prepared by stirring a THF solution (100 cm^3) of $Cp_2Fe_2(CO)_4$ (1.6 g, 4.6 mmol) with 1%

Na/Hg (0.3 g Na, 2.1 cm^3 Hg) at room temperature for 1 hour. After removing the excess Na/Hg amalgam, CpFe(CO)(CNBu^t)I (3.2 g, 9.2 mmol) was added to the orange coloured solution of the anion, and the mixture was stirred for 2 hours, during which time the colour of the mixture turned dark brown. The solvent was evaporated off in vacuo and the residue was chromatographed over alumina (Grade III). Elution with a 20:80 mixture of dichloromethane and petroleum ether brought down a trace of $Cp_2Fe_2(CO)_4$ (0.36 g, 4.2%) closely followed by the major product of the reaction $Cp_2Fe_2(CO)_3(CNBu^t)$ (2.30 g, 31.9%). Further elution with dichloromethane gave a small amount of $Cp_2Fe_2(CO)_2(CNBu^t)_2$ (0.30 g, 3.5%).

The analogous reactions of $[CpFe(CO)_2]$Na and CpFe(CO)(CNR)X (R = Pr^i, Et, X = I; R = Bu^t, X = Br) were carried out in a similar manner. The products and yields obtained are given in Table .

Reaction of CpFe(CO)(CNBu^t)I with $[CpMo(CO)_3]$Na

The anion $[CpMo(CO)_3]$Na was prepared by stirring a THF solution (70 cm^3) of $Cp_2Mo_2(CO)_6$ (0.46 g, 0.9 mmol) and Na/Hg amalgam (0.1 g Na, 0.3 cm^3 Hg) for 2 hours. After removing the excess Na/Hg amalgam, CpFe(CO)(CNBu^t)I (0.40 g, 1.3 mmol) was added to the anion and the mixture was stirred for 5 hours. Most of the solvent was evaporated off and the reddish brown residue was chromatographed over alumina (Grade III). Elution with a 50:50 mixture of dichloromethane and petroleum ether brought down traces of $Cp_2Fe_2(CO)_4$ and $Cp_2Mo_2(CO)_6$. Further elution with dichloromethane brought down the red band of $CpMo(CO)_2(CNBu^t)I$. After evaporating off the solvent, the crude yield of $CpMo(CO)_2(CNBu^t)I$ was found to be 0.08 g

[33% based on $Cp_2Mo_2(CO)_6$]. Considerable decomposition of the reaction products seemed to occur on the column.

The reaction of $CpFe(CO)(CNPr^i)I$ with $[CpMo(CO)_3]Na$ was carried out in an analogous manner. $CpMo(CO)_2(CNPr^i)I$ was obtained with a yield of 37%.

Reaction of $CpMo(CO)_2(CNPr^i)I$ with $[CpFe(CO)_2]Na$.

The anion $[CpFe(CO)_2]Na$ was prepared from $Cp_2Fe_2(CO)_4$ (3.0 g, 8.4 mmol) as described before. To the THF solution of the anion was added $CpMo(CO)_2(CNPr^i)I$ (6.0 g, 14.5 mmol) and the mixture was stirred at room temperature for 3 hours. The solvent was evaporated off and the reddish brown residue was chromatographed over alumina (Grade III). Elution with a 60:40 mixture of dichloromethane and petroleum ether gave $Cp_2Fe_2(CO)_4$ (1.9 g, 63%), $Cp_2Fe_2(CO)_3(CNPr^i)$ (0.17 g, 5%) and $CpMo(CO)_2(CNPr^i)I$ (0.91 g, 15%). A fourth red band decomposed before it could be collected.

Reaction of $CpFe(CO)(CNBu^t)I$ with $[Co(CO)_4]Na$.

$[Co(CO)_4]Na$ was prepared by stirring a THF solution (150 cm^3) of $Co_2(CO)_8$ (3.2 g, 9.3 mmol) with an excess of 1% Na/Hg amalgam for 2 hours. After removal of the excess amalgam, $CpFe(CO)(CNBu^t)I$ (6.7 g, 18.9 mmol) was added and the mixture was stirred at room temperature for 4 hours, i.e. till infrared spectroscopy indicated that all of the iodide had reacted. The solvent was evaporated off and the yellowish brown residue was chromatographed over alumina (Grade III). A 40:60 mixture of dichloromethane and petroleum ether eluted $Co_2(CO)_8$ (0.57 g, 18%) and $Cp_2Fe_2(CO)_4$ (0.77 g, 22%). Further elution with a 70:30 mixture of dichloromethane and petroleum ether yielded $Cp_2Fe_2(CO)_3(CNBu^t)$ (0.71 g, 17%) and $Cp_2Fe_2(CO)_2(CNBu^t)_2$ (0.31 g, 7%). A yellowish green band decomposed on the column before it could be collected.

Reaction of $CpFe(CO)\{P(OMe)_3\}I$ with $[CpMo(CO)_3]Na$

To a THF solution (40 cm^3) of $[CpMo(CO)_3]Na$, prepared by reduction of $Cp_2Mo_2(CO)_6$ (0.91 g, 1.9 mmol) (with Na/Hg amalgam as described before), was added $CpFe(CO)\{P(OMe)_3\}I$ (1.30 g, 3.3 mmol) and the mixture was stirred for 3 hours. The solvent was evaporated off and the yellowish brown residue was chromatographed over alumina (Grade III). Elution with a 20:80 mixture of dichloromethane and petroleum ether gave $Cp_2Fe_2(CO)_4$ (0.07 g, 12%), a small trace of $CpMo(CO)_3Me$ and $Cp_2Mo_2(CO)_6$ (0.61 g, 67%). Further elution with dichloromethane yielded the starting material, $CpFe(CO)\{P(OMe)_3\}I$ (0.81 g, 62%). A yellow band decomposed on the column before it could be collected.

The reaction of $CpFe\{P(OPh)_3\}_2I$ with $[CpMo(CO)_3]Na$ was carried out similarly. After removal of the solvent from the reaction mixture, an orange red residue was obtained which, on chromatography using alumina (Grade II) and a 40:60 mixture of dichloromethane and petroleum ether, yielded a trace of $Cp_2Fe_2(CO)_4$, $Cp_2Mo_2(CO)_6$ (19%), $CpMo(CO)_3I$ (21%) and $Cp_2Fe_2\{P(OPh)_3\}_4$ (57%). Two red bands remained on the column and eventually decomposed before they could be collected.

Reaction of $CpFe(CO)\{P(OPh)_3\}I$ with $[CpFe(CO)_2]Na$

To a THF solution (100 cm^3) of $[CpFe(CO)_2]Na$, prepared by reduction of $Cp_2Fe_2(CO)_4$ (0.48 g, 1.4 mmol) with Na/Hg amalgam as described before, was added $CpFe(CO)\{P(OPh)_3\}I$

(1.61 g, 2.7 mmol), and the mixture was stirred at room temperature for 2 hours. The solvent was evaporated off and the brown residue was chromatographed over alumina (Grade III). Elution with a 30:70 mixture of dichloromethane and petroleum ether gave $Cp_2Fe_2(CO)_4$ (0.53 g, 55%) and $Cp_2Fe_2(CO)_3P(OPh)_3$ (0.18 g, 11%).

The reaction of $CpFe(CO)\{P(OMe)_3\}I$ with $[CpFe(CO)_2]Na$, which was carried out in a similar manner, yielded $Cp_2Fe_2(CO)_4$ (36%) and $Cp_2Fe_2(CO)_3P(OMe)_3$ (20%).

The reaction of $CpFe\{P(OPh)_3\}_2I$ with $[CpFe(CO)_2]Na$ yielded $Cp_2Fe_2(CO)_4$ (18%) and $Cp_2Fe_2\{P(OPh)_3\}_4$ (28%). The two products were separated by chromatography using an alumina (Grade III) column and a 30:70 mixture of dichloromethane and petroleum ether.

Reaction of $Cp_2Fe_2(CO)_3P(OPh)_3$ with Bu^tNC

A mixture of $Cp_2Fe_2(CO)_3P(OPh)_3$ (1.3 g, 2.0 mmol) and Bu^tNC (1.5 cm , 12.0 mmol) was stirred in 40 cm^3 of benzene at room temperature for 3 hours. The colour of the solution changed to reddish brown to deep green. The solvent was evaporated off and the residue was chromatographed on alumina (Grade III). Elution with a 50:50 mixture of dichloromethane and petroleum ether gave a single green band which was identified as $Cp_2Fe_2(CO)_2(CNBu^t)_2$. Yield 0.35 g (46%).

The same reaction, when carried out using only 3-fold excess of Bu^tNC, gave a trace of $Cp_2Fe_2(CO)_3(CNBu^t)$ as well as the major product $Cp_2Fe_2(CO)_2(CNBu^t)_2$. The two complexes were separated by chromatography, using the same conditions as stated above.

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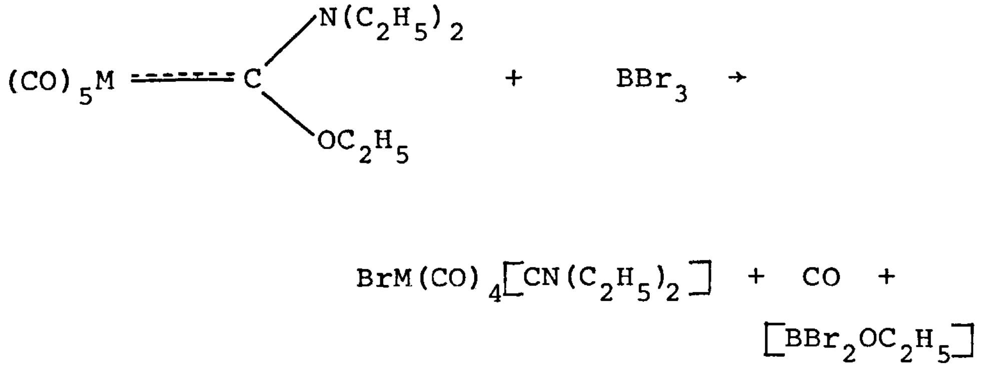
CHAPTER 4

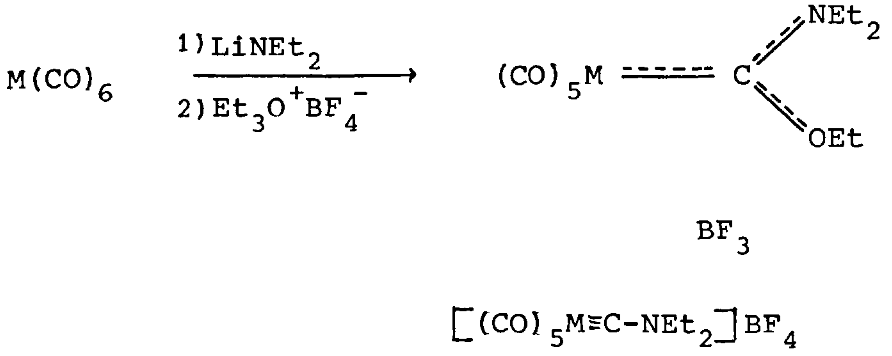
SYNTHESIS AND FLUXIONAL CHARACTER OF SOME POLYNUCLEAR CARBONYL COMPLEXES.

I Introduction

There is currently much interest in the chemistry of transition metal clusters containing carbene, carbyne and carbide species. Their possible relevance as simple models for the catalytic hydrogenation of carbon monoxide has been discussed in Chapter 1. In recent years, several examples of the preparation of complexes containing the dialkylamino carbyne (CNR_2) group, bound in a terminal, μ_2- or μ_3- fashion, have been reported. The complexes trans - $BrM(CO)_4[CNEt_2]$ (M = Cr, W) have been prepared by the reaction of diethylamino-ethoxycarbenepentacarbonyl complexes of chromium and molybdenum with boron trihalides (Scheme 1)[1,2]. The reaction involves simultaneous removal of the C_2H_5O group and a CO ligand, and introduction of a halogen into the complex. The cationic carbene complexes ,$[(CO)_5 M\equiv CNEt_2]^+$ (M = Cr, Mo, W), have been prepared by the route shown in Scheme 2 .[3]



Scheme 1



Scheme 2

The compounds, trans-$[M(CNR)_2(dppe)_2]$ (M = Mo, W; R = Me, Bu^t, aryl; dppe = $Ph_2PCH_2CH_2PPh_2$), can be protonated at one or both nitrogen atoms to give complexes containing CNHR (carbyne) ligands[4,5]. Bonding of isonitriles to the electron-rich site, $M(dppe)_2$, results in a build up of charge on the isonitrile, thus promoting ready electrophilic attack at its nitrogen atom.

Complexes containing μ_2-CNR_2 species have been prepared by a variety of means. Thus, protonation or alkylation of derivatives of the type $Cp_2M_2(CO)_3(CNR)$ (M = Fe, Ru) yields salts of structure $[Cp_2M_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNRR^1)]X$ (R^1 = H, alkyl)[6,7], while alkylation of $Fe_2(CNEt)_9$ with alkyl halides yields a salt of structure $[Fe_2(CNEt)_6(\mu_2\text{-}CNEt)(\mu_2\text{-}CNEtR)_2]X_2$ (R = Me, Et)^8. The triruthenium cluster complex, $HRu_3(CO)_{10}(CNMe_2)$, has been prepared by the reaction of $Me_2NCH_2SnMe_3$ with $Ru_3(CO)_{12}$ ^{9}. The cleavage reaction of $Me_2NCH_2SnMe_3$ produces the ruthenium cluster which contains both a $CNMe_2$ ligand in a μ_2-bridging mode and a bridging hydride ligand (Fig. 1).

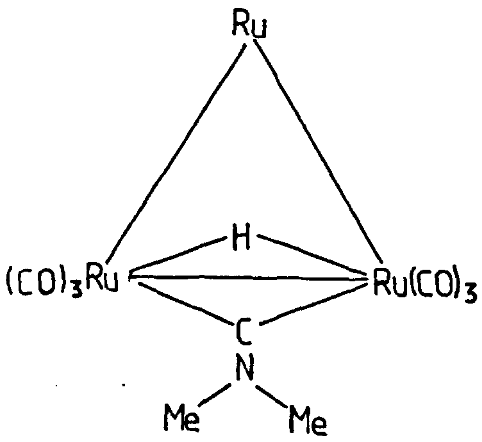


Fig. 1 . $HRu_3(CO)_{10}(CNMe_2)$

Trimethylamine and N, N-dimethylbenzylamine react with $Os_3(CO)_{12}$ by elimination of hydrogen to give $HOs_3(CO)_{10}(CNMe_2)$ as one of the products (Scheme 3)^{10}.

$(CH_3)_3N + PhCH_2N(CH_3)_2 + Os_3(CO)_{12} \rightarrow$

$HOs_3(CO)_{10}(\mu_2\text{-}RC{=}NMe)$ (R = H, Ph)

+

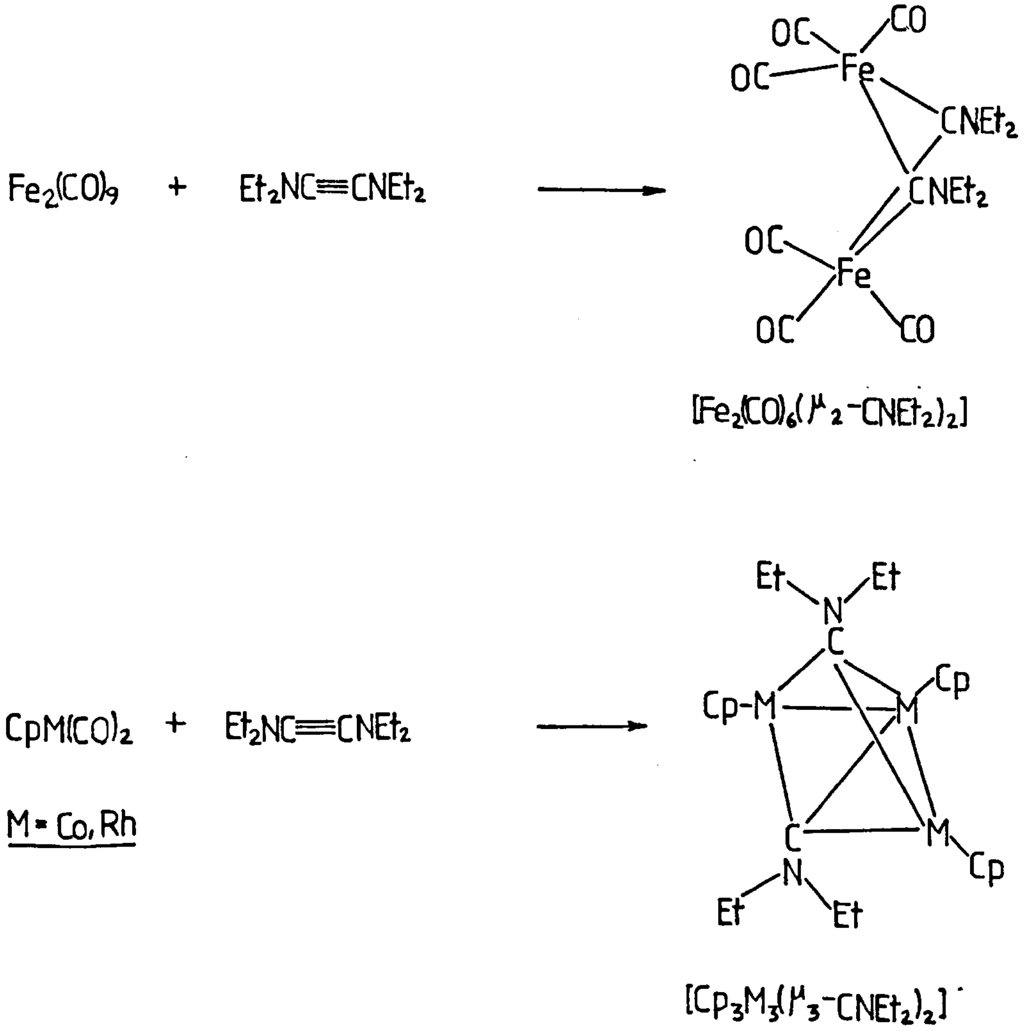
$HOs_3(CO)_{10}(\mu_2\text{-}CNMeR)$ (R = Me, $PhCH_2$)

+

$HOs_3(\mu_3\text{-}HC{=}NMe)(CO)_9$

Scheme 3 .

The complex $HOs_3(CO)_{10}(\mu_2\text{-}CNHR)$ may be prepared by thermolysis of the isonitrile adducts $H_2Os_3(CO)_{10}(CNR)$ [11]. The reaction involves the transfer of one of the bridging hydride ligands to the isonitrile. The iron complex $HFe_3(CO)_{10}(CNMe_2)$ has been isolated from the reaction of $Fe_3(CO)_{12}$ with benzoyl chloride in dimethylformamide[29], and from the probably related reaction of $Fe_3(CO)_{12}$ with $[Me_2N{=}CHCl]Cl$ [30]. A crystal structure determination of this complex has recently been reported, and it has been shown to have a structure similar to that of the ruthenium analogue (Fig. 1)[15]. The carbon-carbon triple bond in $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ undergoes complete cleavage in its reaction with $Fe_2(CO)_9$ and $CpM(CO)_2$ (M = Co, Rh) (Scheme 4)[12,13].



