Kinetics of some reactions of cationic organotransition-metal complexes

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DEDICATION

To my husband, my children

and

to my parents

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A general introduction is given to clarify the different ways in which nucleophilic attack on organotransition-metal cationic complexes takes place.

Kinetics of the reactions between: $[Mn(MeC_5H_4)(CO)_2(NO)]^+PF_6^-$ and some phosphine ligands were followed by infrared spectroscopy. From the results, a bimolecular mechanism is suggested for this reaction which is confirmed by measuring the activation parameters $\Delta H^\ddagger, \Delta S^\ddagger$.

The reaction between (6-phenylhexa-3,5-dien-2-ol) tricarbonyl iron and trifluoroacetic acid was studied kinetically by infrared spectra. The results obtained show that the rate law equation is as follows:

$$\text{Rate} = k_2[Fe^+]\,[Acid]$$

N.m.r. spectra for the iron compound and for the product formed with trifluoroacetic acid were recorded at ambient temperature. A proposed mechanism is discussed in the light of both the kinetic and the spectroscopic data.

The reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and methoxide ion was investigated by stopped-flow techniques over a range of 25-45°C. The plots of k_{obs} v. OMe^- give straight lines with positive intercepts which are interpreted as a parallel reaction with the solvent methanol according to the following mechanism:

$$\text{Rate} = \left\{k' + k_2[OMe^-]\right\}[Co]^+$$

The activation parameters were determined for the reaction of cobalt compound with both the methoxide ion and methanol. The structure of the cobalt compound was confirmed by the use of double resonance technique.

In the final chapter another kinetic study by stopped-flow is described for the reaction between $[M(C_7H_7)(CO)_3]^+BF_4^-$, M = Cr, Mo or W, and methoxide ion. The reactions were found to proceed through two steps as in

$$[M^+]+OMe^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{intermediate} \xrightarrow[\text{slow}]{k_2} \text{products}$$

Values of k_1, k_{-1} and k_2 were determined, the last being found to decrease in the order Cr > Mo > W.

The nature of the intermediate is discussed in terms of correlations between CO stretching force constants in the carbonyl complexes and their tendency to form carbamoyl and carboxyl complexes.

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CHAPTER ONE

PATTERNS OF NUCLEOPHILIC ATTACK ON SOME ORGANOTRANSITION-METAL COMPLEXES

CHAPTER 1

Patterns of nucleophilic attack on some organotransition-metal complexes

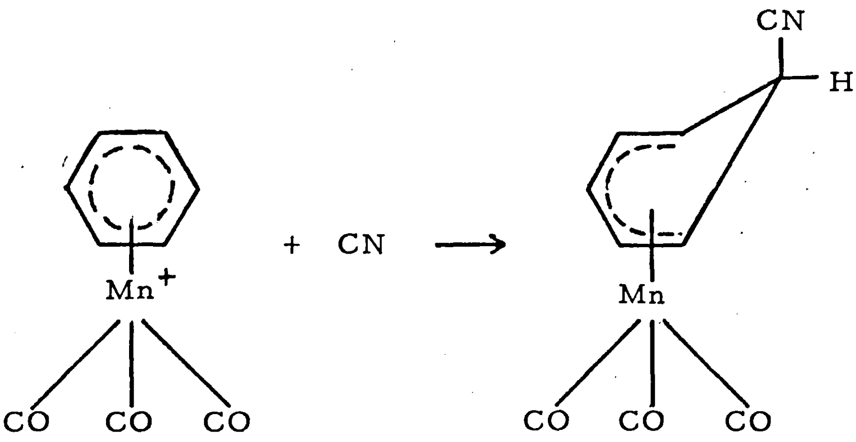
This chapter will review the relevant literature concerning nucleophilic attack on cationic organotransition-metal complexes. This topic has been investigated by many authors who include Green, Kane-Maguire, Lewis, Mawby, Pauson, Pearson and Salzer. A review which relates to the subject has been published.[1] Nucleophiles have been shown to react with the cationic organotransition-metal complexes in several different ways. Some of these are illustrated by the behaviour of the compound $[Mn(C_6H_6)(CO)_3]^+BF_4^-$ The following reaction pathways have been observed. Other examples are given in the following chapters.

a) Addition to the organic ligand.
b) Attack at the metal with displacement of arene..
c) Attack at the metal with replacement of a carbonyl ligand.
d) Addition to the carbon atom of a carbonyl group.

Each of these kinds is now discussed in further detail.

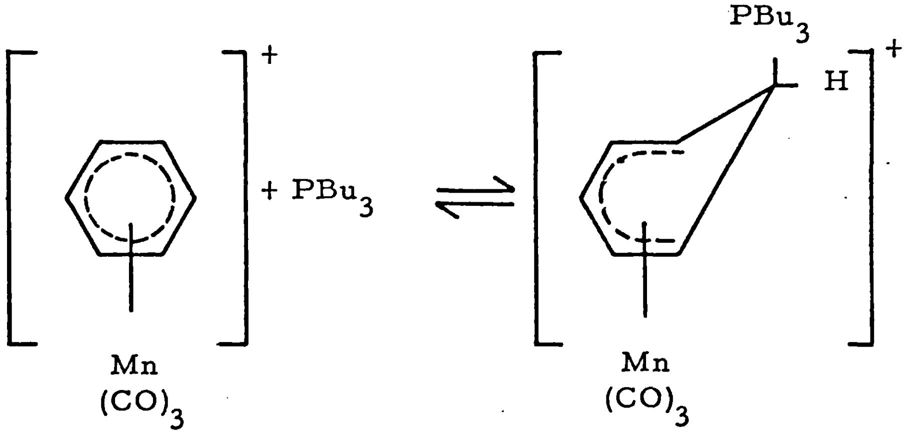
a) Nucleophilic attack on the arene:-

Mawby and Walker[2] have reported many examples of nucleophilic attack on coordinated arenes. The products from the reactions of the cations $[Mn(arene)(CO)_3]^+$, (arene = benzene, p-xylene, 1,2,3 trimethylbenzene, mesitylene; 1,2,3,4 tetramethylbenzene, and 1,2,4,5 tetramethylbenzene) with cyanide ion in aqueous solution were found to have the empirical formula $[Mn(arene.CN)(CO)_3]$. N.m.r. spectroscopy showed that addition of cyanide to the arene to yield cyanocyclohexadienyl complexes had occured:



The complex $[Mn(C_6H_6)(CO)_3]BF_4$ reacts with the anion $(EtO_2C)_2CH^-$ in ethanol at room temperature to yield $[Mn\{C_6H_6CH(CO_2Et)_2\}(CO)_3]$. The n. m. r. data showed chemical shifts for the ring protons similar to those observed for the cyanocyclohexadienyl complex $[Mn(C_6H_6CN)(CO)_3]$, indicated that the reaction again involves nucleophilic addition to the benzene ring. The acetylacetonate anion reacts with $[Mn(C_6H_6)(CO)_3]BF_4$ in the same way. The similarity in the infrared spectrum of the product in the terminal C-O stretching region to that of $[Mn(C_6H_6CH(CO_2Et)_2)(CO)_3]$ showed that addition had again occurred affording the compound $[Mn\{C_6H_6CH(COMe)_2\}(CO)_3]$. The cation $[Mn(C_6H_6)(CO)_3]^+$ likewise undergoes many other reactions with anions such as $Y^- = N_3^-$, OMe^-, PPh_2^- and NCS^- at room temperature in suitable solvents to yield products of general formula $[Mn(C_6H_6Y)(CO)_3]$ as shown from their infrared and n. m. r. spectra.

Kane-Maguire and Sweigart[3] carried out a study of the reaction between $[Mn(arene)(CO)_3]BF_4$ and PBu_3. They found that when the reaction is performed under nitrogen in the dark or in air (dark or light), rapid reversible formation of the phosphonium ring addition compound takes place as follows:



^{1}H n.m.r. data supported the above structure, which is in accord with the first kind of nucleophilic attack.

b) Nucleophilic attack on the metal:-

The cation $[Mn(C_6H_6)(CO)_3]^+$ was found to react with triphenyl phosphine in acetone with evolution of carbon monoxide and formation of $[Mn(C_6H_6)(CO)_2(PPh)_3]^+$ which could be isolated as its fluoroborate salt. However, as mentioned above, Kane-Maguire and Sweigart in a later study, reported that under specific conditions only (under nitrogen and light exposure), the final product is $[Mn(C_6H_6)(CO)_2(PBu_3)]BF_4$. This is because of a photochemical conversion of the manganese adduct $[Mn(arene.PBu_3)(CO)_3]^+$ to $[Mn(arene)(CO)_2(PBu_3)]^+$, which agrees with Mawby's observations. All the products were identified from their n.m.r. and infrared spectra.

c) Nucleophilic attack on the metal with loss of the arene:-

When the complex $[Mn(arene)(CO)_3]BF_4$ was heated under reflux in acetonitrile,$_2$ the product $[Mn(CO)_3(NC\,Me)_3]\ BF_4$ was obtained. Mawby et.al. gave n.m.r. data of this compound which showed a single resonance for the three sets of methyl protons, indicating that it has the fac-configuration. The results from the infrared spectrum of the same compound were in agreement with those from the n. m. r. spectrum. Two bands in the C-O stretching region were observed. Another weak band at 2323 cm^{-1} was assigned to a C-N stretching mode of the acetonitrile ligand.

The reaction was followed kinetically by n. m. r. spectroscopy in acetonitrile. A new peak at 7.28δ was assigned to free benzene instead of one at 6.45δ which was due to complexed benzene. The reaction is represented as follows:-

$$[Mn(C_6H_6)(CO)_3]^+ + 3MeCN \longrightarrow [Mn(CO)_3(NCMe)_3]^+ + C_6H_6$$

Series of analogous complexes (toluene, p-xylene and mesitylene derivatives) were also studied. All these reactions were found to be first order with respect to the arene complex. It was observed that the rate of arene displacement by acetonitrile ligands decreases with increasing methyl substitution on the arene. This could be attributed to increasing the bond strength between arene and metal, or probably increasing the steric hindrance to attack by the incoming ligand. It was noticed too, that the rate of the reaction of the cation $[Mn(C_6H_6)(CO)_3]^+$ increases with the increasing size of the anion present. This may suggest the existence of ion pairing in the acetonitrile, and the increase in rate with anion size is interpreted as a decrease in the extent of ion pairing with large anions.

d) Nucleophilic addition at the carbon atom of a carbonyl group:-

Although the reaction of the cation $[Mn(C_6H_6)(CO)_3]^+$ with methoxide ion in ether yielded the methoxycyclohexadienyl complex $[Mn(C_6H_6OMe)(CO)_3]$, a change in solvent from ether to methanol was sufficient to alter the site of attack from the arene to a carbonyl group. The product given the formula

$[Mn(C_6H_6)(CO)_2(CO_2Me)]$ was identified by measuring the infrared and n. m. r. spectra in deuterated acetone.

Attack on the carbonyl group of arene complexes was also reported by Angelici and Blacik[4]. Similarly, amines attack coordinated CO in the cation $[Mn(C_6H_{6-n}Me_n)(CO)_3]^+$ to yield carboxamido complexes having the structure $[Mn(C_6H_{6-n}Me_n)(CO)_2(CONHR)]$.