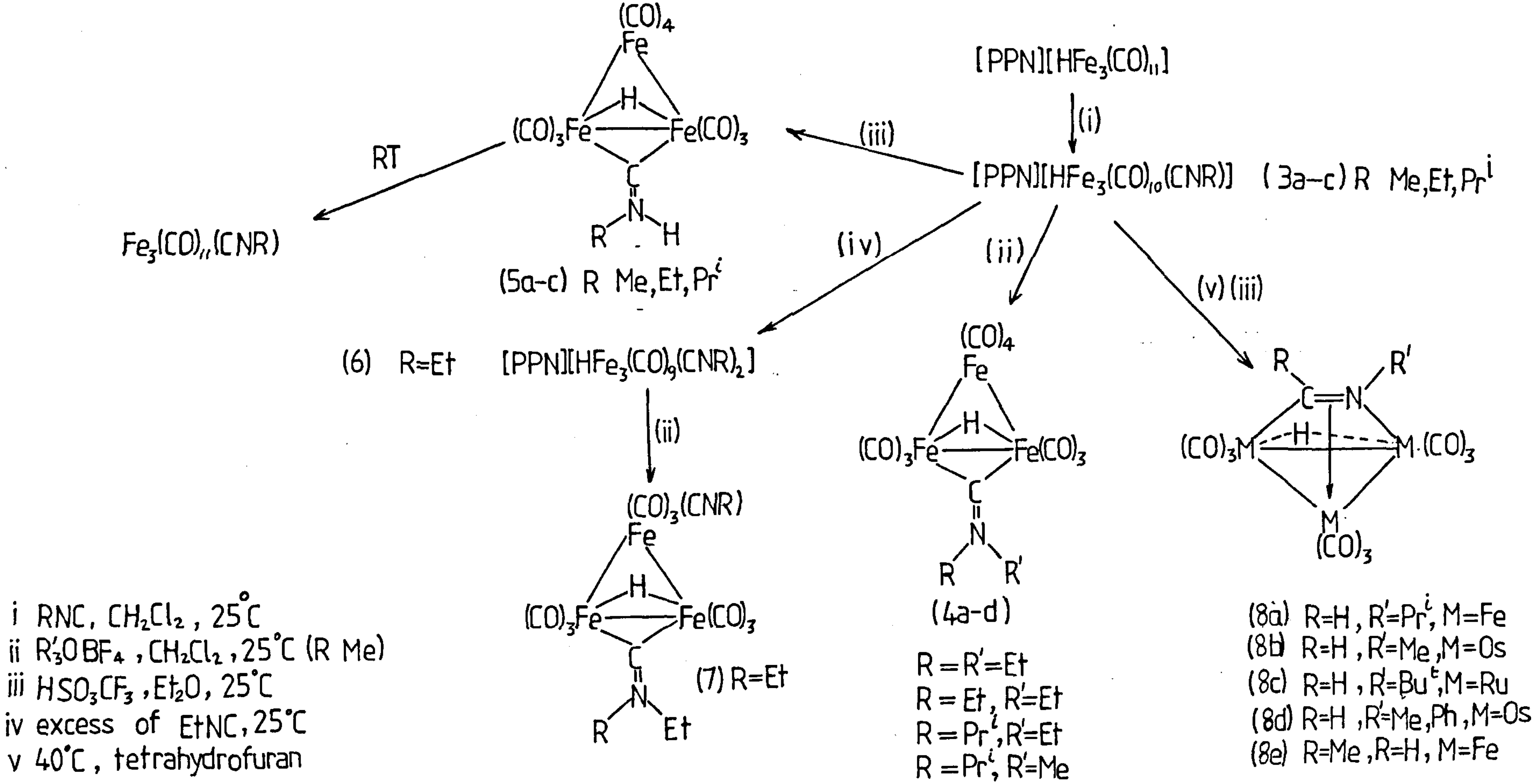
Scheme 4.

We present in this Chapter a potential general method for the synthesis of neutral clusters containing the CNR_2 moiety, namely the isonitrile substitution of an anionic cluster, followed by alkylation. Herein, we describe the application of this method to the $HFe_3(CO)_{11}^-$ anion.

II Discussion

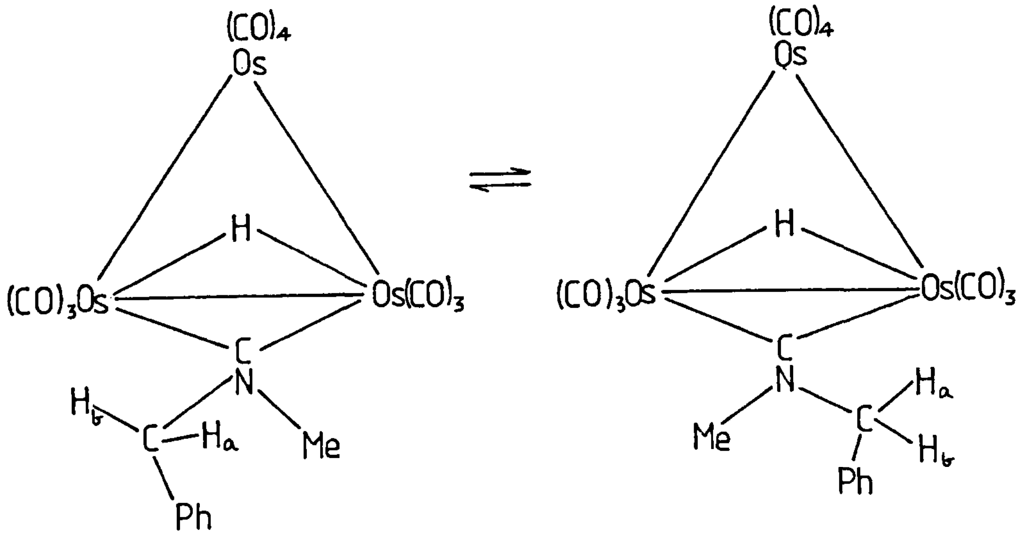
Reaction of triethylamine with iron pentacarbonyl in water at 80°C yields the triiron carbonyl cluster anion, $[HFe_3(CO)_{11}][NHEt_3]$ in good yield[32]. However, reactions of this anion with isonitriles only give very low yields of isonitrile substituted complexes of the type $[HFe_3(CO)_{11-n}(CNR)_n][NHEt_3]$ (n = 1,2). In contrast, the anion in the form of bis (triphenylphosphiniminium) salt, $[HFe_3(CO)_{11}][PPN]$, which is obtained by metathesis of $[HFe_3(CO)_{11}][NHEt_3]$ with $[PPN]C\ell$ in dichloromethane at room temperature, reacts with excess of RNC (R = Me, Et, Pr^i) at room temperature to give, after alkylation with $R^1_3O^+BF_4^-$ (R^1 = Et, Me), products of the type $[HFe_3(CO)_{10}(CNRR^1)]$ in good yields (Scheme 5). The neutral carbyne-containing clusters, as obtained by this method, were purified by chromatography and recrystallisation or sublimation to give air stable red-purple solids. Microanalytical and infrared data are given in Tables 1 and 2 .

Crystallographic determinations of six of the complexes previously mentioned[2,6,9,11b,12,15] have shown that the CN bond length (1.28-1.30 Å) is very close to the CN double bond length of 1.27 Å in diacetyl dioxime[14]. In addition, n.m.r. data on the complexes $[HOs_3(CO)_{10}(\mu_2\text{-}CN(Me)(CH_2Ph)]$ [10] and $[Cp_2Fe_2(CO)_3(CNRR^1)]X$ [7] have shown that C-N bond rotation is slow, at least on the n.m.r. timescale. Thus, the non-equivalent nature of the benzylic hydrogen atoms is evident from the AB quartet in the proton n.m.r. spectrum of the osmium complex. A rotation of 180° about the C-N bond would result in racemization and H_a, H_b interchange (Scheme 6).



i RNC, CH_2Cl_2, 25°C
ii R'_3OBF_4, CH_2Cl_2, 25°C (R Me)
iii HSO_3CF_3, Et_2O, 25°C
iv excess of EtNC, 25°C
v 40°C, tetrahydrofuran

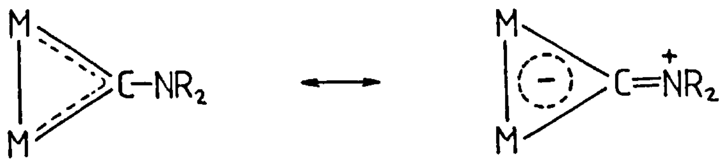
Scheme 5.



Scheme 6 .

For the complexes $[Cp_2Fe_2(CO)_3(CNRR^1)]X$, when R = $CH(CH_3)_2$, R^1 = H the proton n.m.r. spectrum at -10°C shows a doublet of doublets for the $CH(\underline{CH_3})_2$ resonance. Also, when R = CH_2CH_3, R^1 = $CH(CH_3)_2$, the spectrum shows an AB multiplet associated with the CH_2 group, and again, a doublet of doublets for the $CH(\underline{CH_3})_2$ resonance.

The crystallographic and the n.m.r. data for the complexes mentioned thus have been interpreted primarily in terms of the immonium structure (II) shown below.

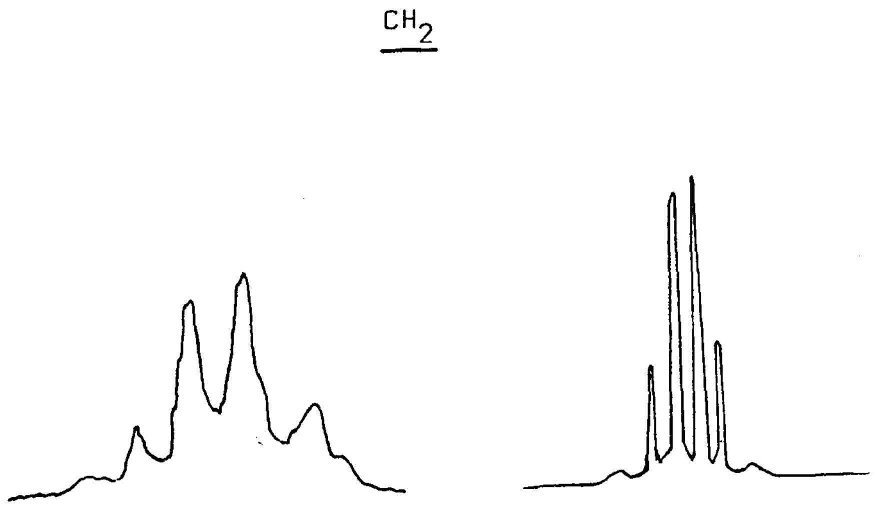


(I) (II)

Fig.2

We have found, however, that restricted C-N bond rotation in (4a-d) is evident in their variable temperature n.m.r. spectra; those of (4c) best exemplify the phenomenon (Fig I). At -60°C, the diastereotopic nature of the $CH\underline{(CH_3)_2}$ resonance can be seen in the form of two doublets (although superimposed on the $CH_2\underline{CH_3}$resonance), while the AB nature of the $\underline{CH_2}CH_3$ resonance is clear. The computer simulated spectrum of (4c) has confirmed the AB nature of the $\underline{CH_2}CH_3$ resonance (Fig. II), (δ_{HA} 4·12, δ_{HB} 4·28, δ_{CH_3} 1·59, J_{gem} -14 Hz, J_{vic} 7·4 Hz). On warming, changes typical of an exchanging system are observed. Thus, there is a broadening and eventual coalescence of the two doublets due to the $CH(\underline{CH_3})_2$ resonance to give a single sharp doublet. This is accompanied by broadening and coalescence of the multiplet peaks due to the $\underline{CH_2}CH_3$ resonance to give eventually a sharp quartet. From the coalescence temperature of the isopropyl resonance, an activation energy of 54 kJ mol^{-1} has been calculated[16]. Throughout, the M-H resonance at -18δ remains sharp. The spectra of complex (4d) exhibit analogous behaviour.

For complex (4b), the $\underline{CH_2}CH_3$ resonance (Fig. 3) shows an apparent simple quartet at -60°C. However, small resonances on either side of the quartet are apparent, and the experimental ABX_3 spectrum can be simulated by computer (δ_{HA} 4·30, δ_{HB} 4·34, δ_{CH_3} 1·42, J_{gem} -14 Hz, J_{vic} 7·5 Hz). At room temperature, only a simple quartet is visible.



Experimental spectrum

Computer simulated spectrum

Fig. 3

Complex (4a) exhibits only a simple quartet at all temperatures, implying that the chemical shift difference between A and B is too small to affect the overall shape of the spectrum (ie. $\delta_A - \delta_B < 0{\cdot}02$ ppm).

The related complexes $HM_3(CO)_{10}COR$ (M = Fe, Ru, Os; R = Me, Et)[17] (Fig. 4) have been shown by variable temperature ^{13}C n.m.r. spectra to display restricted C-OR bond rotation. The COR ligand in these complexes can be regarded as a μ_2-carbyne ligand, thus contributing three electrons to the cluster skeleton.

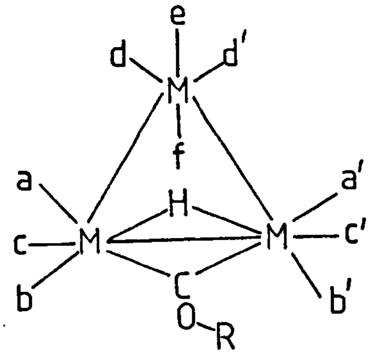
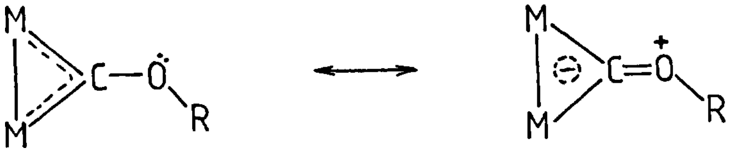


Fig. 4 . $HM_3(CO)_{10}COR$

The bonding situation in $HM_3(CO)_{10}COR$ can be considered as a resonance hybrid of the following mesomeric forms:



I II

This bonding picture is supported by infrared and crystallographic data. Thus, the C-OR stretching vibration is observed to lie between the characteristic regions for organometallic CO double and single bonds. The C-O bond length is found to be intermediate between normal single and double bond values. A partial π character of the C-OR bond, as a result of the above mentioned representation of the ligand bonding, is thus expected to allow hindered rotation, as is observed. C-O bond rotation in $[HFe_3(CO)_{10}(COMe)]$ is still rapid on the n.m.r.

time scale at -112°C, but the ^{13}C spectra of the Ru and Os analogues indicate an increased barrier to rotation of the C-OR bond in these complexes. The lower activation energy for the rotation of the C-OR bond in $HFe_3(CO)_{10}COR$ than in the ruthenium and osmium analogues implies that the mesomeric form I is significantly more important in the case of the iron complex than for the ruthenium and osmium analogues. An alternative mechanism for the flipping of the R group of the bridging COR moiety is that of inversion at oxygen atom involving a linear COR intermediate. It has been suggested that in binuclear transition metal complexes containing bridging CNR groups it is the inversion at nitrogen that is more likely than rotation around the C-N bond because of the short C-N bond length[31]. The C-O bond length of the COMe group in $HOs_3(CO)_9(CNBu^t)COMe)$ complex indicates considerable multiple bond character, and here too, inversion at oxygen is possible. However, in complexes containing bridging CNR_2 moieties, inversion at nitrogen is not possible, and rotation around the C-N bond is the only mechanism by which the two R groups can interchange sites. In view of this, it is very likely that rotation around the C-O bond of the COR group is probably more likely than inversion at the oxygen atom.

The CNR_2 group may also best be regarded as a μ_2-carbyne ligand; a partial π-character of the $C-NR_2$ bond, resulting from representation of the ligand bonding as a resonance hybrid of the two mesomeric forms (I) and (II) (Fig. 2), would be expected to allow hindered rotation, as observed.

Mechanisms involving reversible bridge cleavage of the $M(\mu-H)(\mu-CNR_2)M$ moiety, or inversion of the bridging ligands through the M_3 plane are not consistent with the variable temperature ^{13}C spectra, which show that the inequivalence of the two axial carbonyls of the unique $Fe(CO)_4$ group is maintained in spectra taken at temperatures significantly higher than those of the fast exchange proton spectrum. While a rotation of the complete CNR_2 ligand cannot be ruled out, this process seems unlikely.

Infrared data support these conclusions. The ν_{CN} value observed for (4b) (1540 cm^{-1}, nujol) is intermediate between accepted values for $\nu_{C=N}$ of 1640-1690 cm^{-1} for imines, oximes[18] or immonium salts $[(R_2CHCR=\overset{+}{N}R_2)X]$ [19] and accepted values for ν_{C-N} of 1360-1310 cm^{-1} for tertiary amines[20]. The complex $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMeEt)]BF_4$ exhibits an analogous absorption at 1595 cm^{-1}, [7] the shift to higher frequency being consistent with the cationic nature of the complex.

Protonation of (3a-c) using CF_3SO_3H yields the expected complexes (5a-c). Only (5a) has been isolated in a reasonable state of purity, as these compounds decompose in the solid state over a period of hours to give $[Fe_3(CO)_{11}(CNR)]$.* It is known that protonation of (2) at −80°C yields the analogous $[HFe_3(CO)_{10}(COH)]$ which decomposes above −30°C to give $Fe_3(CO)_{12}$ [22]. Although the N-H proton itself could not be detected in the n.m.r. spectrum of (5a), its presence is evident in the coupling observed to both the methyl and the M-H resonances, and in the ν_{N-H} observed at 3330 cm^{-1} in the nujol mull infrared spectrum[18].

An independent fluxional process is apparent from the ^{13}C spectra (Fig. III). For (4a), a six line carbonyl spectrum

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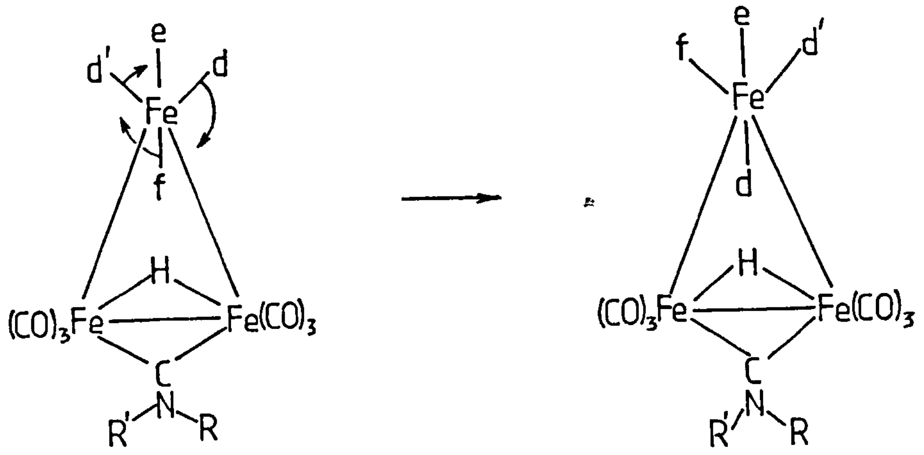
* See page 155 of this Chapter.

in the ratio of 1:1:2:2:2:2 , consistent with the static structure, is obtained at -70°C. On the basis of intensities, the resonances at 218.3 and 216.5 ppm may be assigned to carbons (e & f), while dd' may be associated with the resonance at 207.3 ppm which is the only peak of relative intensity two not to show proton coupling (Table 4). The $Fe(CO)_3$ resonances may be assigned according to the magnitude of the difference in chemical shift of the pairs nn' (n = a, b, c) when $R \neq R'$ as in (4b-d). Examination of molecular models indicates that the order of difference in chemical shift should be cc' $\gtrsim$ bb' >> aa'. As the lowest field resonance at c.a. 215 ppm occurs as a single peak in both (4b,c), this is assigned to the aa' pair. It is not possible to make an unambiguous assignment of bb' and cc', since the relevant resonances show a reversed order of chemical shift difference in (4b) as compared to (4c). As aa' occurs at lower field than cc' the lower of the two resonances belonging to the axial $Fe(CO)_4$ carbons is assigned to e.

On initial warming, two fluxional processes are observed to occur at approximately equal rates: a) a polytopal rearrangement of the $Fe(CO)_3$ carbonyls, and b) a polytopal rearrangement of three of the four $Fe(CO)_4$ carbonyls (d, d' and f). This preferential exchange of three carbonyls can be explained by a trigonal twist mechanism involving the triangular dd'f face (Scheme 7). On further warming, the resonance due to e also broadens, implying a higher activation energy for the trigonal twist involving the dd'e face.



Scheme 7.

At +90°C only a single broadened resonance is observed, consistent with complete carbonyl scrambling over the cluster.

The ^{13}C spectrum of $[HFe_3(CO)_{10}(COEt)]$, which was prepared by the reaction of the anion $[HFe_3(CO)_{11}][PPN]$ with $Et_3O^+BF_4^-$, displays six resonances of relative intensity 1:1:2:2:2:2 at -50°C. Thus, the two low intensity peaks can be assigned to the two axial carbonyls (e & f) of the $Fe(CO)_4$ moiety, (Fig. V).

Polytopal carbonyl rearrangement at cluster $M(CO)_3$ units is a well established process. Rearrangement at an $M(CO)_4$ moiety may proceed via a pseudo-fourfold or pseudo-threefold mechanism. Recent results suggest that it is the pseudo-threefold (trigonal twist) mechanism which is evident here[23].