Green et. al.[5] have given some proposals in the form of three rules for predicting the site of nucleophilic attack on 18-electron organotransition-metal cations containing polyene ligands.

Rule 1: Nucleophilic attack occurs preferentially at even coordinated polyenes which have no unpaired electrons in the H. O. M. O's, highest occupied molecular orbitals.

Rule 2: Nucleophilic addition to 'open' coordinated polyenes is preferred to addition to 'closed' polyenes.

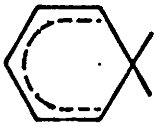
Rule 3: For even 'open' polyenes nucleophilic attack at the terminal carbon atom is always preferred, for odd 'open' polyenyls attack at the terminal carbon atom occurs only if ML_n^+ is a strong electron withdrawing group.

These rules should be applied sequentially. Before showing many examples which illustrate the rules, it might be relevant to clarify what is meant by even and odd polyenes.

In butadiene for example, the number of electrons which is formally donated by the ligand is an even number, four electrons. The allyl group, however, formally contributes only three electrons, so it is an odd polyene.

The term 'open' and 'closed' refer to the π-electron systems. Thus benzene and the cyclopentadienyl group are 'closed' polyenes, whereas butadiene, and the allyl and cyclohexadienyl groups are 'open'.

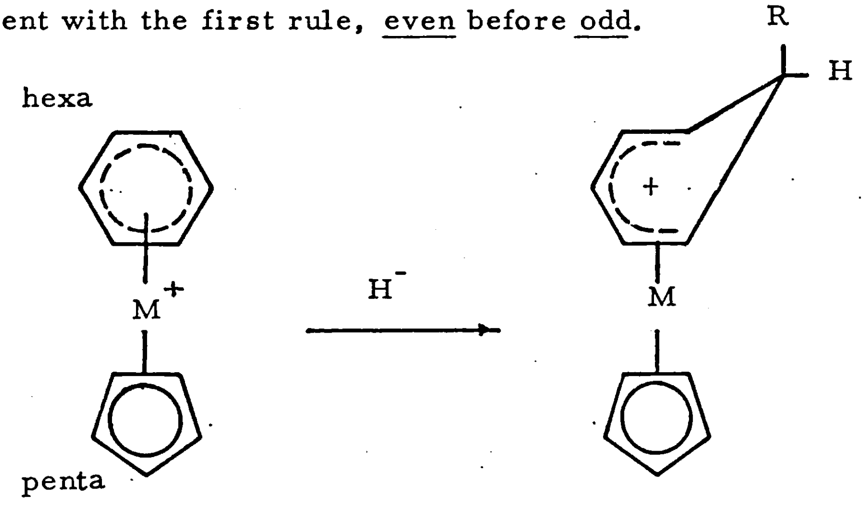
cyclopentadienyl
'closed' polyene



cyclohexadienyl
'open' polyene

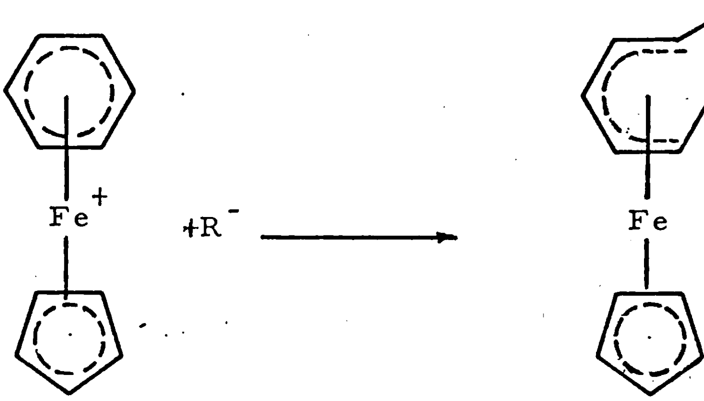
Some examples from the literature are given below which show that the regioselectivity of nucleophilic attack on 18 electron organotransition-metal cationic complexes is consistent with Green's rules.

Rule 1: The attack of the nucleophile upon the arene cyclopentadienyl-iron cation, normally occurs exclusively at the arene ring, in agreement with the first rule, even before odd.



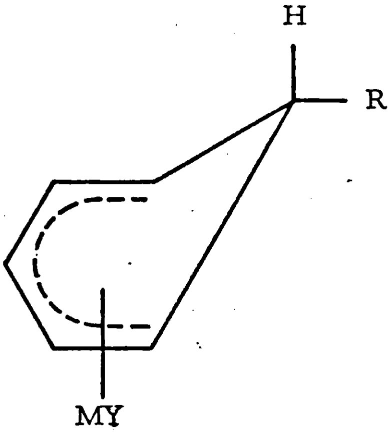
The fact that nucleophilic addition to the arene ring in the cationic complexes usually takes place from the exo-side to the metal was first indicated by crystallographic study.[6]

Pauson and his coworkers[7] investigated some reactions of cyclopentadienyliron salts. They found that the products have the following structure.