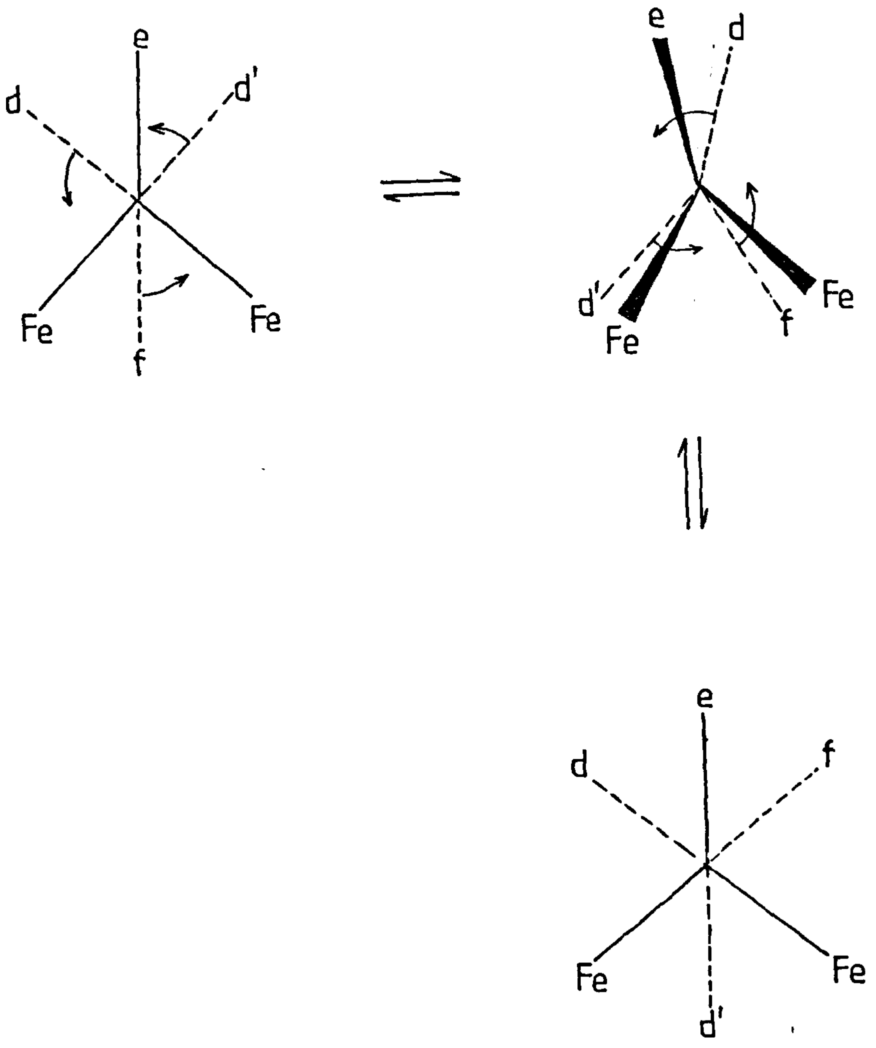


Fig 5.

The mechanism involves rotation of one of the faces of an octahedron relative to the opposite face (Fig. 5). However, as applied to the polytopal rearrangement of the Fe(CO)$_4$ moiety, it is evident from Fig. 6 that due to the fixed Fe-Fe bonds, there are only two faces which may undergo rotation (face edd' and face dd'f).

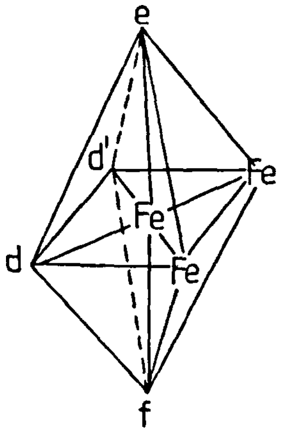
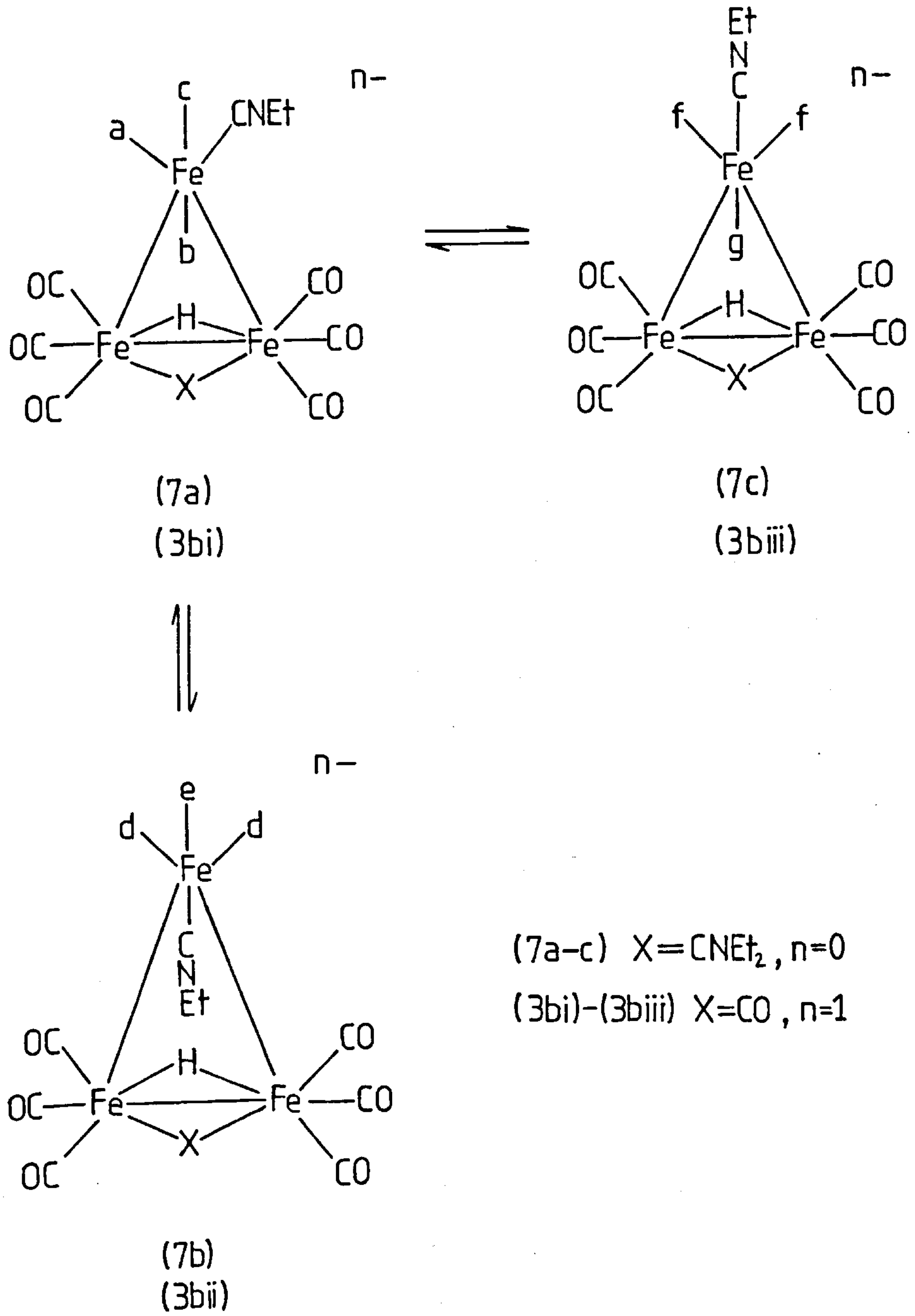


Fig 6.

Initial warming of a solution of $HFe_3(CO)_{10}COEt$ results in broadening and coalescence of one of the low intensity peaks and one other pair. The only reasonable choice for the latter is dd' and it is on the basis of this observation that the assignment of dd' is made. On raising the temperature, the peak due to the other axial carbonyl also begins to broaden, and a single broad resonance due to $Fe(CO)_4$ carbonyls is observed at 0°C. Thus, the polytopal rearrangement of the $Fe(CO)_4$ group clearly occurs as a two step process. Initially, there is exchange of carbonyls between the two equatorial sites and only one of the axial sites. This can be accounted for by the trigonal twist mechanism in which rotation about one three-fold axis has a lower activation energy than that about the other. The remaining three peaks are assigned to aa', bb' and cc'. At +20°C, these three peaks begin to broaden and coalesce, implying a higher activation energy for the polytopal rearrangement at $Fe(CO)_3$ groups than at the $Fe(CO)_4$ group. At +85°C a single, reasonably sharp peak is observed, indicating total carbonyl scrambling at this temperature.

More prolonged reaction of $[HFe_3(CO)_{11}]^-$ with EtNC, followed by alkylation and purification, yielded the monosubstituted complex $[HFe_3(CO)_9(CNEt)(CNEt_2)]$ (7), presumably via the intermediary of the disubstituted anion, $[HFe_3(CO)_9(CNEt)_2]^-$ (6). The complexity of the infrared spectrum (Table 2) indicates the presence of isomers, and at -65°C in the proton n.m.r. spectrum, three M-H resonances of unequal intensities are observed (Fig.VI). The temperature dependence of the three resonances is most consistent with the three isomers (7a-c) (Fig.7). Initial warming to -25°C results in broadening and coalescence of the highest and lowest field resonances, while further warming yields eventually a single resonance at +75°C. The results imply an initial exchange of two of the three possible isomers, and can be explained in terms of the trigonal twist mechanism previously outlined. Thus, an initial twist about the abCNEt face of (7a) or the dCNEtd face of (7b) results in exchange between (7a) and (7b); a similar twist about the fgf face of (7c) results in axial ⇌ equatorial site exchange, but not in isomer interchange. At higher temperatures, rotation about the alternate faces cis to the M-H-M bridge (acCNEt, ded and fCNEtf) results in exchange between all three isomers. The resonance of greatest intensity at -17.4 δ may thus be assigned to (7c), and it is of interest to note that in the related complex $HOs_3(CO)_9(COMe)(CNBu^t)$ only the isomer of analogous structure is observed in the solid state and in solution[17a]. Unambiguous assignment of (7a) and (7b) is not possible, although steric considerations would suggest a lower population for the axially substituted (7b). Variable temperature ^{13}C spectra are



(7a)
(3bi)

(7c)
(3biii)

(7b)
(3bii)

(7a–c) X=$CNEt_2$, n=0
(3bi)-(3biii) X=CO, n=1

Fig 7.

consistent with this interpretation (Fig. VII). Thus, the spectrum at -60°C displays three $\underline{C}NCH_2CH_3$ resonances at 150.7, 154.7 and 157.8 ppm, due to the three isomers (7a-c). On warming, broadening and coalescence of the highest and lowest field resonances occurs to give a broad resonance at 0°C. This implies an initial interchange of only two of the three isomers. At room temperature, the resonance due to the third isomer begins to broaden and coalesce with the broad resonance, thus implying exchange between all three isomers at higher temperatures. The same process can be seen from the $\underline{C}N(CH_2CH_3)_2$ resonances. At -60°C, three resonances at 322.3, 319.6 and 318.1 ppm can be seen, the resonance due to the least abundant isomer appearing at a higher field than that due to the most abundant isomer. This order of resonances for two of the isomers is the reverse of that for the $\underline{C}NCH_2CH_3$ resonances. On warming initially, the two highest field resonances broaden and coalesce to give a single broad resonance at 0°C. At room temperature, the resonance due to the third isomer begins to broaden and coalesce with this broad resonance, thus again indicating the two-stage interchange process between the three isomers.

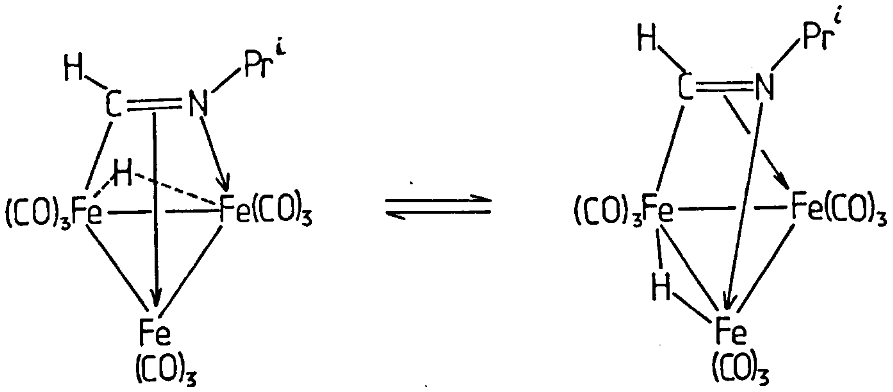
The ^{13}C spectrum of (7a-c) at low temperature would also be predicted to display four resonances for the axial carbonyls a, b, e and g of the three isomers. In the axial carbonyl region, 220-219 ppm, three distinct resonances are clearly observed, while the fourth one is probably under one of these resonances. On initial warming, while the resonance at 219.9 ppm remains unchanged, the other axial carbonyl resonances begin to broaden and coalesce with the resonance at 209.9 ppm which, on the basis of the previous discussion and on its position relative to other carbonyl peaks, may be assigned to an equatorial carbonyl. The resonance at 219.9 ppm can be assigned to the axial carbonyl g of isomer (7c). Further warming results in broadening and coalescence of the remaining resonances, and at +25°C, a single very broad resonance is obtained.

It is of interest to compare these results with those for the initial isonitrile substitution of $[HFe_3(CO)_{11}]^-$. Because of the sequential substitution, pure samples of (3a-c) could not be obtained. However, it is possible to determine the position of substitution by n.m.r. techniques. In the ^1H n.m.r. spectrum, reaction of (2) over 30 minutes at room temperature with a 4:1 excess of EtNC results in replacement of the M-H resonance of (2) (-15.0 δ) with a new resonance at -14.5 δ, assignable to (3b), which on cooling to -65°C yields three resonances of unequal intensity at -14.0, -14.6 and -14.8 δ (Fig. VI). The similarity in pattern to (7a-c) is apparent, and the resonances may be assigned tentatively to the analogous isomers (3bi-iii) (Fig.7) .In contrast, however, only one isomer is present in reasonable abundance, and on the basis of the previous discussion, this resonance may be assigned to (3b iii). ^{13}C spectra conclusively demonstrate the axial substitution. The spectrum of $[HFe_3(CO)_{11}][PPN]$ at -110°C (Table 4)^{21} exhibits two resonances of unit intensity at 223.8 and 221.3 ppm due to the axial carbonyls (e & f); in the spectrum of $[HFe_3(CO)_{10}(CNEt)][PPN]$ taken at -70°C, only one axial resonance is observed, together with the appearance of a terminal isonitrile resonance at 160.5 ppm. Resonances due to the two minor isomers are not observed , (Fig. VIII) .

Chemically, the results imply an alkylation of (3a-c) at the terminal isonitrile rather than bridging carbonyl, followed by structural rearrangement; the presence of a small amount of bridging isonitrile isomer cannot be discounted, however.

If the solvent and excess isonitrile are removed from a sample of (3c), and (3c) is heated in tetrahydrofuran, protonation yields complex (8a) instead of the carbyne derivative (5c). This complex is clearly derived from initial insertion of coordinated isonitrile into the M-H-M bond, as the n.m.r. spectrum of the complex obtained on deuteration shows > 90% incorporation of hydrogen into the $\underline{CH}NPr^i$ position. Several isostructural examples have been recently prepared and characterised. Thus, reaction of $Os_3(CO)_{12}$ with NMe_3 yields (8b)[10], while hydrogenation of $Ru_3(CO)_{11}(CNBu^t)$ yields (8c)[24]. Reaction of $H_2Os_3(CO)_{10}$ with RNC yields the substituted complexes $H_2Os_3(CO)_{10}(CNR)$ and $H_2Os_3(CO)_9(CNR)$ (R = Me, Ph, Bu^t) which on further heating in poor donor solvents (R = Me, Ph only) yield edge bridging $HOs_3(CO)_{10}(\mu_2\text{-}CH{=}NR)$ and face bridging (8d) complexes[11a,25]. Reaction of $[HFe_3(CO)_{11}]^-$ with moist acetonitrile, followed by protonation yields (8e), isomeric with the complex reported herein[26-28]. Interestingly, (8e) isomerises on heating to the complex $HFe_3(CO)_9[\mu_3\text{-}N{=}C(H)Me]$. Deuteration studies were not conclusive as to whether the N-H or the M-H proton is transferred to carbon. Complex (8a), however, does not exhibit such an isomerisation, implying that it is the N-H proton which is transferred.

Complex (8a) is also fluxional. Thus, the proton n.m.r. spectrum at -50°C exhibits the two doublets expected for the $CH(\underline{CH_3})_2$ group on the basis of a static structure. On warming, broadening and coalescence yield eventually a single sharp doublet at 0°C. The mechanism most likely responsible involves a concurrent flipping of the hydride ligand and twisting of the CH=NPr^i group (Scheme 8), thus generating an apparent plane of symmetry through the isopropyl moiety.



Scheme 8.

From the coalescence temperature of the isopropyl resonance, an activation energy of 52 kJ mol^{-1} is calculated.

An independent fluxional process is apparent from the ^{13}C n.m.r. spectra. On the basis of a static structure, all nine carbonyls are inequivalent. At -60°C, the ^{13}C spectrum exhibits five sharp resonances at 209.0, 207.2, 205.8, 204.1 and 202.4 ppm in the ratio of 1:1:2:1:1 , together with a much broader resonance at 210.9 ppm which broadens further on cooling to -90°C. The proton coupled spectrum shows that all the sharp resonances exhibit proton coupling, and that the resonance of relative intensity two is in fact two coincident resonances. Thus, the broad peak at 210.9 ppm is assigned to the $Fe(CO)_3$ moiety not involved in the M-H-M bridge. The broadness indicates a significantly lower barrier for polytopal rearrangement of the carbonyl ligands at this iron atom. Warming to room temperature results in broadening and coalescence to yield two signals in the ratio of 2:1 at 207.8 and 206.2 ppm, consistent with polytopal exchange of carbonyls at each iron atom, accompanied by the flipping of the metal hydride and $CH=NPr^i$ ligand described earlier. Carbonyl exchange between the iron atoms is not evident. Throughout, the $\underline{C}H=NPr^i$ resonance at 174.9 ppm remains sharp.

As discussed in Chapter 1, the use of metal clusters in the catalytic hydrogenation of CO or CNR must initially involve a reduction of the $C\equiv O$ or $C\equiv NR$ bond order. The results discussed above demonstrate the partial reduction of the $\bar{C}\equiv\overset{+}{N}R$ bond on an anionic cluster by alkylation or M-H insertion. Thus, the triiron clusters discussed in this Chapter may not only serve as models for surface catalysed hydrogenation of isonitriles, but they can also be regarded as supports on which such reactions may occur.

By coordination of the isonitrile to a metal atom followed by alkylation or protonation, the CN bond order has been reduced. Further reduction of the CN bond followed by release of the organic group from the complex will thus provide a potential method for the reduction of isonitriles on metal complexes. Therefore, it would be interesting to investigate reactions of coordinated isonitriles with the hope of finding a general method for their reduction on cluster complexes.

Attempted preparation of complexes of the type $HFe_2(CO)_7(CNR_2)$ by isonitrile substitution of the anion $HFe_2(CO)_8^-$, followed by alkylation, resulted in the isolation of trinuclear complexes. Thus, the reaction of $HFe_2(CO)_8^-$ with EtNC, followed by alkylation with $Et_3O^+BF_4^-$ gave $HFe_3(CO)_{10}CNEt_2$ as the major product with traces of $HFe_3(CO)_{10}COEt$ and $HFe_3(CO)_{10}CN(H)Et$ also being formed. Similarly, the reaction of the dianion $Fe_2(CO)_8^{2-}$ with EtNC, followed by alkylation with $Et_3O^+BF_4^-$ resulted in the formation of $HFe_3(CO)_{10}CNEt_2$ and $HFe_3(CO)_{10}CN(H)Et$ in approximately equal proportions. The attempted preparation of $Fe_2(CO)_6(CNEt_2)_2$ from the reaction of the dianion with $[Cl_2CNEt_2]Cl$[33] gave $Fe_3(CO)_{12}$ as the only product.

The formation of trinuclear complexes from the reactions of binuclear compounds is not completely unknown. For instance, Wilkinson[38] has recently reported the formation of $Fe_3(CO)_9(MeCO)^-$ (Fig. 26ii, page 24) from the interaction of $Fe_2(CO)_8^{2-}$ with methyl iodide. Also, it is known that the monoanion, $HFe_2(CO)_8^-$, decomposes to give the trinuclear anion $HFe_3(CO)_{11}^-$, and Collman et al[37] have proposed the following mechanism for the decomposition.

$$HFe_2(CO)_8^- \rightarrow HFe(CO)_4^- + [Fe(CO)_4]$$

$$[Fe(CO)_4] \rightarrow \tfrac{1}{2}[Fe_2(CO)_8]$$

$$[Fe_2(CO)_8] + HFe_2(CO)_8^- \rightarrow HFe_3(CO)_{11}^- + Fe(CO)_5$$

$$\overline{3HFe_2(CO)_8^- \rightarrow 2HFe(CO)_4^- + HFe_3(CO)_{11}^- + Fe(CO)_5}$$

It is probable that the formation of $Fe_3(CO)_{12}$ from $Fe_2(CO)_8^{2-}$ also involves neutral species produced in fragmentation reactions.

It has recently been reported[35,36] that the reaction of the tetranuclear dianion $[Fe_4(CO)_{13}][PPN]_2$ with methylating agents gives $[Fe_4(CO)_{12}COMe]PPN$ in which the COMe ligand μ_3- caps a face of the Fe_4 tetrahedron (Fig. 8).

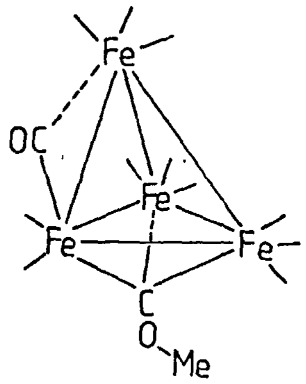


Fig. 8

Protonation of the methylated anion gives $HFe_4(CO)_{12}COMe$, in which the COMe group coordinates to the Fe atoms via the C and O atoms.

It would thus seem reasonable to assume that the reaction of $HFe_4(CO)_{13}^-$ with isonitrile, followed by alkylation would yield a tetranuclear complex containing a CNR_2 moiety. However, such a reaction using EtNC and $Et_3O^+BF_4^-$ gave the trinuclear complex, $HFe_3(CO)_{11}CNEt_2$ as the major product, with a trace of $HFe_3(CO)_{10}COEt$. A similar degradation is known to occur when $Fe_4(CO)_{13}^{2-}$ reacts with NaOH and aqueous NH_4Cl to give $HFe_3(CO)_{11}^-$ [40].

In order to fully ascertain the identity of the decomposition product of $HFe_3(CO)_{10}CN(H)Pr^i$, the monosubstituted complex $Fe_3(CO)_{11}(CNPr^i)$ was prepared by the room temperature reaction of $Fe_3(CO)_{12}$ and Pr^iNC. The infrared spectrum of the product thus obtained was found to be identical to that of the decomposition product of $HFe_3(CO)_{10}CN(H)Pr^i$. The spectrum in hexane shows a terminal isonitrile band at 2175 cm^{-1}, terminal carbonyl bands at 2079 (w), 2059 (m), 2038 (s), 2031 (s), 2010 (m), 1995 (m) and 1969 (m) cm^{-1}, and bridging carbonyl bands at 1815 (w) and 1813 (w) cm^{-1}. Comparison of this spectrum with that of pure $Fe_3(CO)_{11}CNBu^t$, which has previously been prepared by treatment of $Fe_3(CO)_{12}$ with Bu^tNC [39], and of $Fe(CO)_4CNPr^i$ [41] (Fig. XIII), indicates $Fe_3(CO)_{11}CNPr^i$ to contain $Fe(CO)_4(CNPr^i)$ as an impurity. At room temperature, $Fe_3(CO)_{11}(CNPr^i)$ decomposes in solution completely over a period of hours to give $Fe(CO)_4(CNPr^i)$, the infrared spectrum of which in hexane shows the following bands: ν_{CN} 2173 cm^{-1}, ν_{CO} 2059 (s), 1995 (s), 1969 (s) and 1929 (w) cm^{-1}. The spectrum of $Fe_3(CO)_{11}(CNPr^i)$ shows no presence of bridging isonitrile ligands and so, the complex probably exists in solution as a mixture of the four isomers shown in Fig. 9 .

In order to study the effect of CNR on the rate of exchange of CO between different sites, a ^{13}C n.m.r. study of $Fe_3(CO)_{11}(CNPr^i)$ was carried out. At -80°C, the spectrum (Fig. XIV) shows a single carbonyl resonance at 210.7 ppm and a single $CNPr^i$ resonance at 147.6 ppm. The $\underline{C}H$ and $\underline{C}H_3$ resonances have chemical shifts of 21.1 and 48.5 ppm respectively. Thus, even at this low temperature, carbonyl scrambling between metal atoms is still fast on the n.m.r. time scale. That the complex decomposes to $Fe(CO)_4(CNPr^i)$ can be seen from the appearance of a resonance at 213.7 ppm, which increases in

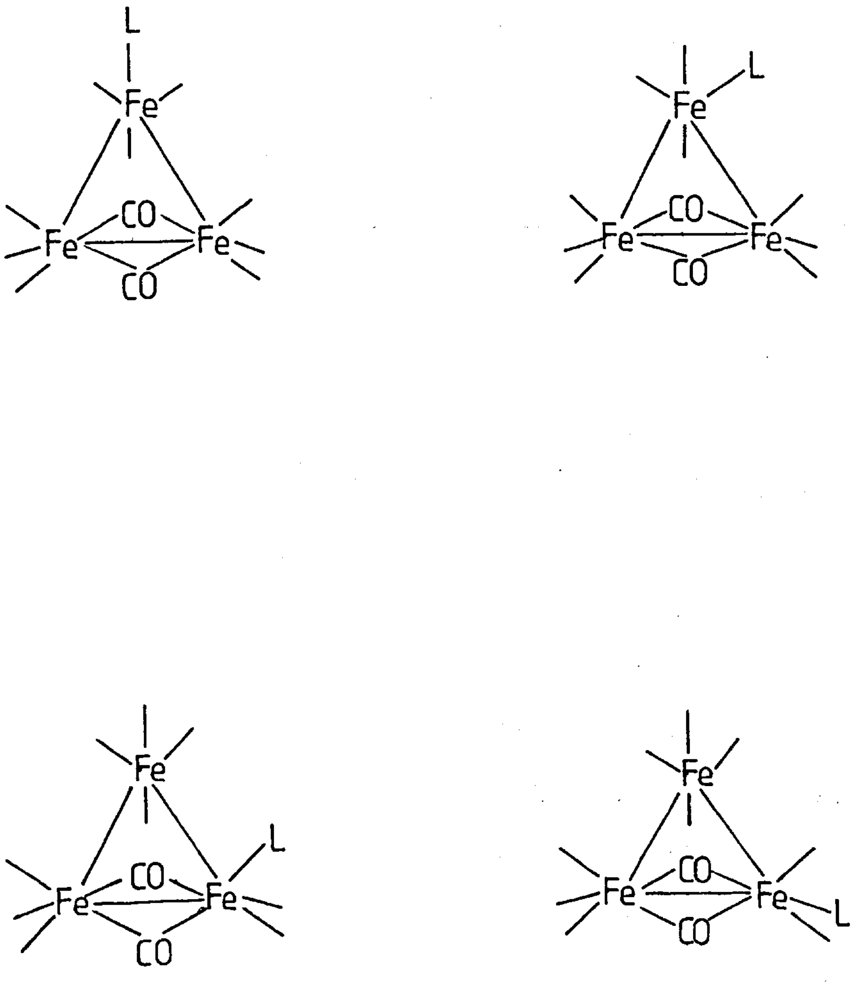
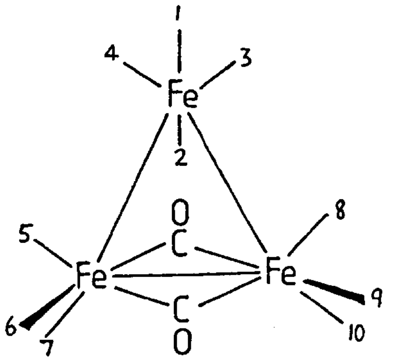


Fig. 9.

intensity with time. The spectrum of pure $Fe(CO)_4(CNPr^i)$ at 0°C exhibits resonances at 212.2, 152.4, 49.6 and 22.4 ppm, assignable to CO, $\underline{C}NPr^i$, CH and CH_3 respectively. It is interesting to note that in the spectrum of $Fe(CO)_4(CNPr^i)$, C-N coupling is retained (J_{CN} 19.5 Hz) after coordination of the isonitrile to the metal. Isonitriles are one of the few compounds to show clear CN coupling, with J_{CN} in free isonitriles being of the order of 6 Hz. This is the first case in which we have resolved the coupling in a complexed isonitrile, although it may be observed that resonances of complexed isonitriles are generally broader than carbonyl resonances.

Prolonged reaction of $Fe_3(CO)_{12}$ with Pr^iNC produced the disubstituted complex, $Fe_3(CO)_{10}(CNPr^i)_2$. The greater stability of this complex enabled it to be purified by chromatography and recrystallisation to give a green crystalline solid, which was characterised by i.r. and n.m.r. spectroscopy. The infrared spectrum in hexane shows two terminal isonitrile bands at 2157 and 2143 cm^{-1}, terminal carbonyl bands at 2053 (m), 2023 (s), 2012 (s), 2007 (sh), 1987 (sh), 1981 (m) and 1977 (sh) cm^{-1}, and bridging carbonyl bands at 1833 (w) and 1797 (w) cm^{-1}. The spectrum is identical to that reported for the analogous Bu^tNC complex[39]. There is no evidence for bridging isonitrile and the possible isomeric forms in which the complex may exist are summarised in Fig. 10 .



Possible sites of the two isonitrile ligands:

1,2	1,5 1,8 2,7 2,10	1,6 1,9 2,6 2,9	1,7 1,10 2,5 2,8	3,5 3,7 4,8 4,10	3,8 3,10 4,5 4,7
1,3 1,4					
3,4					
3,6 4,9	3,9 4,6	5.6 8,9	5,7 8,10	5,8 7,10	5,9 6,8
	5,10 8,7	6,9			

Fig. 10. Possible isomers of $Fe_3(CO)_{10}(CNPr^i)_2$

^1H n.m.r. spectrum of $Fe_3(CO)_{10}(CNPr^i)_2$ in $CD_2C\ell_2$ at 0°C (Fig. XVI) shows a $CH(\underline{CH_3})_2$ doublet at δ 1.46 ppm and a $\underline{CH}(CH_3)_2$ septet at δ 4.18 ppm. The ^{13}C spectrum (Fig. XVII) at room temperature shows a single $\underline{C}NPr^i$ resonance at 153.4 ppm and a single broadened CO resonance at 216.6 ppm which on cooling to -80°C yields the spectrum shown in Fig. XVII. As no characteristic resonance due to bridging CO (c.a. 270 ppm) is yet evident, it is obvious that a limiting low temperature spectrum has not been reached, but because of the obvious presence of isomers, it is not possible to draw any definite conclusions, except to say that increasing isonitrile substitution again results in an increase in the activation energy to carbonyl scrambling.

III Experimental

The same reaction conditions and instrumentation were employed as specified in Chapter 2. $[HFe_3(CO)_{11}][NHEt_3]$[32], $Fe_3(CO)_{12}$[42], $[PPN]C\ell$[43], $[C\ell_2CNEt_2]C\ell$[33], Et_3OBF_4[44], $[Fe_2(CO)_8][Et_4N]_2$, $[HFe_2(CO)_8][Et_4N]$[40] and $[HFe_4(CO)_{13}][Hpy]$[45] were prepared as described in literature. All other chemicals were purchased commercially. Proton decoupled ^{13}C spectra were run in the presence of $Cr(acac)_3$; coupled spectra were run without $Cr(acac)_3$ at low temperature (< - 50°C) using slightly longer pulse intervals. Spectra at or below room temperature were run in $CD_2C\ell_2$; those above room temperature were run in $C_6D_5CD_3$.

Preparation of $[PPN][HFe_3(CO)_{11}]$ (2)

This compound has been reported[22], but details of its preparation have not been given. To a solution of $[HNEt_3][HFe_3(CO)_{11}]$ (36 g, 0.062 mol) in $CH_2C\ell_2$ (200 ml) was added $[PPN]C\ell$ (50 g, 0.087 mol) and the mixture was stirred at room temperature for 3 hours. The solvent was removed to give a red oily mass which solidified on addition of 20 ml of petroleum ether.

The crude product was washed several times with warm water and dried in vacuo to give, after recrystallisation from $CH_2C\ell_2$-petroleum ether, dark red-purple crystals (45 g, 72%).

$[HFe_2(CO)_8][PPN]$, $[Fe_2(CO)_8][PPN]_2$ and $[HFe_4(CO)_{13}][PPN]$ were prepared similarly from $[HFe_2(CO)_8][NEt_4]$, $[Fe_2(CO)_8][NEt_4]_2$ and $[HFe_4(CO)_{13}][Hpy]$ respectively.

Preparation of $HFe_3(CO)_{10}(CNEt_2)$ (4a)

[PPN][$HFe_3(CO)_{11}$] (5 g, 5 mmol) and 1.80 ml (20 mol) of EtNC were stirred in 100 ml of $CH_2C\ell_2$ at room temperature. The reaction was monitored by reaction of 1 ml aliquots of the reaction mixture with Et_3OBF_4, followed by thin layer chromatography to detect the product $HFe_3(CO)_{10}(CNEt_2)$. When monosubstitution of the anion was complete, the $CH_2C\ell_2$ and the excess EtNC were removed in vacuo. The purple-red residue was dissolved in dichloromethane, and 1.2 g (5.5 mmol) of Et_3OBF_4 was added. The mixture was stirred at room temperature for 10 minutes, the solvent was evaporated off, and the residue was chromatographed on a silica gel column. Elution with petroleum ether-benzene (90:10) yielded a trace of red $HFe_3(CO)_{10}(COEt)$ followed by the purple $HFe_3(CO)_{10}(CNEt_2)$ (0.7 g, 26%). Further elution with petroleum ether-benzene (20:80) yielded a small amount of the substituted complex $HFe_3(CO)_9(CNEt)(CNEt)_2$ (7). This complex can be isolated as the major product if a larger excess of isonitrile is used, and the reaction is left for a longer period of time. The reaction is monitored by the method described above.

Complexes (4b-c) were prepared in an analogous manner, while (4d) was prepared similarly using Me_3OBF_4. Derivatives (4b-d) were purified by sublimation (0.1 mm, 80°C) or by crystallization from petroleum ether. $HFe_3(CO)_9(CNEt)(CNEt_2)$ would not crystallize and was purified by preparative t.l.c. $HFe_3(CO)_{10}(COEt)$ may be prepared in 79% yield by an analogous alkylation of [PPN] [$HFe_3(CO)_{11}$].

Preparation of $HFe_3(CO)_{10}[CN(Me)H]$ (5a)

2.0 g (2 mmol) of $[PPN][HFe_3(CO)_{11}]$ and 0.22 ml (4 mmol) of MeNC were stirred in 50 ml $CH_2C\ell_2$ at room temperature until titration of an aliquot with Et_3OBF_4 indicated that monosubstitution was complete. Solvent and excess isonitrile were evaporated off, and the residue was dissolved in diethyl ether. 0.4 ml (2 mmol) of CF_3SO_3H dissolved in 10 ml of diethyl ether was added and the mixture was stirred at room temperature for 10 minutes. After evaporation of solvent, the residue was chromatographed on a silica gel column. Elution with petroleum ether yielded a trace of Fe_3-$(CO)_{12}$, after which the purple $HFe_3(CO)_{10}[CN(Me)H]$ was eluted with petroleum ether-benzene (90:10). The product was purified by preparative t.l.c.

Preparation of $HFe_3(CO)_9[C(H)NPr^i]$ (8)

A mixture of 7.5 g (7.5 mmol) of $[PPN][HFe_3(CO)_{11}]$ and 2.7 ml (29 mmol) of Pr^iNC were stirred in 150 ml of $CH_2C\ell_2$ at room temperature until titration with Et_3OBF_4 indicated that monosubstitution was complete. Solvent and excess isonitrile were removed, and the residue was dissolved in THF and heated at 40°C for 2 hours. 2 g (10 mmol) of CF_3SO_3H dissolved in 30 ml of diethylether was added at room temperature and the mixture was stirred for 30 minutes. After removal of solvent, the residue was chromatographed on a silica gel column. A trace of $Fe_3(CO)_{12}$ was eluted by using petroleum ether, while further elution using petroleum ether-benzene (90:10) yielded orange $HFe_3(CO)_9[C(H)NPr^i]$ which was recrystallized from petroleum ether (1.5 g, 41%).

Deuteration in the same manner using CF_3CO_2D yields the deuterated analogue $DFe_3(CO)_9[C(H)NPr^i]$.

Reaction of $Fe_3(CO)_{12}$ with Pr^iNC

A mixture of $Fe_3(CO)_{12}$ (1.1 g, 2.2 mmol) and Pr^iNC (0.30 cm^3, 2.6 mmol) in benzene (35 cm^3) was stirred at room temperature for 1 hour. The solvent and excess isonitrile were removed in vacuo and the resulting green mass was chromatographed on an alumina column (Grade II). Elution with a 5:95 mixture of dichloromethane and petroleum ether separated a trace of yellow $Fe(CO)_4(CNPr^i)$ from the green $Fe_3(CO)_{11}(CNPr^i)$. Further elution with 20:80 dichloromethane:petroleum ether mixture yielded the second green compound, the disubstituted $Fe_3(CO)_{10}(CNPr^i)_2$. $Fe_3(CO)_{11}(CNPr^i)$ decomposes in solution and in the solid state over a period of hours to $Fe(CO)_5$ and $Fe(CO)_4(CNPr^i)$. The disubstituted complex is more stable and was recrystallised from dichloromethane and petroleum ether to give dark green crystals with a yield of 0.31 g (22%).

$Fe_3(CO)_{11}(CNBu^t)$ was prepared in a similar manner.

Table 1. Analytical Data

Complex	C	H	N
(2)	55.7(55.6)	3.00(3.06)	1.39(1.38)
(4a)	33.7(33.8)	2.03(2.06)	2.66(2.63)
(4b)	32.5(32.4)	1.70(1.73)	2.66(2.70)
(4c)	35.0(35.2)	2.45(2.38)	2.79(2.56)
(4d)	34.0(33.8)	2.06(2.06)	2.80(2.63)
(5a)	30.7(29.3)	1.17(1.02)	2.66(2.85)
(7)	36.8(36.4)	3.05(2.86)	5.05(5.00)
(8a)	31.7(31.8)	1.72(1.83)	2.77(2.85)

$HFe_3(CO)_{10}COEt$ C 31·2 (30·8), H 1·06 (1·19)

Calculated values in parentheses

Table 2. Infrared Data (2200-1700 cm^{-1})

Complex	$\underline{\nu}_{CO}$
(2)[a]	2000(s), 1971(m), 1723(w).
(4a)[b]	2082(m), 2035(s), 2023(s), 2004(m), 1994(m), 1989(sh), 1974(m), 1958(m).
(4b)[b]	2082(m), 2035(s), 2023(s), 2004(m), 1994(m), 1989(sh), 1974(m), 1958(m).
(4c)[b]	2082(m), 2035(s), 2023(s), 2004(m), 1994(m), 1989(s), 1974(m), 1958(m).
(4d)[b]	2082(m), 2035(s), 2023(s), 2004(m), 1994(m), 1989(s), 1974(m), 1958(m).
(5a)[b]	2083(w), 2039(s), 2028(s), 2010(s), 1999(s), 1987(m), 1979(m), 1963(m).
(7)[b]	2058(m), 2016(s), 2008(s), 2000(m), 1993(m), 1990(m), 1982(m), 1976(s), 1972(sh), 1966(sh), 1960(m), 1950(w), 1938(w).
(8a)[b]	2083(w), 2051(s), 2021(s), 2011(s), 1995(m), 1987(w), 1967(w), 1959(w).
$HFe_3^-(CO)_{10}COEt$[b]	2087(w), 2045(s), 2033(s), 2012(s), 2003(sh), 1994(m), 1983(m), 1969(w), 1903(br)

[a] CH_2Cl_2 solution

[b] Hexane solution

Table 3. ^{1}H Nmr Spectral Data[a]

Complex	Temperature (°C)	M-H	Other	
(2)	+25	-15.0(s)	PPN	7.33-7.50(m)
(4a)	-60	-18.0(s)	$\underline{CH_2}CH_3$	4.32(q,J=7.5)
			$CH_2\underline{CH_3}$	1.42(t)
(4b)	-60	-18.0(s)	$\underline{CH_2}CH_3$	4.26(q,J=7.3)
			$CH_2\underline{CH_3}$	1.48(t)
			CH_3	3.88(s)
(4c)	-60	-18.0(s)	$\underline{CH_2}CH_3$	4.13(m)
			$CH_2\underline{CH_3}$	1.51(t,J=7.5)
			$CH(\underline{CH_3})_2$	1.51 1.41 (d,J=6.6)
			$\underline{CH}(CH_3)_2$	4.99(sept)
(4d)	-60	-18.0(s)	$CH(\underline{CH_3})_2$	1.37 1.50 (d,J=6.8)
			$\underline{CH}(CH_3)_2$	4.92(sept)
			CH_3	3.72(s)
(5a)[b]	+25	-18.0(d,J=2.5)	CH_3	2.7=(d,J=4.6)

(7)	-65	-17.2		$CN(\underline{CH_2}CH_3)_2$	4.29 (m)
		-17.4	(s)	$CN\underline{CH_2}CH_2$	3.55-3.97 (m)
		-17.5		$CNCH_2\underline{CH_3}$	1.38 (m)
				$CN(CH_2\underline{CH_3})_2$	
(8a)[b]	-50	-26.7(s)		$\underline{CH}NCH(CH_3)_2$	8.10(s)
				$CHN\underline{CH}(CH_3)_2$	2.38(sept)
				$CHNCH(\underline{CH_3})_2$	0.61 0.35 (d,J=6.8)

[a] $CD_2C\ell_2$ solution unless otherwise indicated; ppm from TMS; s = singlet, d = doublet, t = triplet, q = quartet, sept = septet.