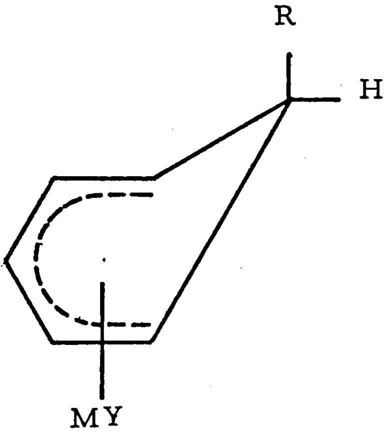
$(R^- = H^-, Me^- Ph^-)$

Spectroscopic characteristics are useful in the identification of the stereoisomeric structures. In the infrared spectrum a strong C-H stretching band appears at near or below 2800 cm^{-1} for all complexes of the type, where the tetrahedral carbon bears an exo-hydrogen atom.



endo-substituent

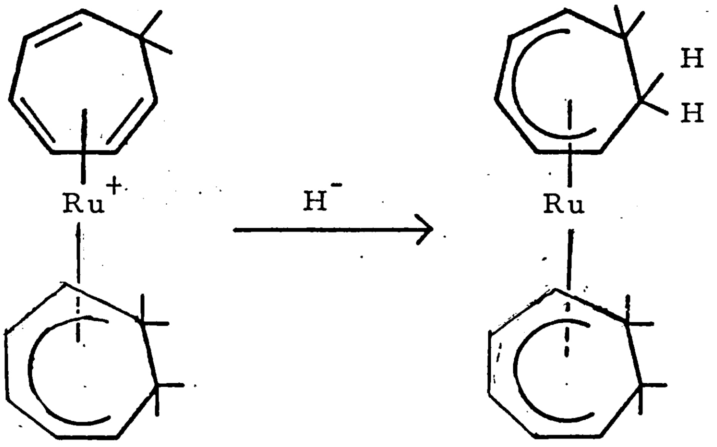
This absorption is absent in the spectra of all the exo-substituted compounds of the type.



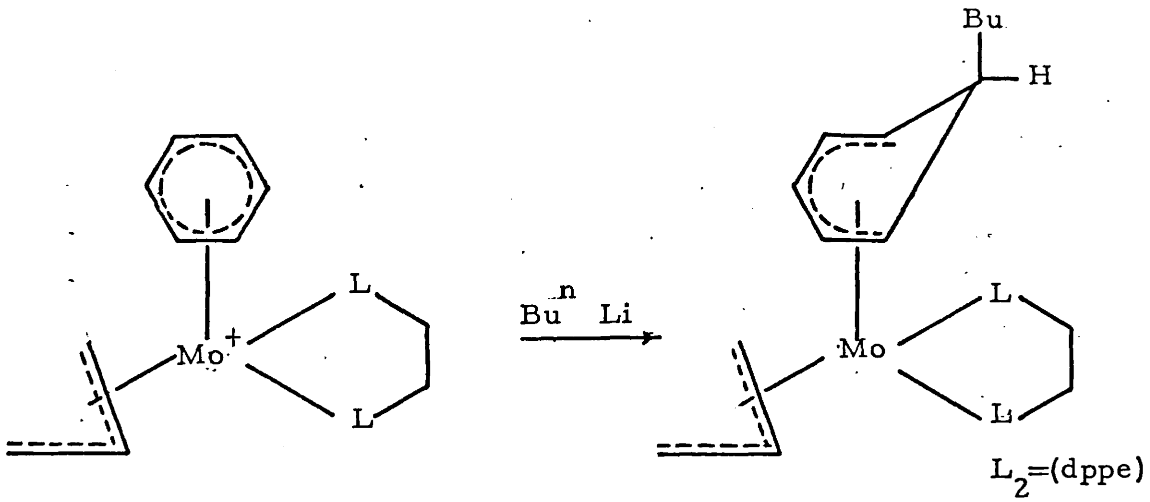
exo-substituent

In the endo substituted compounds, the C-H$_{exo}$ stretching frequency may be lowered because of overlapping between the C-H$_{exo}$ bond through orbital interaction. In the ^{1}H n.m.r. spectra, the protons of substituents attached to the tetrahedral carbon atom in the exo complexes are more shielded compared with endo-substituents.

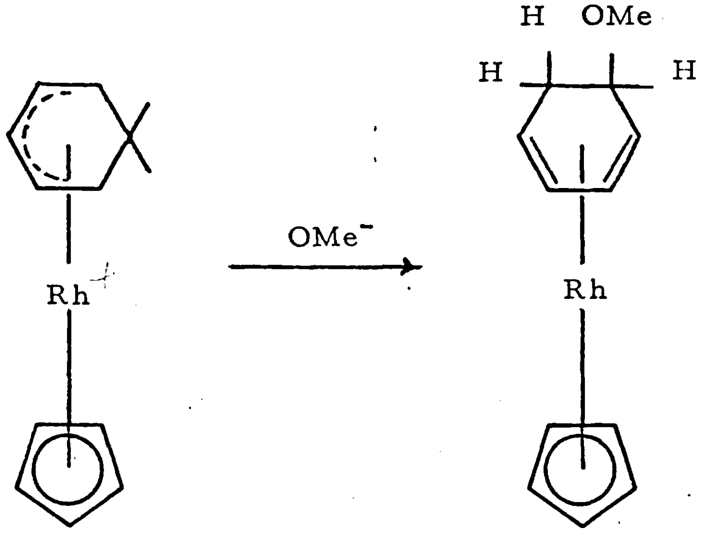
It is noticed also in the reaction between (cycloheptadienyl)-(cyclohepta-1,3,6-triene) ruthenium[8] and nucleophiles such as H$^-$ that the attack occurs preferentially at the cycloheptatriene ligand, that is, at the even 6-electron polyene. This can be illustrated by the equation shown below.



When the complex $[Mo(C_6H_6)(\eta\text{-}C_3H_5)(dppe)]^+$ [9], reacts with sodium cyanide, it gives yellow crystals. The product was examined by n.m.r. spectroscopy which suggests the structure $[Mo(C_6H_6CN)(\eta\text{-}C_3H_5)(dppe)]$, dppe = $Ph_2.PCH_2CH_2PPh_2$. This indicates that the cyanide ion attacks the benzene ring and not the η-allyl group. Again the regioselectivity here is in accord with the first rule.