[b] $C_6H_5CD_3$ solution

Table 4. ^{13}C Nmr Spectral Data[a]

Complex	Temperature (°C)	Terminal Carbonyls[b]	Other	
(2)[d]	-120	223.8(1)	μ-CO	285.7
		221.3(1)		
		219.3(2)		
		215.8(2)		
		210.4(2)		
		208.9(2)		
(3b)	-70	222.9(1)	μ-CO	279.4
		220.4(2)	$\underline{C}NEt$	160.5
		217.4(2)		
		211.7(2)		
		208.9(2)		
(4a)	-70	(aa') 215.6(2)(J=10.4)	CN	317.3(J=13.7)
		(bb') 204.8(2)(J=5.2)	$(\underline{CH_2}CH_3)_2$	57.4
		(cc') 211.2(2)(J=3.4)	$(CH_2\underline{CH_3})_2$	11.2
		(dd') 207.3(2)		
		(e) 218.3(1)		
		(f) 216.5(1)(J=3.5)		

(4b)	-70	(aa') 214.6(2)	CN	316.6
		(bb') 204.1,203.7(2)	CH_3	48.6
		(cc') 210.5(2)	$\underline{C}H_2CH_3$	62.1
		(dd') 206.5(2)	$CH_2\underline{C}H_3$	11.2
		(e) 217.4(1)		
		(f) 215.6(1)		
(4c)	-70	(aa') 214.9(2)	CN	318.4
		(bb') 204.2,204.4(2)	$\underline{C}H_2CH_3$	c
		(cc') 210.6,210.1(2)	$CH_2\underline{C}H_3$	13.4
		(dd') 206.5,205.7(2)	$\underline{C}H(CH_3)_2$	c
		(e) 217.6(1)	$CH(\underline{C}H_3)_2$	20.47, 19.0
		(f) 216.1(1)		
(7)	-60	205.1(s)	$\underline{C}N(CH_2CH_3)_2$	318.1, 319.6, 322.3
		207.5-209.9(m)	$\underline{C}NCH_2CH_3$	150.7, 154.7, 157.8
		211.7-213.4(m)	$CN\underline{C}H_2CH_3$	39.8-40.7(m)
		216.3-218.1(m)	$CN(\underline{C}H_2CH_3)_2$	c
		219.0-219.9(m)	$CN(CH_2\underline{C}H_3)_2$ $CNCH_2\underline{C}H_3$	11.9-14.6(m)

(8a)	-60	203.1(1)(J=9.4)	$\underline{C}H{=}N[CH(CH_3)_2]$	173.8
		204.8(1)(J=5.4)	$CH{=}N[\underline{CH}(CH_3)_2]$	69.7
		206.5(2)(m)	$CH{=}N[CH(\underline{CH}_3)_2]$	23.3, 26.1
		207.9(1)(J=9.2)		
		207.9(1)(J=9.2)		
		209.5(1)(J=13.6)		
		210.9(3)(broad)		

[a] $CD_2C\ell_2/CH_2C\ell_2$ solution; ppm from TMS

[b] relative intensities and coupling constants in parentheses; (a-f) refer to Figure 2.

[c] not detected; may be under solvent resonance at 53.8 ppm.

[d] data from reference 21.

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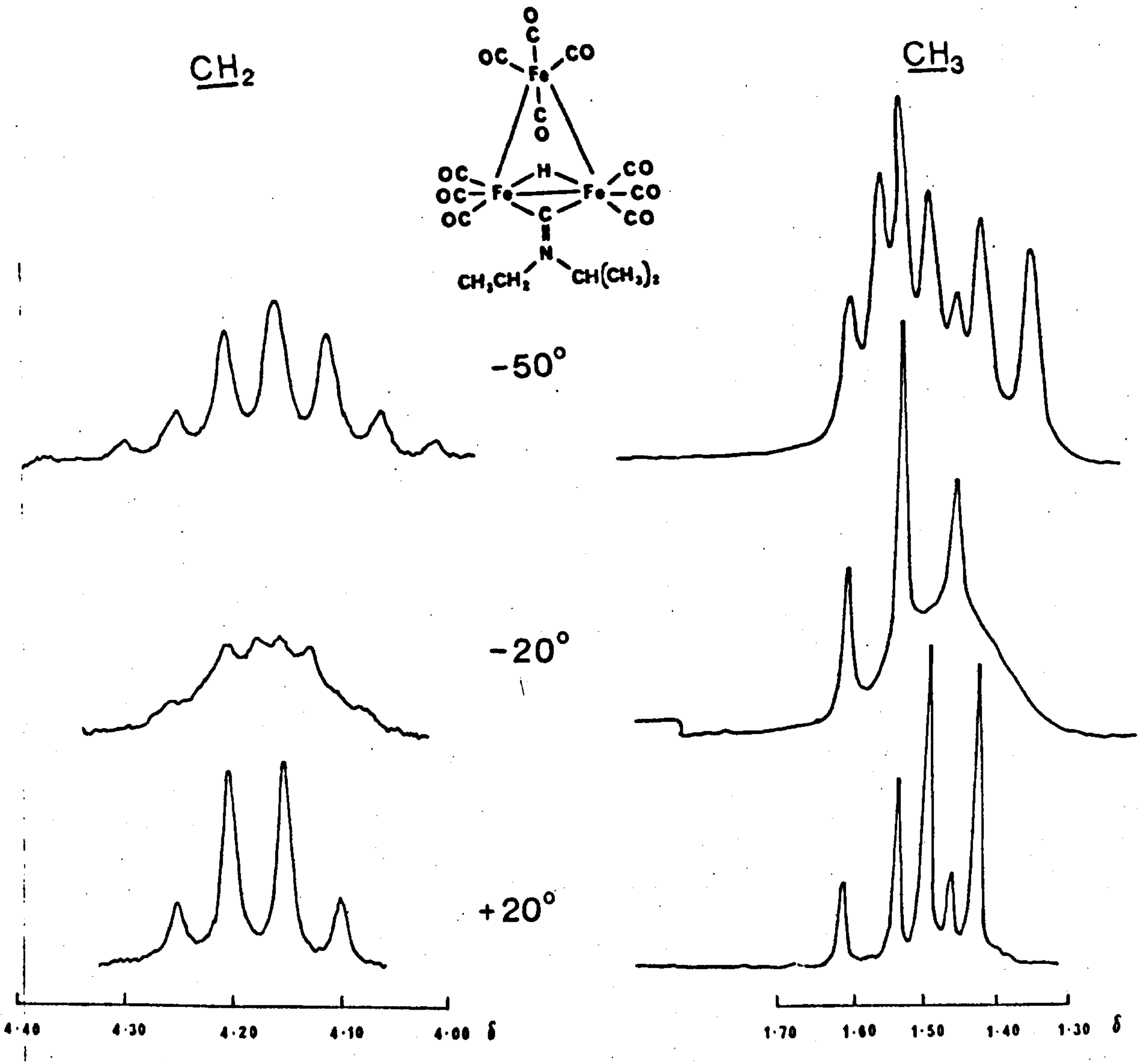
Fig I Variable temperature ^1H NMR spectra of (4c).



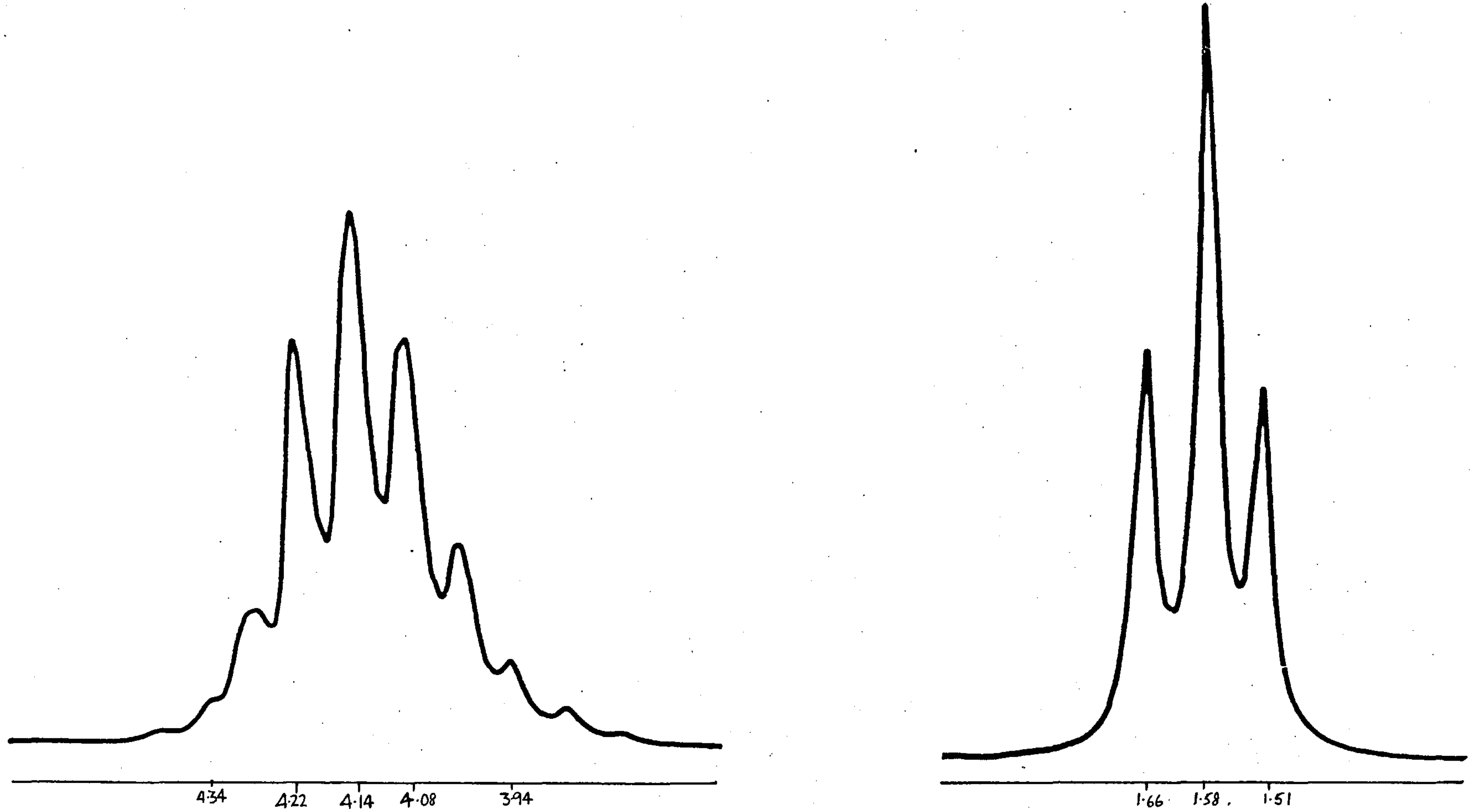


Fig II. Computer simulated spectrum of $HFe_3(CO)_{10}(CNEtPr^i)$.

Fig III. Variable temperature ^{13}C spectrum of (4a) (R' = R = Et).

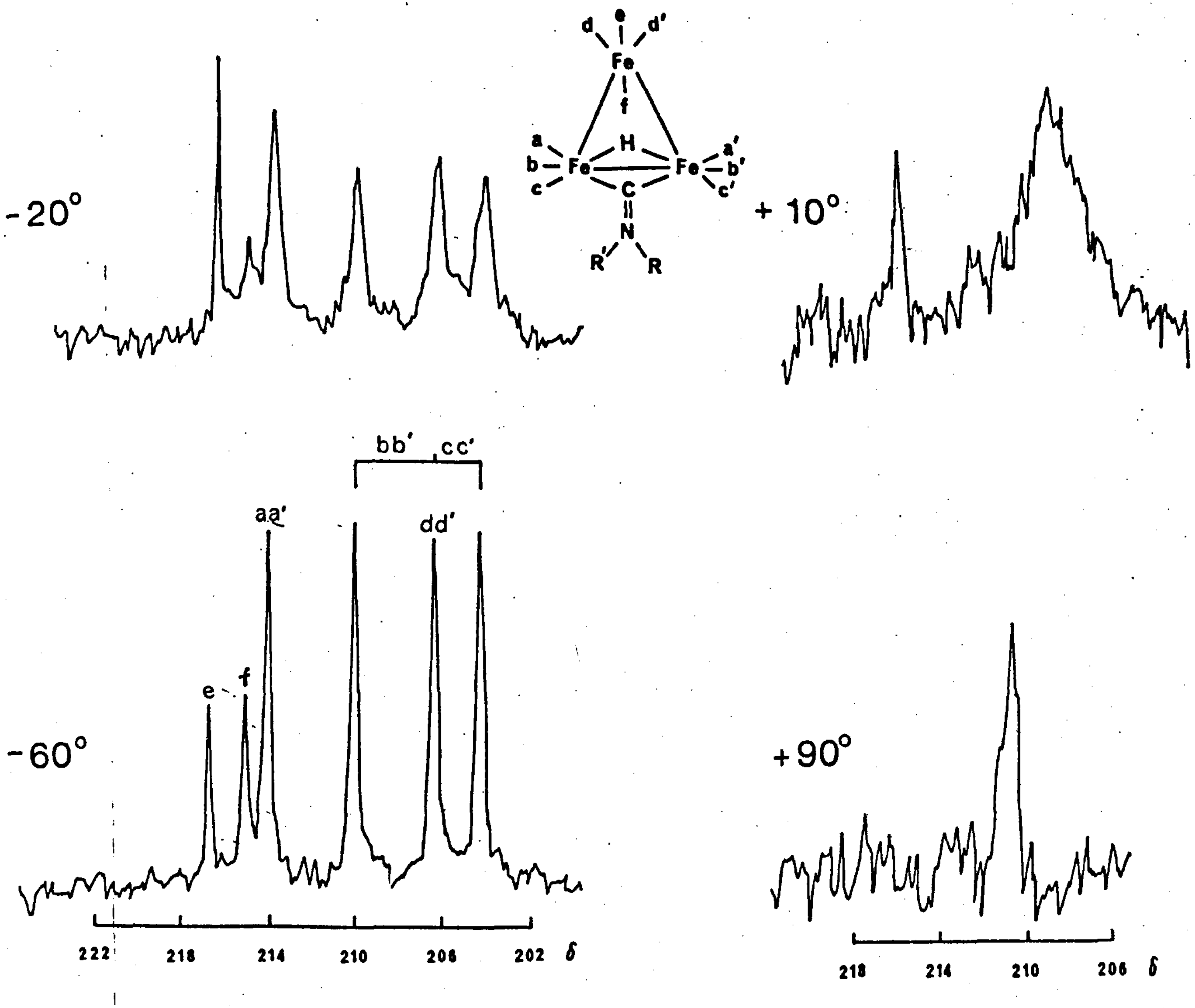
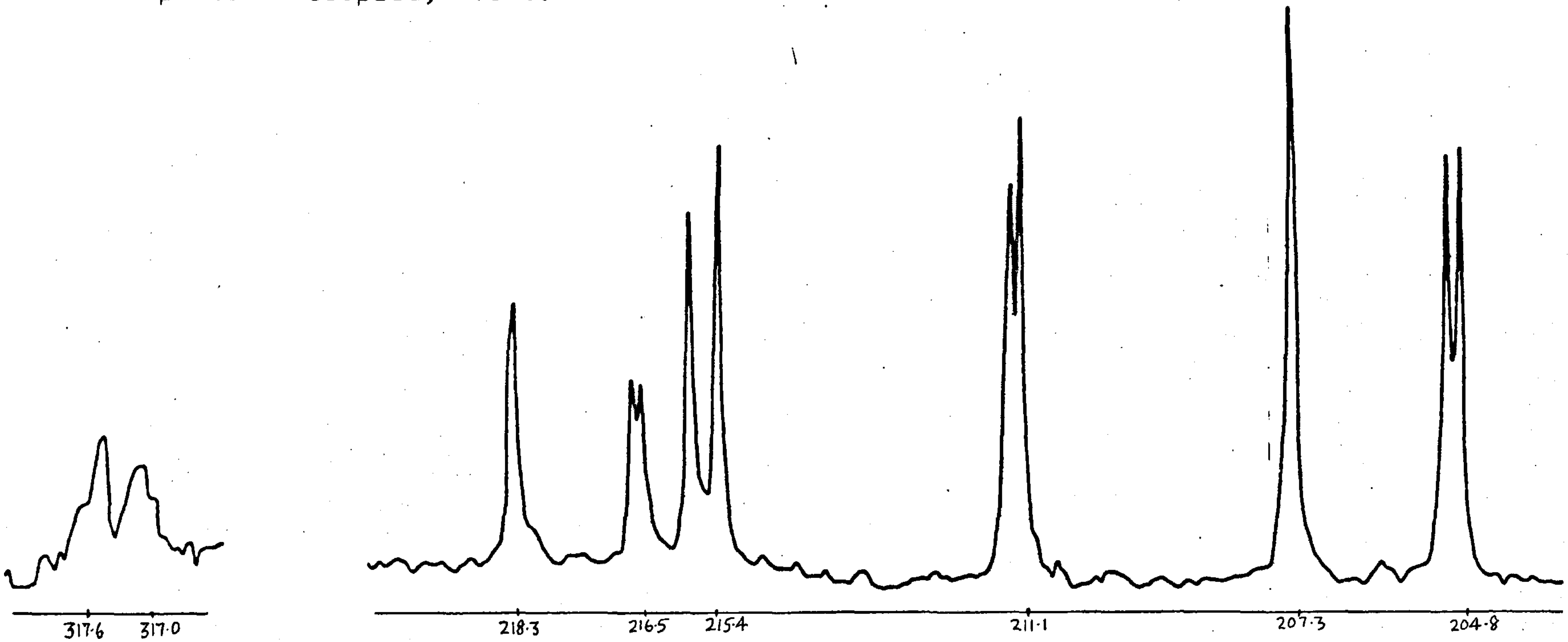


Fig IV ^{13}C NMR spectrum of $HFe_3(CO)_{10}(CNEt_2)$; CD_2Cl_2 /CH_2Cl_2 ; proton coupled; -70°C.



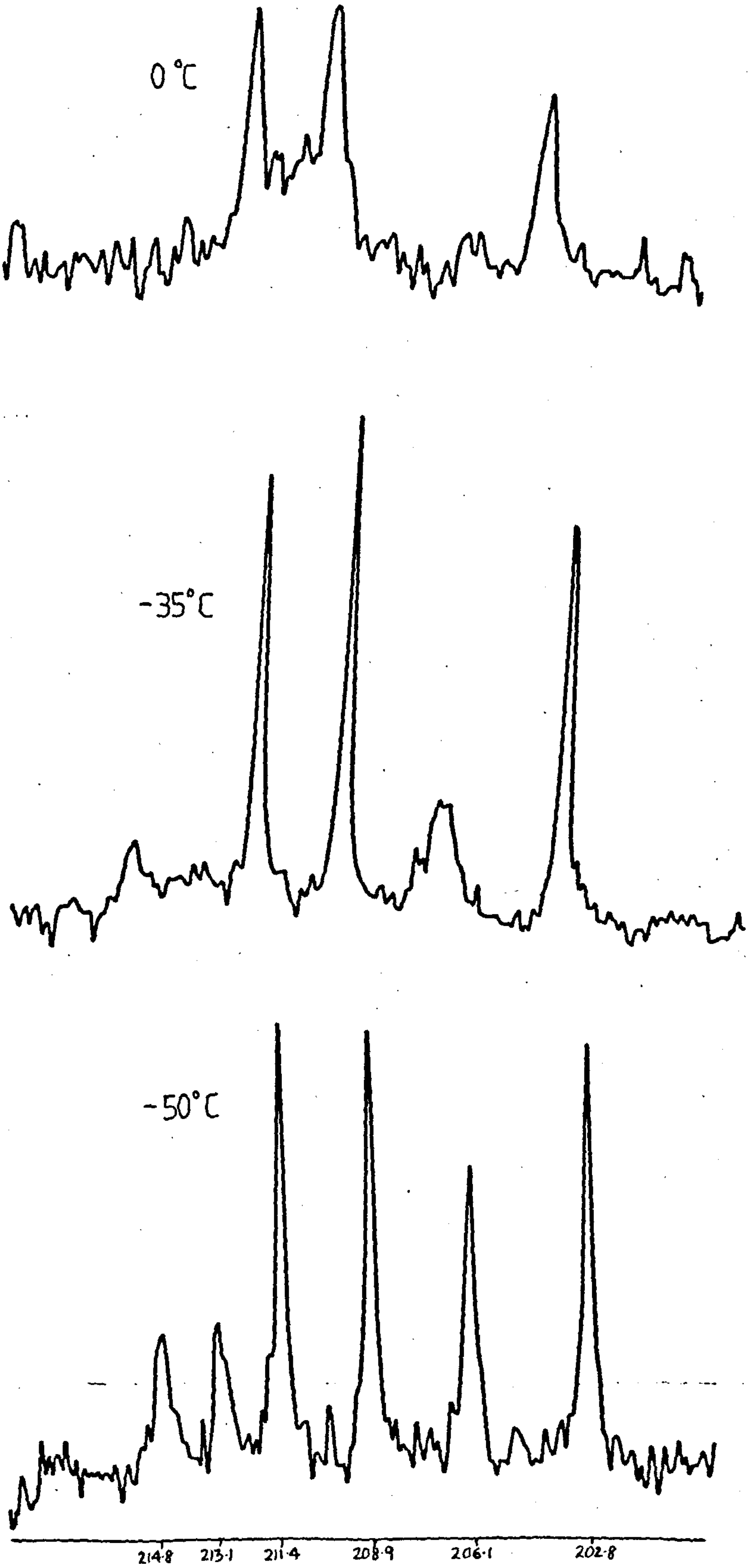


Fig V ^{13}C NMR spectrum of $HFe_3(CO)_{10}(COEt)$; proton decoupled; see also next page...

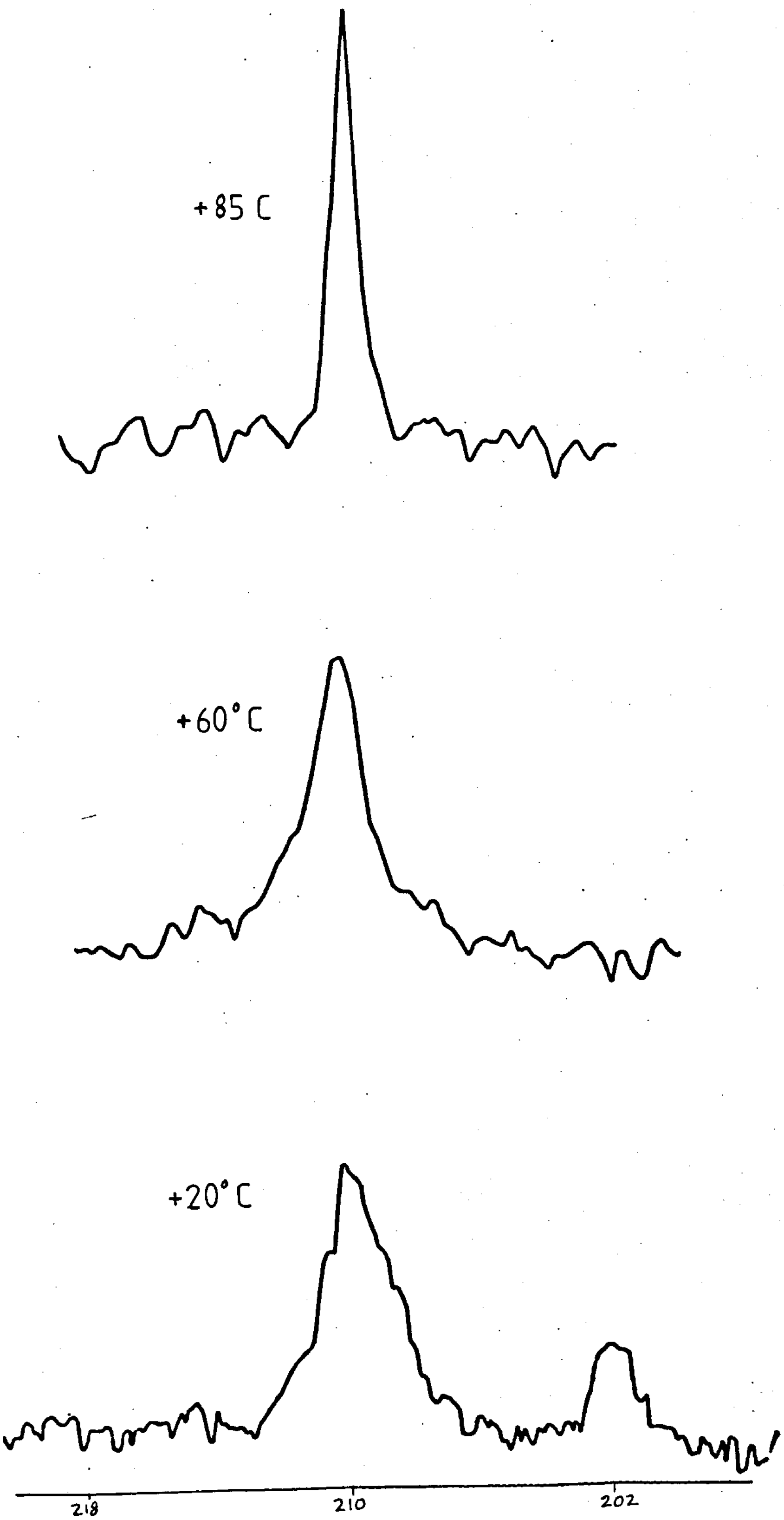


Fig V cont'd.

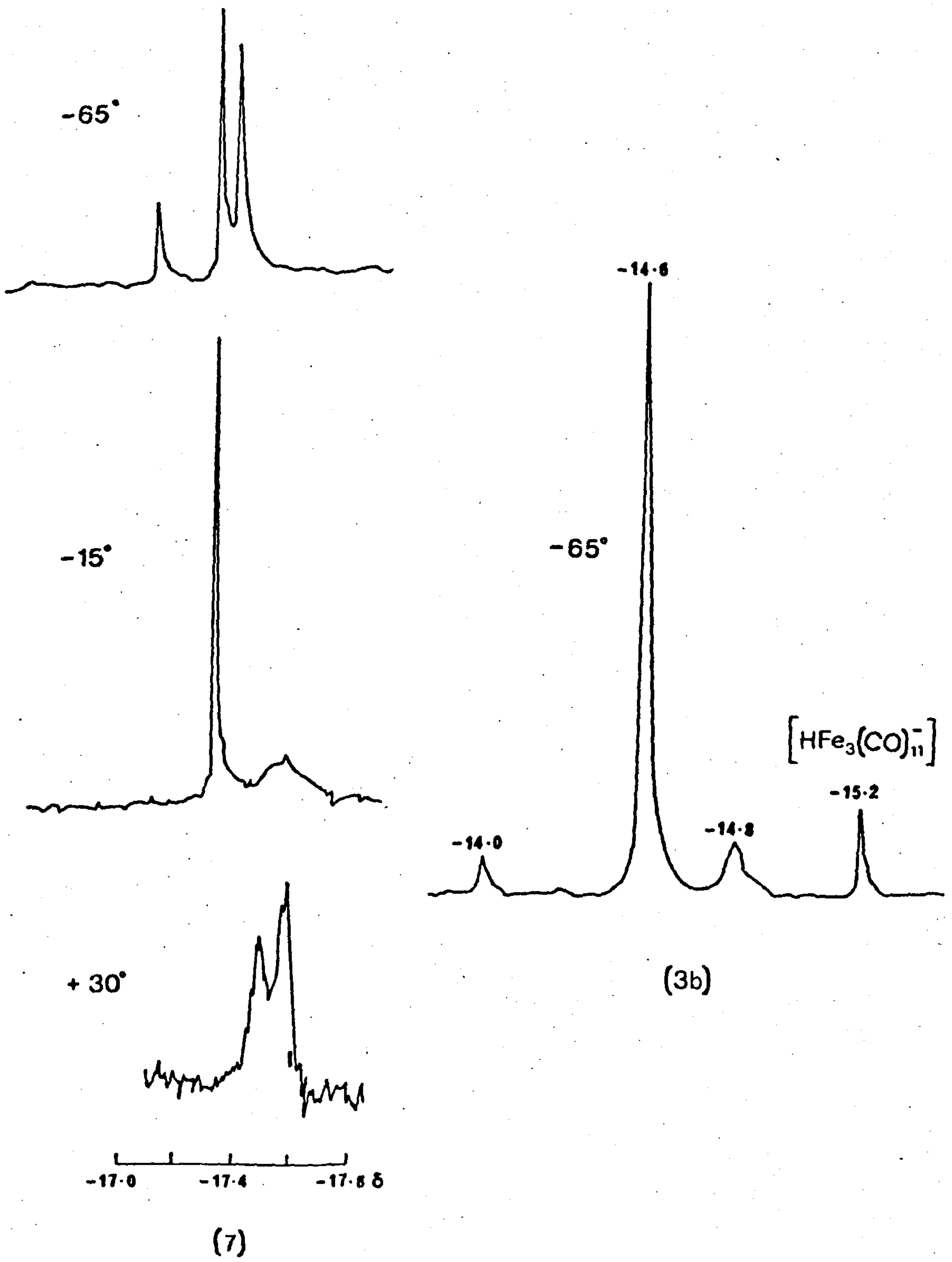


Fig VI. Variable temperature ^{1}H NMR spectrum of (7) and (3b) (Fe - H region only).

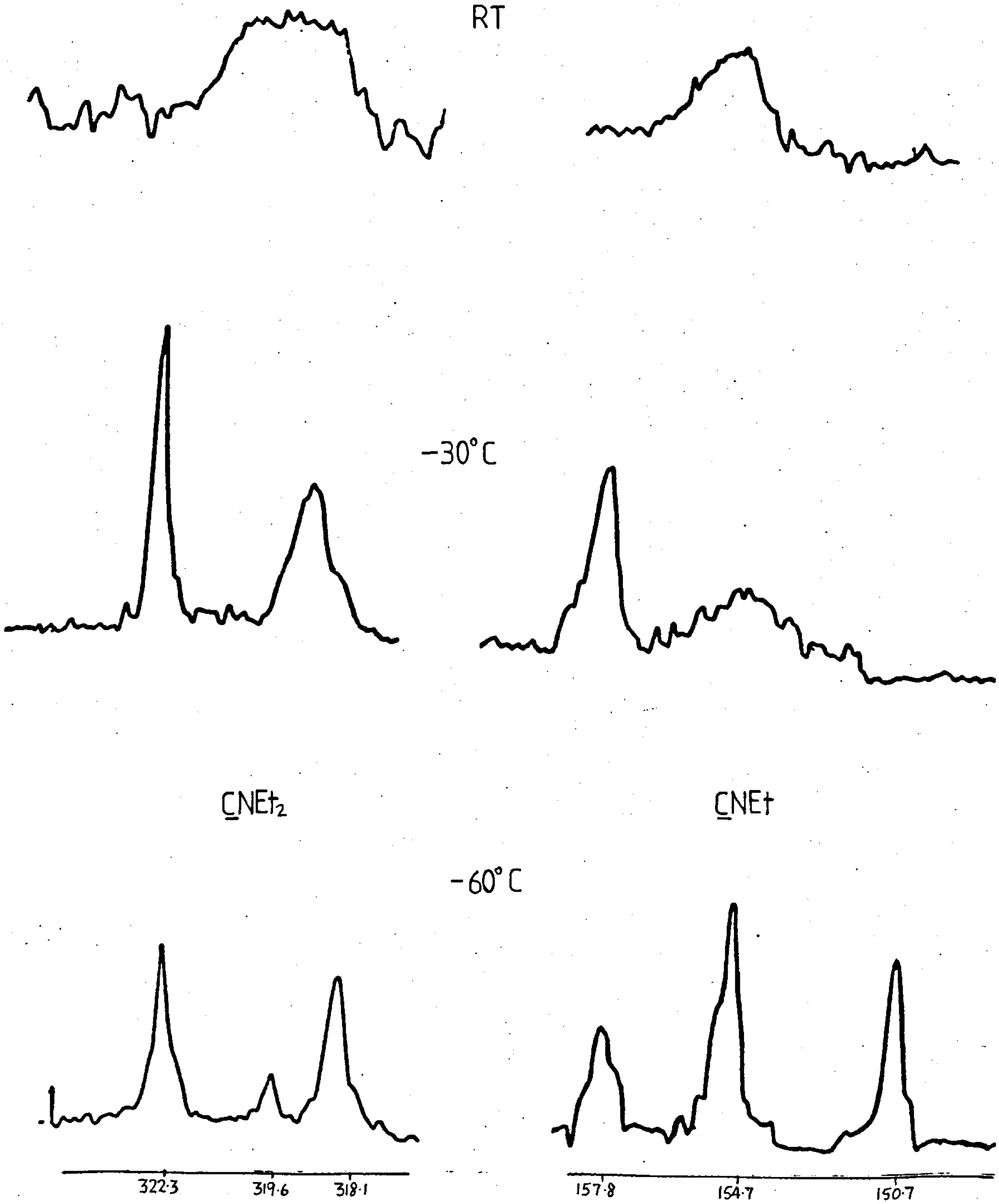


Fig VII. ^{13}C NMR spectra of $HFe_3(CO)_9(CNEt_2)(CNEt)$; proton decoupled.

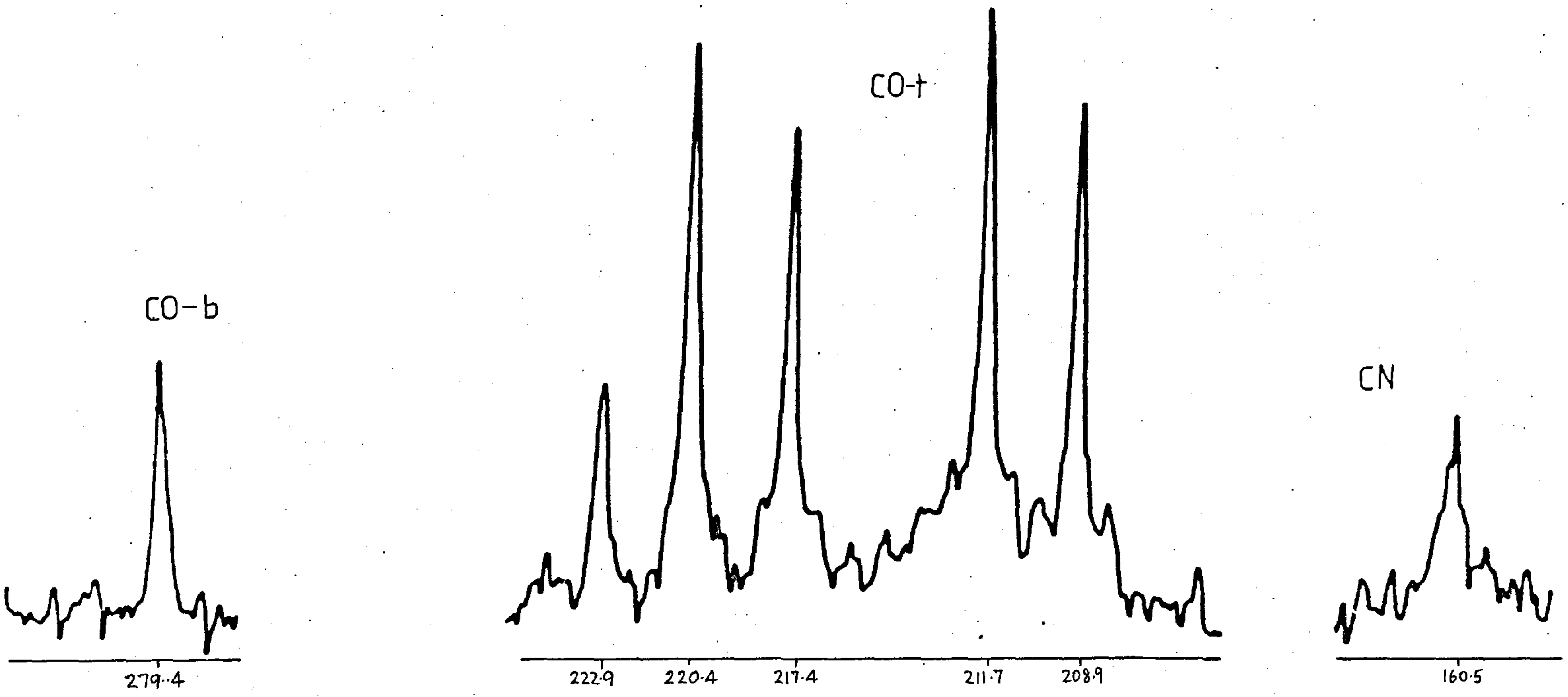


Fig VIII. ^{13}C NMR spectrum of $HFe_3(CO)_{10}(CNEt)^-$; CD_2Cl_2/CH_2Cl_2 ; proton decoupled; 0°C.

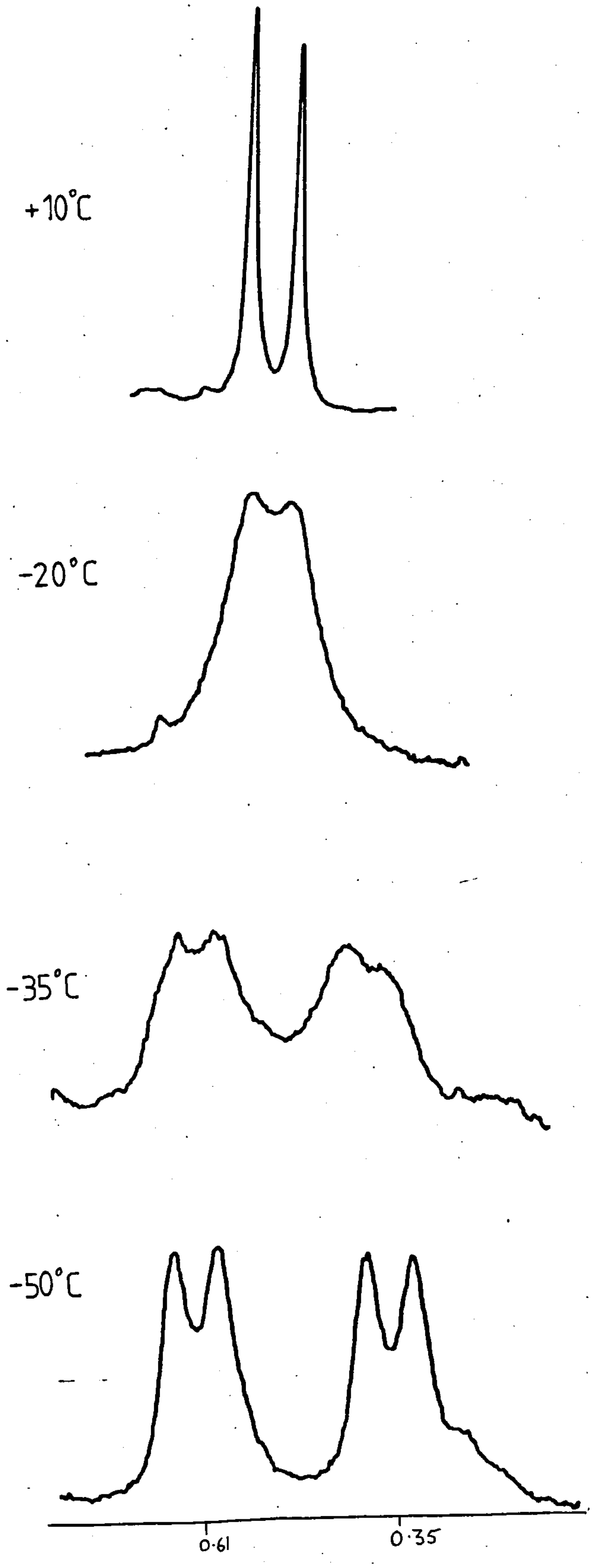
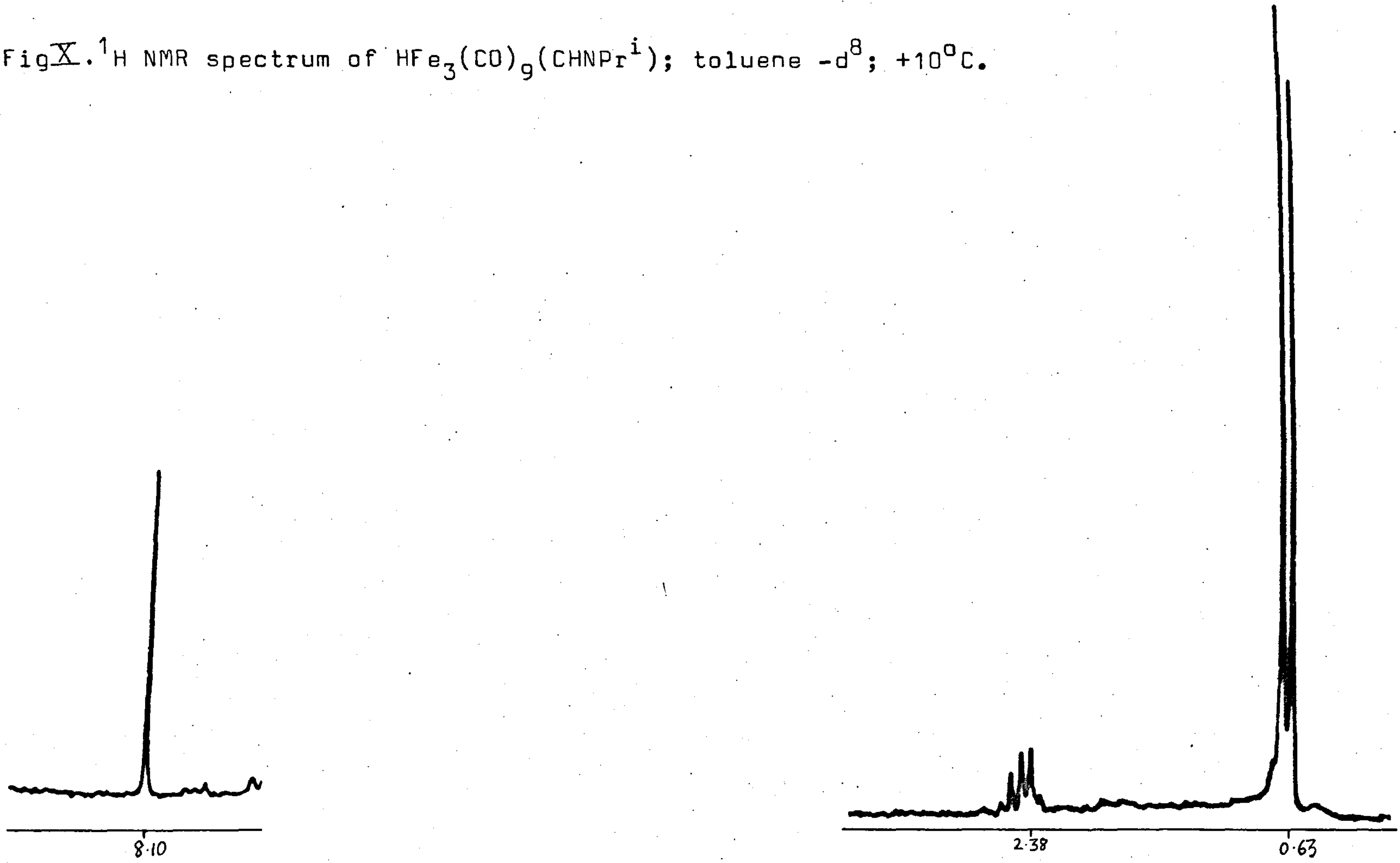