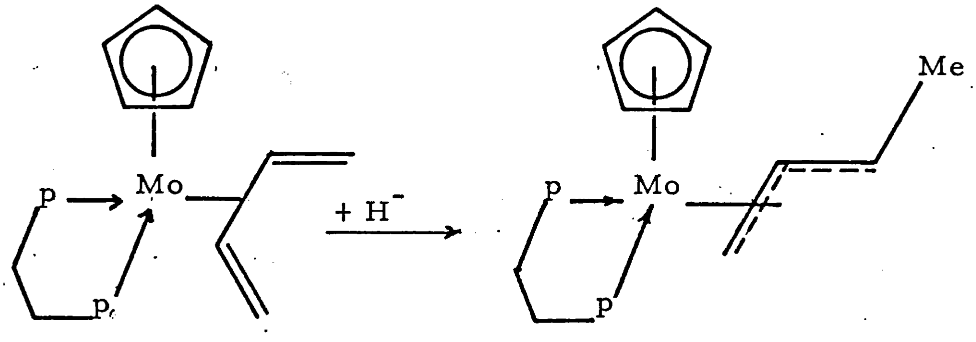


Rule 2: In 1972 Lewis et al[10] carried out a study of the reactions of I with both nucleophiles and electrophiles. Methoxide ion gives (cyclopentadienyl)(5-methoxycyclohexa-1,3-diene) rhodium (I). This shows that the nucleophilic attack occurs at the open cyclohexadienyl ligand rather than at the closed cyclopentadienyl ring which is consistent with rule 2 proposed by Green and his colleagues.



I

Rule 1 and Rule 2: Treatment of the compound II with $Na[AlH_2(OCH_2CH_2OMe)_2]$ gives $[Mo(C_5H_5)(dppe)(\eta^3\text{-}MeCHCHCH_2)]^{11}$, as follows:-

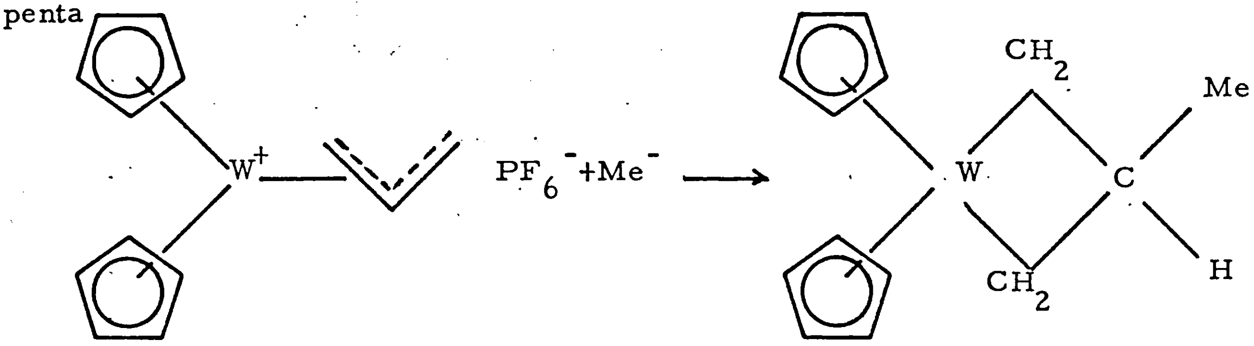


II

This is in accord with rule 2, attack at the 'open' polyene butadiene being favoured over that at the closed cyclopentadienyl group.

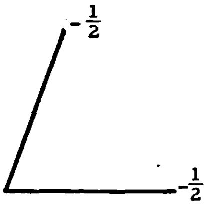
Rule 3: In rule 3 it is suggested that, for <u>even</u> <u>'open'</u> polyenes nucleophilic attack in general occurs at the terminal carbon. The previous example of the Mo compound described above illustrates the rule.

In the case of <u>odd</u> <u>'open'</u> polyenes attack at the terminal carbon atom occurs only if $ML^{+}_{\eta 2}$ is a strong electron withdrawing group. The following example shows that attack on the η-allylcations by H^-, D^- and $CH_2{=}CH{-}\overline{C}H_2$ occurs preferentially on the central 2-carbon:

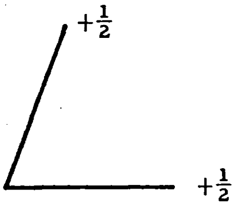


This could be interpreted in terms of bonding in the allyl group.

Three models of bonding might be considered, in other words the allyl group may be present essentially as $C_3H_5^+$, $C_3H_5^\cdot$ or $C_3H_5^-$. When it is $C_3H_5^-$ the positive charge will be more concentrated on the central carbon atom because of location of $-\frac{1}{2}$ at each terminal one.



However, in case of $C_3H_5^+$, nucleophilic attack will prefer terminal carbons because the positive charges are centred there.



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CHAPTER TWO

KINETIC STUDY OF THE REACTIONS BETWEEN METHYLCYCLOPENTADIENYLDICARBONYLNITROSYL MANGANESE HEXAFLUOROPHOSPHATE AND SOME PHOSPHINE LIGANDS

CHAPTER 2.

Kinetic study of the reactions between methylcyclopentadienyldicarbonylnitrosyl manganese hexafluorophosphate and some phosphine ligands.

2.1. Metal carbonyls.

Transition metal carbonyl complexes have been known for over 100 years. In 1871, Schutzenberger reported platinum carbonyl chlorides but it was not until 1890 that the first binary carbonyl, Ni $(CO)_4$ was discovered by Mond. Table I summarises the historical development of the subject.

TABLE I

Metal carbonyl complexes [1]

1871 - 1930

1871	$Pt(CO)_2Cl_2$	P.Schutzenberger
1890	$Ni(CO)_4$	L. Mond, C. Langer and F. Quincke
1891	$Fe(CO)_5$	L. Mond and F. Quincke; M. Berthelot
1905	$Fe_2(CO)_9$	J. Dewar and H. O. Jones
1907	$Fe_3(CO)_{12}$	J. Dewar and H. O. Jones
1910	$Co_2(CO)_8$, $Co_4(CO)_{12}$	L. Mond, H. Hirtz and M. D. Cowap.
1910	$Mo(CO)_6$	L. Mond, H. Hirtz and M. D. Cowap.
1924-26	$[Ru(CO)_2Hal_2]_n$ $Ir(CO)_2Cl_2$;$Os(CO)_3Cl_2$	W. Manchot et. al.
1927-28	$Cr(CO)_6$; $W(CO)_6$	A. Job et. al.
1930	$Fe(C_4H_6)(CO)_3$	H. Reihlen et. al.

The detailed foundations of carbonyl chemistry were laid between 1928 and 1970 by W. Hieber and his group who from 1935 onwards were based in Munich.[1]

Nickel tetracarbonyl $Ni(CO)_4$ can be prepared by the direct reaction between nickel and carbon monoxide. This forms the basis of the Mond process for the refining of the metal.

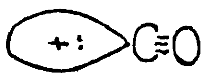
Iron pentacarbonyl also can be formed from carbon monoxide and iron. In fact, carbon monoxide stored in iron cylinders can contain appreciable amounts of $Fe(CO)_5$. This complex is manufactured in tonnage quantities for the preparation of special iron powder by thermal decomposition. Use is also made industrially of the thermal decomposition of molybdenum hexacarbonyl for depositing metallic molybdenum.

The direct reaction between a transition metal and carbon monoxide is very limited in its application to the preparation of carbonyl complexes. Usually they are obtained by reduction of a metal compound such as a halide or acetylacetonate in the presence of carbon monoxide, often under pressure. Reduction can be effected by using sodium, aluminium alkyls, zinc or even a mixture of carbon monoxide itself with hydrogen. Useful reviews of carbonyl chemistry have been published.[2]

The structure and bonding in these compounds is of great interest. The effective atomic number rule which was first formulated by Sidgwick[3] has proved useful in understanding the structure of metal carbonyls.

The carbon monoxide molecule has lone electron pairs on both the carbon and oxygen atoms, the sp orbital of the carbon atom containing its lone electron pair can overlap with a metal hybrid orbital to form a σ-bond, where this lone electron pair of the ligand is donated to the metal atom. Carbon monoxide however is a very poor donor ligand to conventional Lewis acids such as BF_3 or SbF_5. Borine carbonyl $H_3B.CO$ can be prepared but it dissociates readily. This indicates that CO is not normally a strong σ-donor. In transition metal carbonyls, this σ-bond is supplemented by a second bond a reverse π-bond where a filled metal d orbital containing an electron pair can overlap with an empty π^* antibonding orbital of the carbon monoxide ligand.

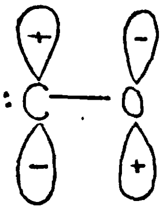
The extent of this π-back donation is quite variable in metal carbonyl derivatives, depending upon the electron density on the metal atom which is affected by various factors, such as the other ligands attached to the metal atom and the charge on the metal carbonyl species. In the case of metal carbonyls, the forward σ-bond between carbon monoxide and the transition metal is sufficiently weak that significant amounts of π-back donation are required to ensure reasonable stability of the compound.



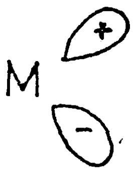
Nonbonding orbital localized on carbon and containing lone electron pair

empty hybrid σ orbital

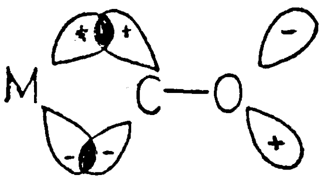
metal-carbon dative σ-bond



Empty antibonding orbital π^* of CO multiple bond



nonbonding metal orbital containing lε pair



metal-carbon back donation bond

The following additional features of the π-back bond in metal carbonyls are also of some importance.

a) Carbon monoxide has two orthogonal antibonding orbitals which can form orthogonal π-back bonds with the metal atom, provided that suitable metal orbitals are available.

b) The π-back donation in metal carbonyls places additional electron density into the antibonding π^* orbitals of the carbon monoxide. This lowers the carbon-oxygen bond order and, therefore, the carbon oxygen stretching force constant. This effect can be measured from infrared frequencies in metal carbonyls and provides a useful means for deducing the amount of back donation.

2.2. Some substitution reactions in metal carbonyls.

Metal carbonyls and metal carbonyl complexes undergo substitution reactions under either thermal or photochemical conditions with a large number of nucleophiles.
These reactions and their products have been reviewed. For example, arene and cyclopentadienyl metal carbonyls have been reviewed by Wilkinson and Cotton,[4] Fischer and Fritz,[5] Pauson[6], and Zeiss[7], olefinic derivatives by Guy and Shaw[8], Bennett[9], Fischer and Werner [10], derivatives of phosphines, arsines and stibines by Booth[11], and finally, the metal carbonyls themselves by Abel[2] and Chatt et al.[12]

Kinetic studies of substitution reactions require attention to the following experimental problems:-

a) Removal of carbon monoxide from the reacting solution either by efficient stirring or the use of an inert gas in which case independent studies of the dependence of rate constant on flow rate of carrier gas are also needed.

b) Efficient removal of oxygen from the solvent especially in studies of photochemical reactions.

c) Elimination of side reactions such as decomposition of complexes.