Fig IX. ^{1}H NMR spectrum of $HFe_3(CO)_9(CHNPr^i)$; toluene - d^8; CH_3 region only.

Fig$\underline{\text{X}}$. ^{1}H NMR spectrum of $HFe_3(CO)_9(CHNPr^i)$; toluene -d^8; +10°C.



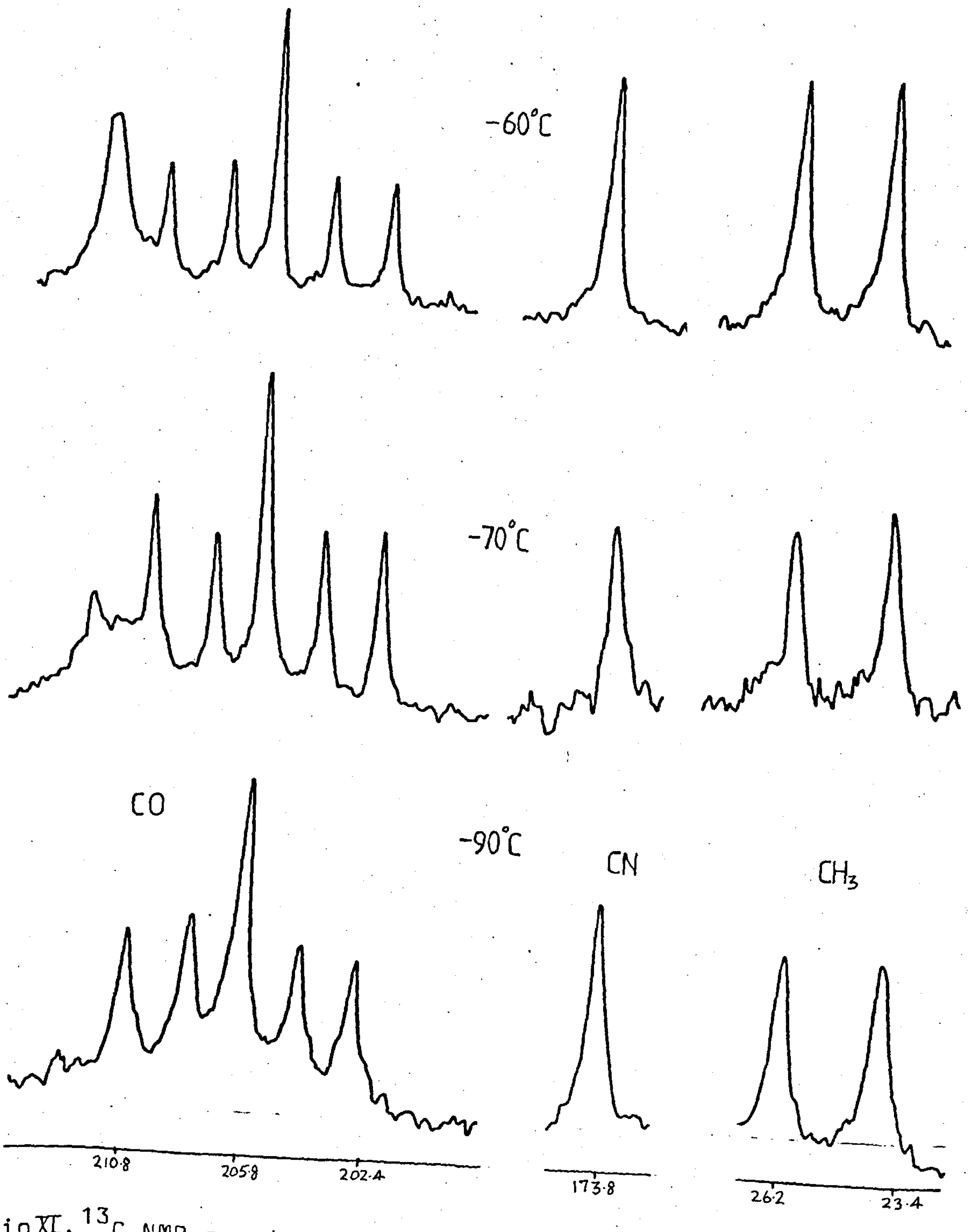


Fig XI. ^{13}C NMR spectra of $HFe_3(CO)_9(CHNPr^i)$; CD_2Cl_2 / CH_2Cl_2 .
(see also next page).

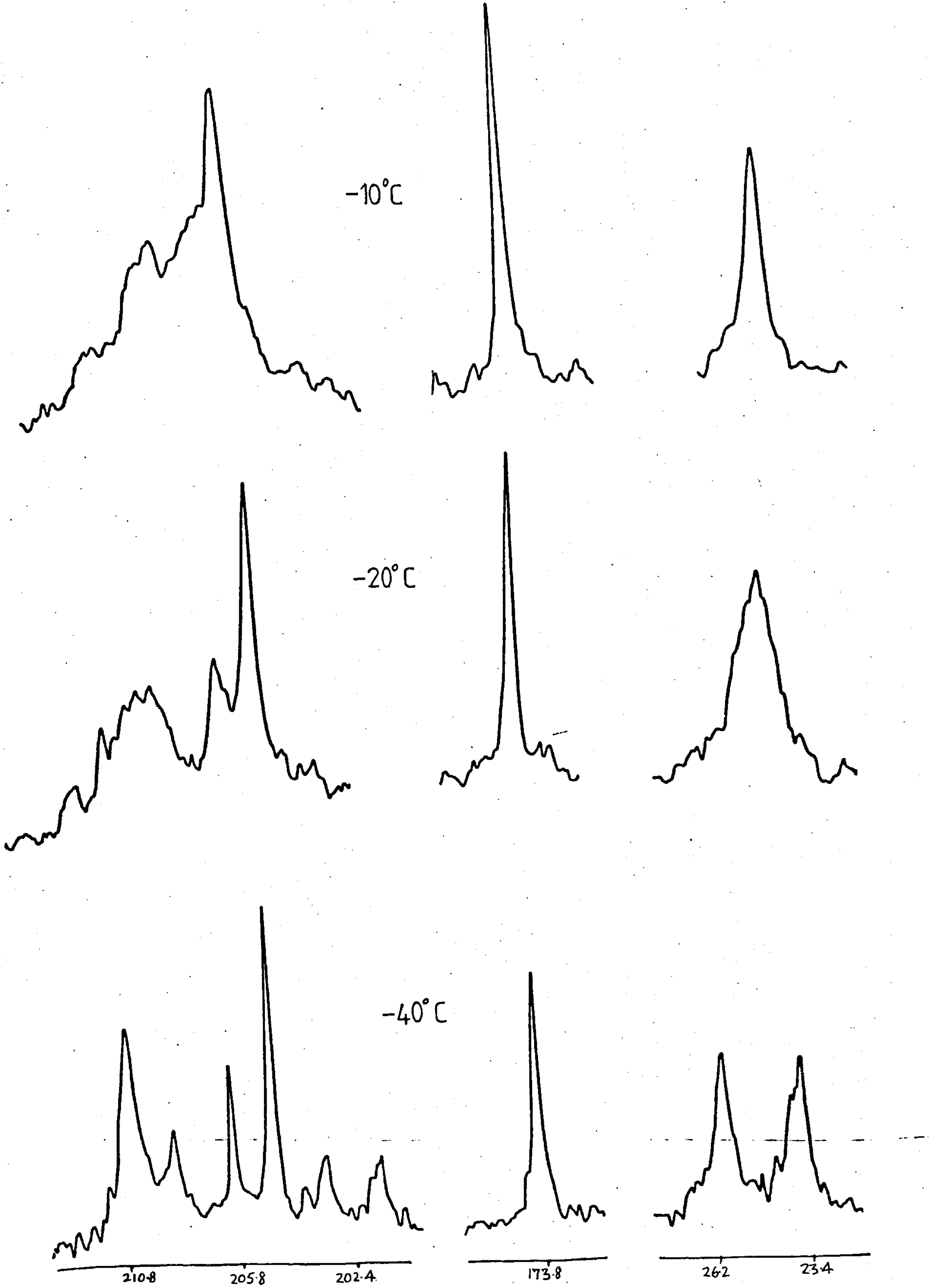


Fig XI. cont'd.

Fig XII. ^{13}C NMR spectrum of $HFe_3(CO)_9(CHNPr^i)$; CD_2Cl_2 ; -60°C; proton coupled.

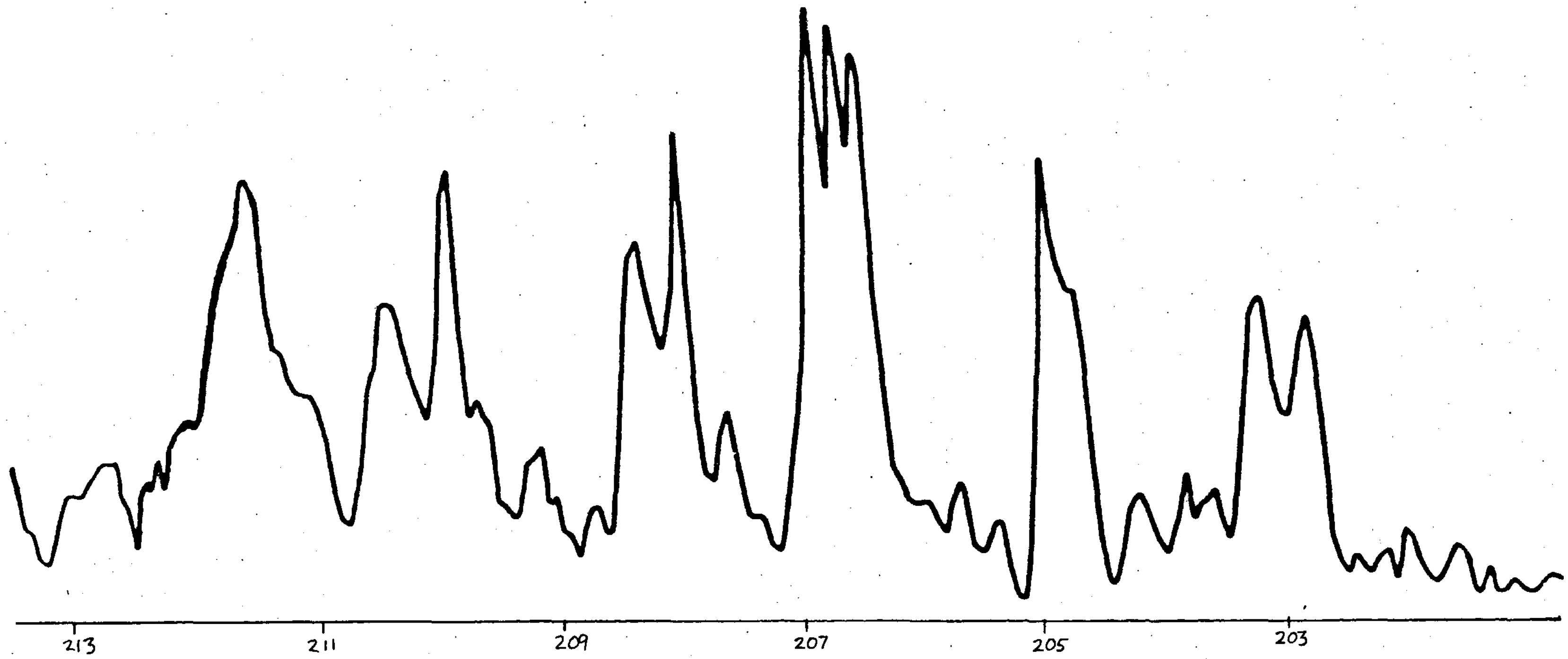


Fig XIII. Infrared spectra (CN and CO regions only).

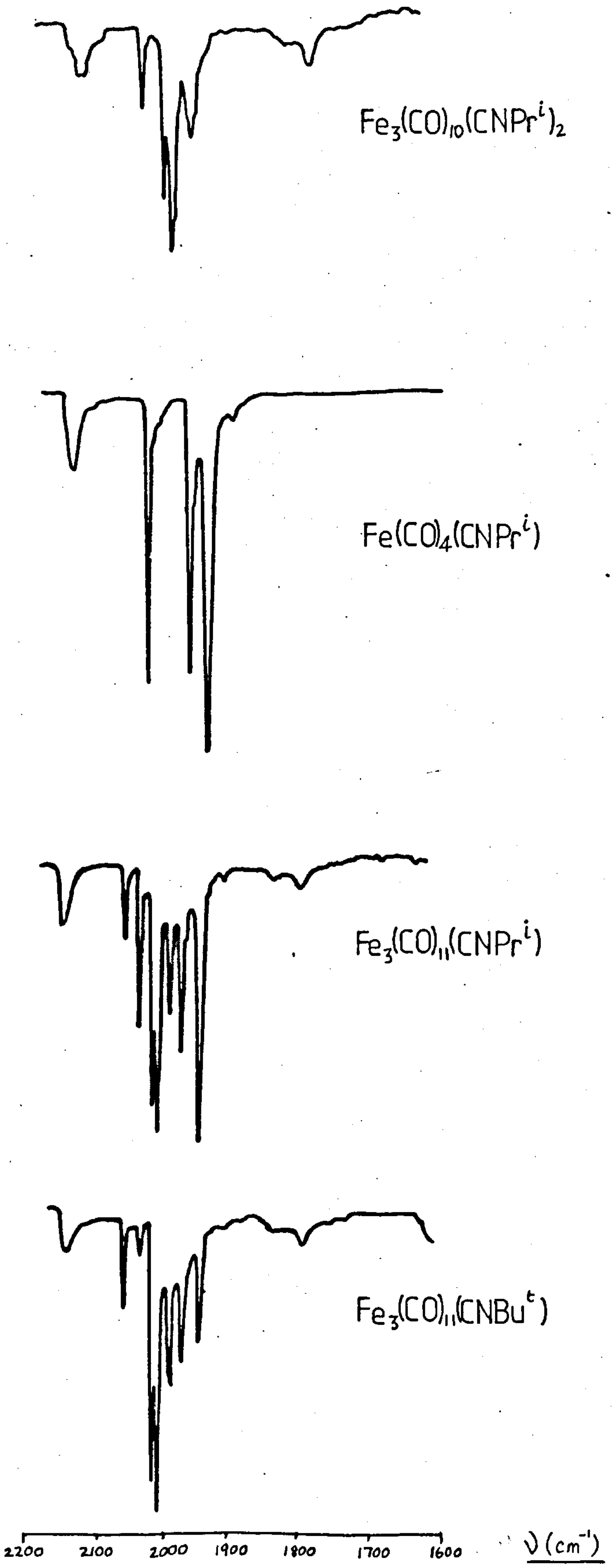


Fig.XIV. ^{13}C NMR spectrum of $Fe_3(CO)_{11}(CNPr^i)$; proton decoupled; 0^oC.

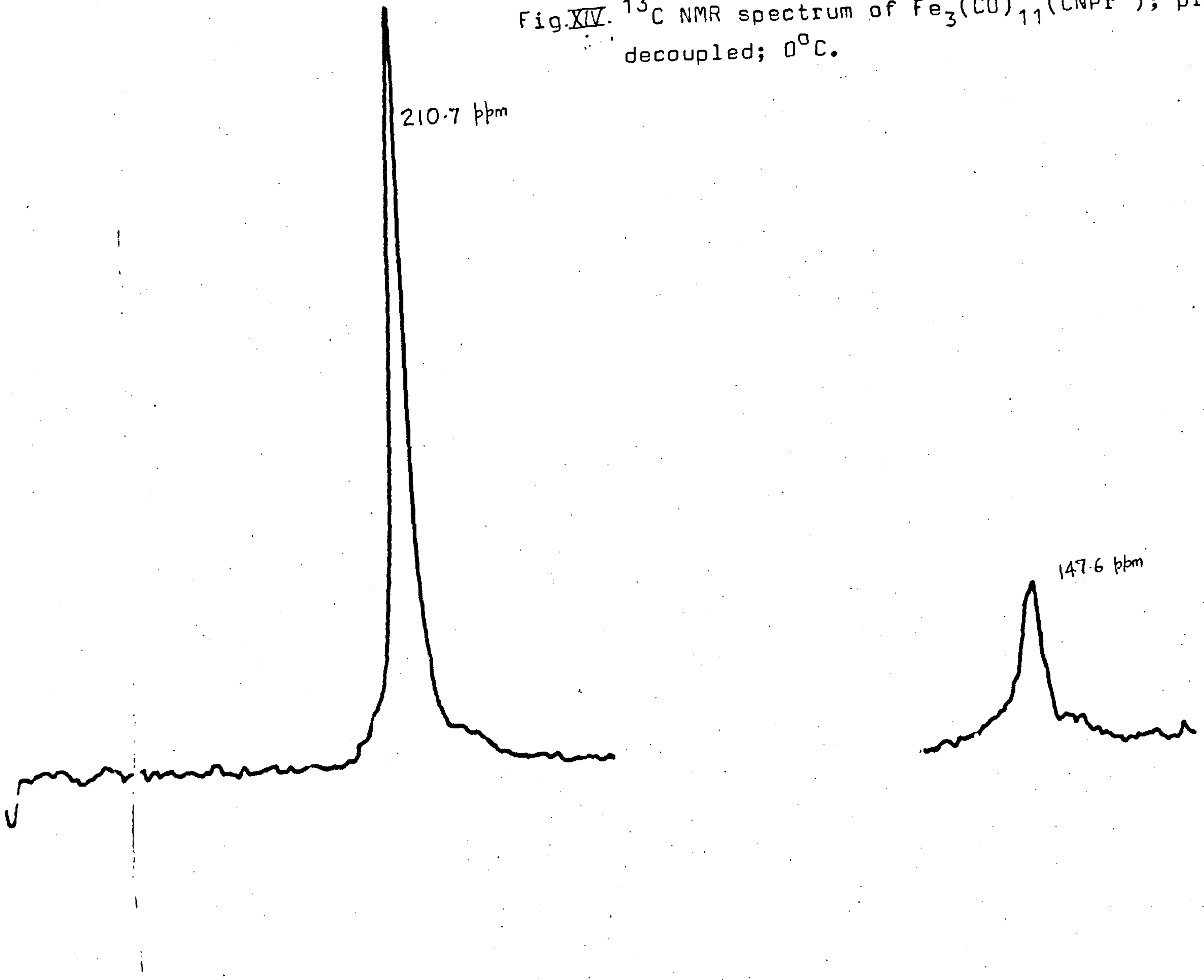


Fig XV. ^{13}C NMR spectrum of $Fe(CO)_4(CNPr^i)$; CD_2Cl_2/CH_2Cl_2 ; proton decoupled; 0°C.

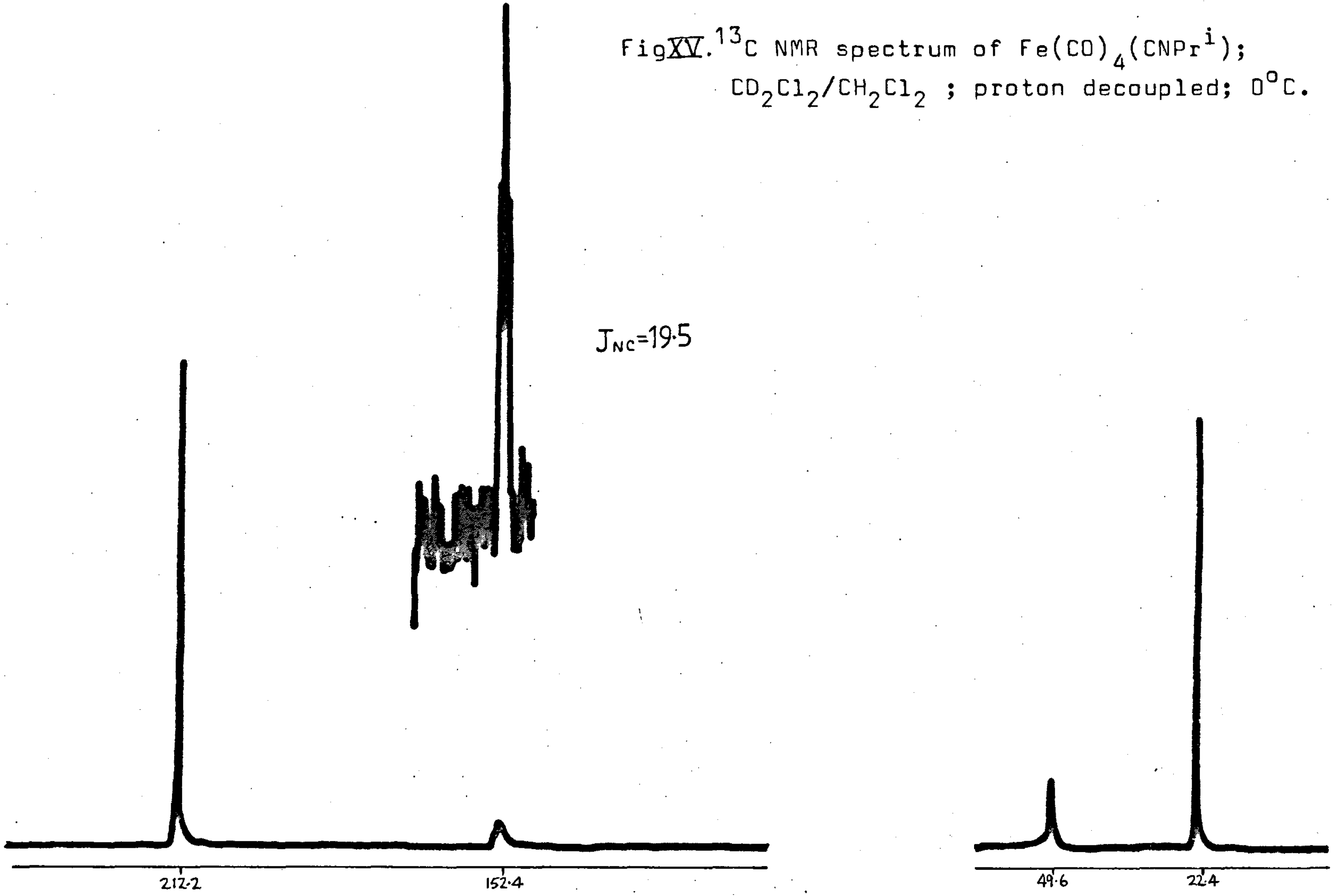
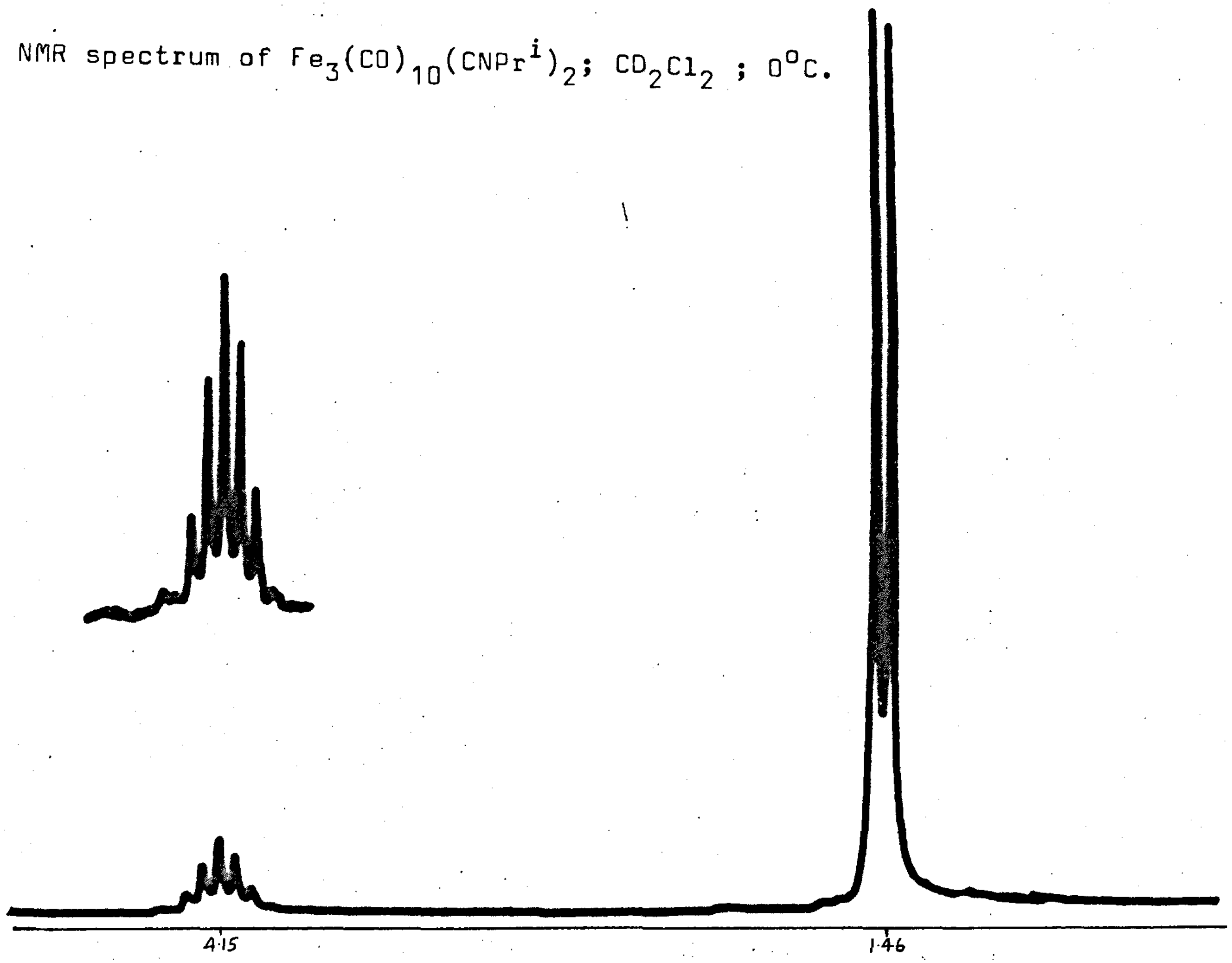


Fig XVI. ^1H NMR spectrum of $Fe_3(CO)_{10}(CNPr^i)_2$; CD_2Cl_2 ; 0°C.



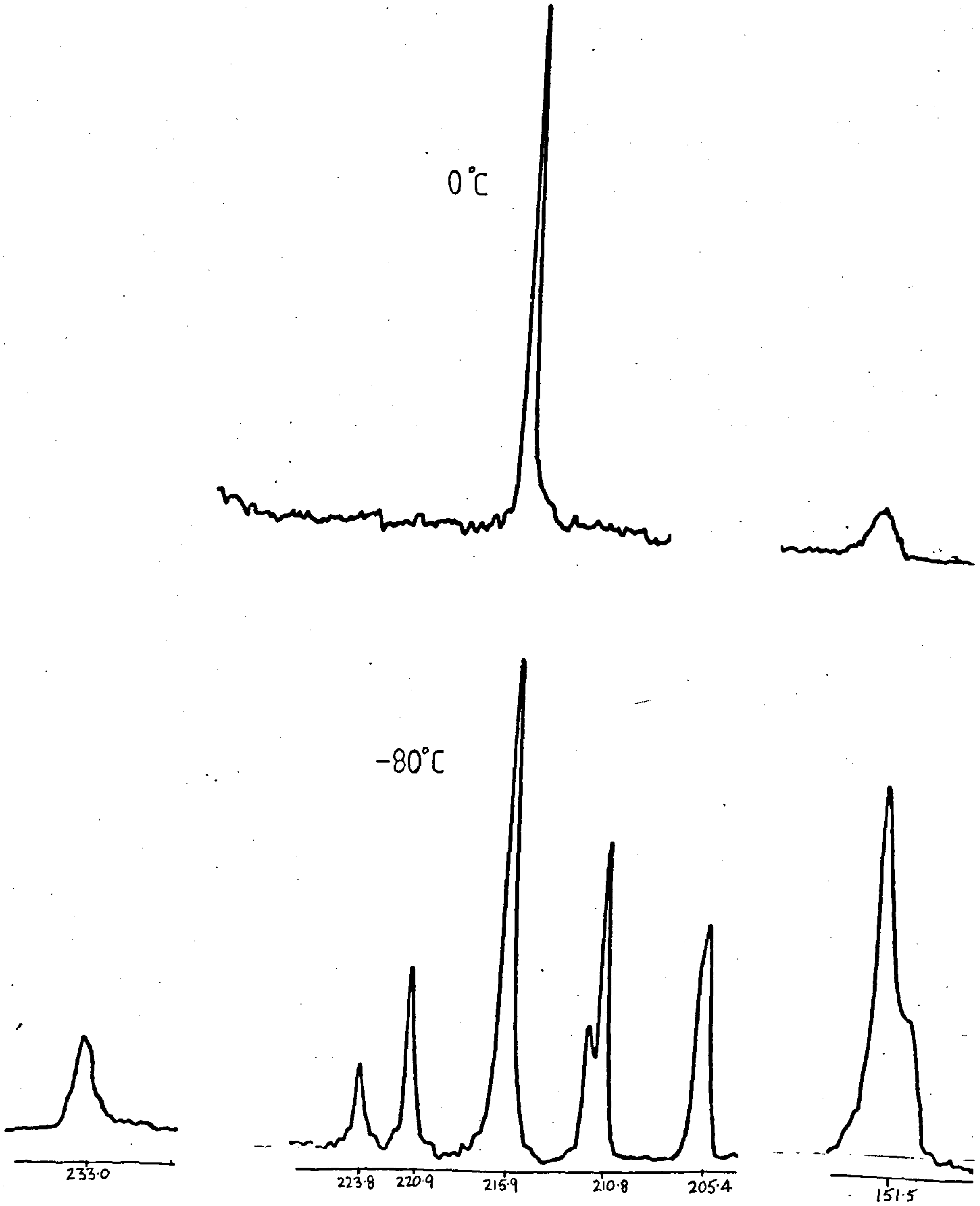


Fig XVII. ^{13}C NMR spectra of $Fe_3(CO)_{10}(CNPr^i)_2$; proton decoupled.

Fig XVIII. ^1H NMR spectrum of $HFe_3(CO)_{10}(CNEt_2)$; CD_2Cl_2 ; -60°C.

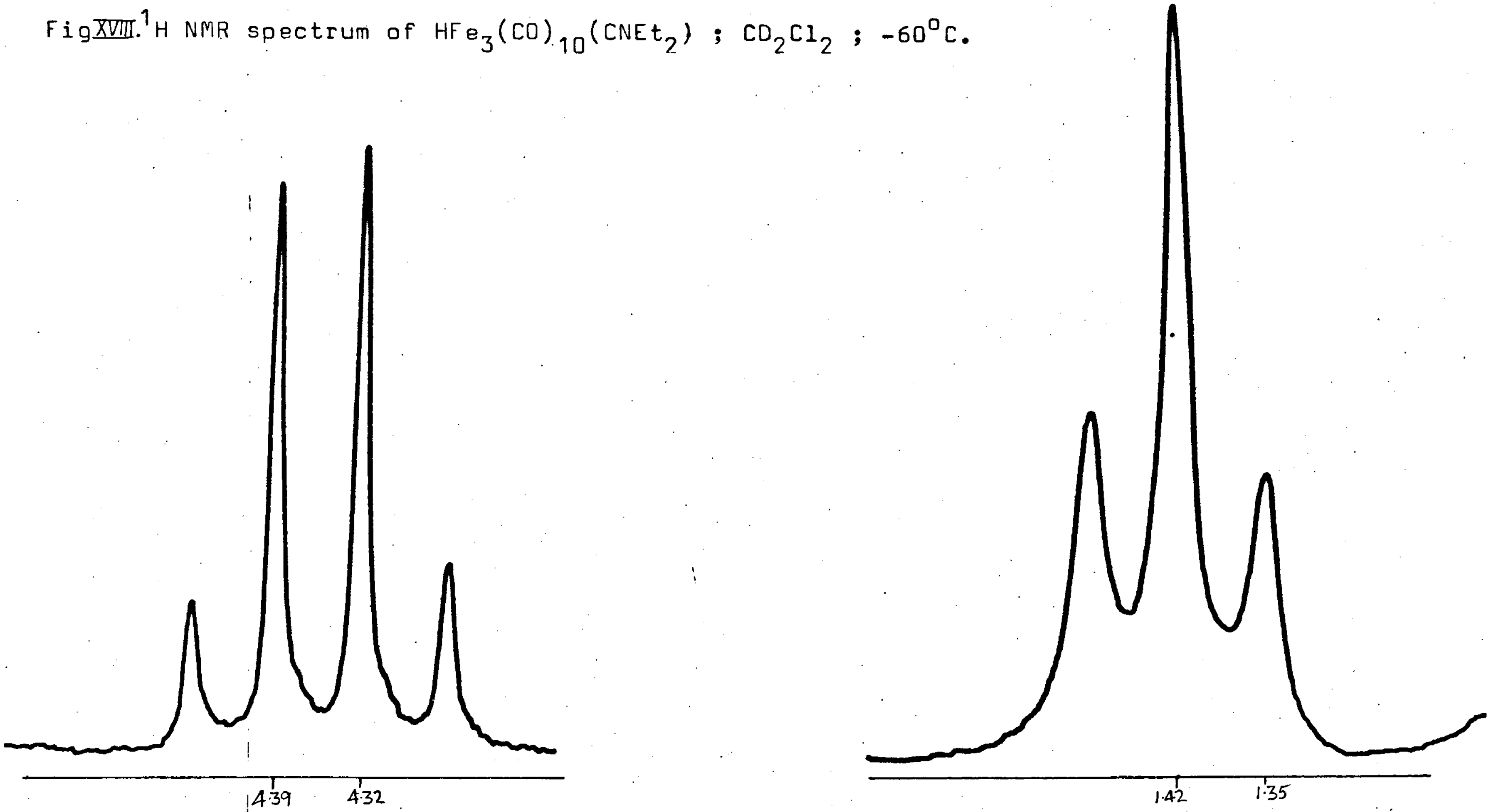
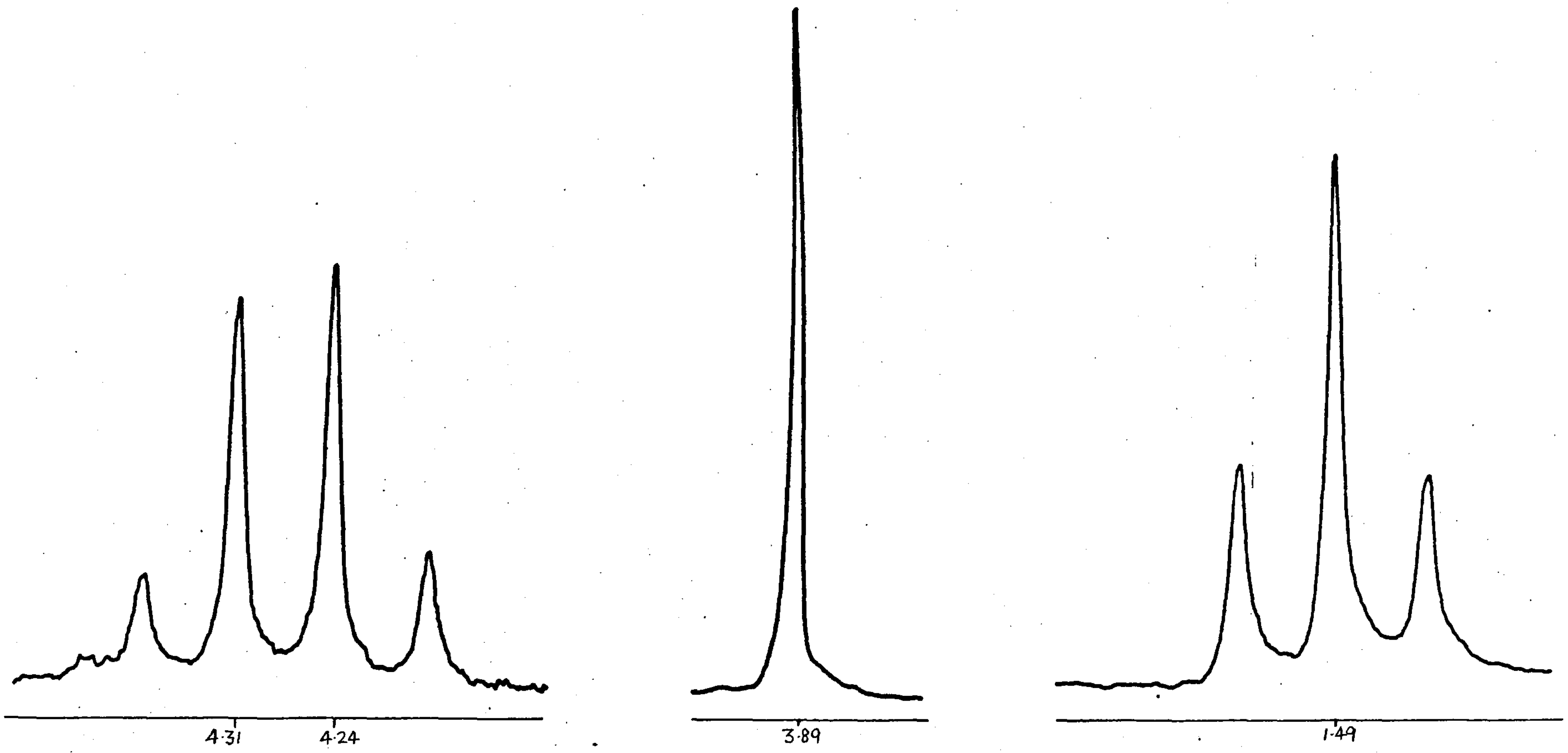


Fig XIX. ^{1}H NMR spectrum of $HFe_3(CO)_{10}(CNMeEt)$; CD_2Cl_2 ; -40°C.



FigXX. ^{1}H NMR spectrum of $HFe_3(CO)_{10}(CNMePr^{i})$; CD_2Cl_2; -60°C.