Nucleophilic substitution reactions can proceed via S_N1 or S_N2 mechanisms according to the classical organic terminology of Hughes and Ingold.[13]

In S_N1 reactions, the dissociation of the metal-ligand bond is the rate determining step followed by a rapid reaction with the attacking group as illustrated by the following equations:

$$ML \overset{\text{slow}}{\rightleftharpoons} M + L$$

$$M + L' \overset{\text{fast}}{\rightleftharpoons} M L'$$

The attacking nucleophile is for example an olefin, acetylene, arene or a ligand containing a donor atom such as O, N, S or P. An example of an S_N1 mechanism is the substitution reaction of manganese pentacarbonylhalides with triphenylphosphine[14] to give mono and disubstituted derivatives. The rates of these reactions are independent of the incoming ligand L.

$$Mn(CO)_5X \xrightarrow[-CO]{\text{slow}} Mn(CO)_4X \xrightarrow[+L]{\text{fast}} Mn(CO)_4LX$$

These reactions have high enthalpies and positive entropies of activation in contrast to a bimolecular process which would be expected to lead to decrease in entropy. The rates for the preceding reaction fall in the sequence Cl>Br>I, following the activation energies. In other words, $E_a(I) > E_a(Br) > E_a(1)$ under the same conditions. This agrees with an increase in the Mn-C bond strength as indirectly shown by the ν(C-O) infrared stretching frequencies, which suggests that the strongest bonding occurs in $[Mn(CO)_5I]$.

In S_N2 substitution reactions, the rates depend on the nature of the attacking nucleophile. The rates of the substitution reactions of Group VI carbonyl complexes by phosphorus donors follow the sequence[15], $PEt_3 \approx PPr^n_3 > PEt_2Ph > PEtPh_2 > P(OMe)_3 > PPh_3 > P(OPh)_3$.

In these reactions the substituting group is weakly bonded to the metal in the transition state. That means that the rate determining step involves both the complex and the attacking nucleophile, as shown by the equation

$$M(CO)_n + L \longrightarrow [\, L \ldots M(CO)_{n-1} \ldots CO \,] \longrightarrow$$

$$LM(CO)_{n-1} + CO.$$

Stepwise substitution reactions of metal carbonyl complexes always become progressively more difficult.[16] This is because the strength of the remaining metal-carbon bonds increases on replacement of CO by a ligand which is a better σ-donor but a poorer π-acceptor. The metal-carbon π-bonding is thus enhanced.

Some examples of substitution reactions which have been studied kinetically are summarized here.

The ^{14}CO exchange of $V(CO)_6$[17, 18] has been reported to be very slow in heptane at 0°C, but no other kinetic data are available for this compound. In group VI metal carbonyls, the exchange reaction of ^{14}CO using toluene as a solvent indicated that hexacarbonyl chromium was much less reactive than either cobalt or nickel carbonyls.[17, 18] It was found that the reaction occurred through a dissociative mechanism. Graham and Angelici[19] reported that the substitutions of $Mo(CO)_6$ and $W(CO)_6$ by various phosphine and phosphite ligands shows a linear dependence of observed rate constants with ligand concentrations, a two term rate law could be applied to describe the reaction

$$\text{Rate} = k_1 [\, Mo(CO)_6 \,] + k_2 [\, Mo(CO)_6 \,][L]$$

The reaction of $Mn_2(CO)_{10}$ with phosphines to form mono and di-phosphine substituents has been observed.[20] The authors suggested that the reaction proceeded via a first order kinetic process.

The substitution of CO in $Ni(CO)_4$ follows an S_N1 mechanism. There was no evidence for any S_N2 pathway. This behaviour could be explained in terms of repulsion of the approaching ligand by a central atom in a d^{10} configuration and also may be due to the fact that $Ni(CO)_3$ fragment is more stable by dπ-pπ bonding compared with $Ni(CO)_4$. The reactions of $Co_2(CO)_8$ was found to go through a dissociative mechanism.[21, 22] This was confirmed by the Arrhenius parameters for the ^{14}CO exchange ($E = 98$ k J mol^{-1} and $\Delta S^{\ddagger} = 55$ J K^{-1} mol^{-1}) , consistent with an S_N1 mechanism.

The exchange reaction of $Fe(CO)_5$ with isotopically labelled carbon monoxide was studied by Keely[23] and Johnson. The reaction was thought to proceed as follows:

$$2\,Fe(CO)_5 \longrightarrow Fe_2(CO)_9 + CO.$$

They suggested that the possibility of photodissociation of $Fe(CO)_5$ went through an intermediate species which exists in equilibrium with the species in the ground state

$$Fe(CO)_5 \longrightarrow Fe(CO)_4 + CO$$

$$Fe(CO)_4 + Fe(CO)_5 \longrightarrow Fe_2(CO)_9$$

The reactions of metal carbonyl phosphines were also reported. For example reactions of mono- and di-substituted nickel carbonyl phosphine with other phosphines were found to be independent of the incoming phosphine ligand and so are assumed to occur by a dissociative mechanism.[24] Also metal carbonyl halide[25] derivatives were found to undergo ^{14}CO exchange by a first order reaction with a rate constant which was independent of the displacing carbonyl concentration.

2.3: Metal carbonyl nitrosyl complexes.

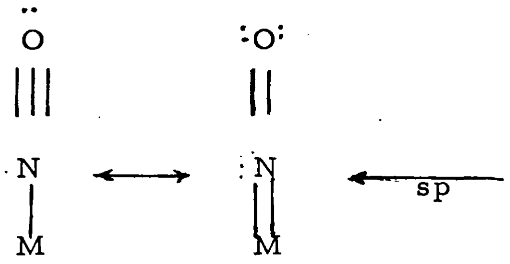
The nitric oxide molecule has one electron in an antibonding molecular orbital which can be easily lost to give the nitrosonium ion, NO^+. The coordination of a nitric oxide molecule to a transition metal atom can formally involve the transfer of the antibonding electron from NO to the metal atom

$$M + NO \longrightarrow M^- + NO^+$$

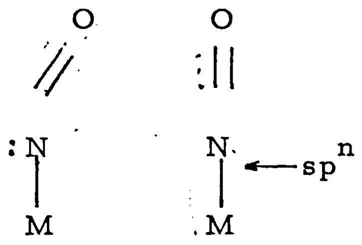
and coordination of the nitrosonium group to M by an electron pair of the nitrogen, that means that three ligand electrons are involved in the metal nitrosyl bond.

Measurements of electronic spectra show that the nitrosyl ligand has a π-acceptor property greater than that of CO or CN^-.[26]

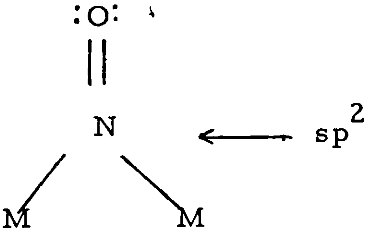
To clarify the bonding of the nitrosyl group to a transition metal, one has to know the different structures of NO in nitrosyl complexes. The nitric oxide molecule can act not only as the common NO^+, a three electron ligand, but also as NO^-, a one electron ligand. Shown below are ways in which the nitric oxide molecule can occur in complexes in several modes.[27]



linear



bent $1 < n < 2$



bridging

In nearly all nitrosyl complexes the M-NO group is essentially linear, and the ligand is bonded formally as NO^+. This is clearly shown by the magnetic moments of nitrosyl cyanides. For example the nitroprusside ion[28] $[Fe(CN)_5(NO)]^{2-}$ is diamagnetic, which indicates that iron is in the +2 oxidation state (d^6). The linear mode of NO coordination is followed also in the nitrosylcarbonyl compounds $[Mn(CO)(NO)_3]$ and $[Fe(CO)_2(NO)_2]$ which form part of the isoelectronic series, $[Cr(NO)_4]$, $[Mn(CO)_3(NO)]$, $[Fe(CO)_2(NO)_2]$, $[Co(CO)_3(NO)]$, $[Ni(CO)_4]$, $[Fe(CO)_3(NO)]^-$. The compound $[V(CO)_5(NO)]$ is isoelectronic with $[Cr(CO)_6]$, $[Mn(CO)_4(NO)]$ with $[Fe(CO)_5]$ and $[Mn_2(CO)_7(NO)_2]$ with $[Fe_2(CO)_9]$. All these compounds and their substituted products obey the eighteen electron rule.

Analysis of the infrared spectra of $[Mn(CO)(NO)_3]$ [29], $[Fe(CO)_2(NO)_2]$[29] and $[Co(CO)_3(NO)]$[30] and salts of $[Fe(CO)_3(NO)]^{-}$[31] suggests that these isoelectronic species have tetrahedral or distorted tetrahedral structures as expected. By the use of infrared spectroscopy also, it is thought that $[Mn(CO)_4(NO)]$[32] has a trigonal-bipyramidal configuration with the nitrosyl group in one of the axial positions.

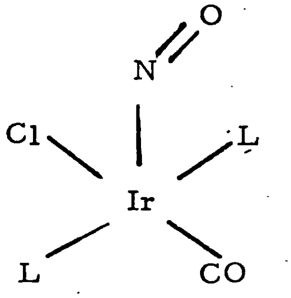
Some of these nitrosylcarbonyl complexes were prepared by the reaction of the metal carbonyl and nitric oxide, e.g.

$$[Co_2(CO)_8] + 2NO \xrightarrow{40^{\circ}C} 2\,[Co(CO)_3(NO)]$$

If $[Co(CO)_3(NO)]$ reacts further with NO, it gives $[Co(NO)_3]$[33]. The compound $[Mn(CO)(NO)_3]$ [29] was obtained by the action of NO on $[Mn(CO)_5I]$ at ca. $100^{\circ}C$, while $[Mn(CO)_4(NO)]$ can be formed from $[Mn_2(CO)_8(PPh_3)_2]$ with nitric oxide at $90^{\circ}C$ in tetralin. On the other hand $[Mn(CO)_4(NO)]$ can be considered as a source for preparing $[Mn(CO)(NO)_3]$ on treatment with nitric oxide.[34]

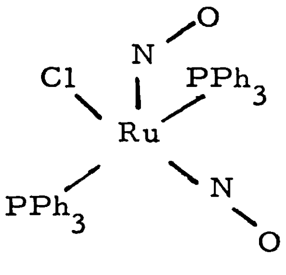
A great number of metal nitrosylcarbonyl compounds with other ligands exist such as $[V(\eta^5\text{-}C_5H_5)(CO)(NO)_2]$[35], $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$[36] or $[Ru(CO)(NO)(PPh_3)(Cl)]$[37]. Cationic and anionic complexes also are known.[38] In anionic species the M-N-O linkage is probably linear and the NO group functions as a σ-donor (Lewis base), back bonding from the metal to the NO group will occur. However in some cationic complexes the NO ligand acts as a σ-acceptor (Lewis acid). Consequently the M-N-O linkage is bent to 125°.

The bent nitrosylcomplex $[Ir(CO)(NO)(PPh_3)Cl]$ was first reported by Ibers and Hodgson.[39] This compound was investigated by X-ray diffraction which confirmed the bent mode of metal nitrosyl bonding,



(Fig i)

A system possessing both linear and bent modes of nitric oxide coordination is $[Ru(NO)_2(PPh_3)_2Cl]^+$, (Fig. ii). This complex is square pyramidal with an angularly coordinated NO^- in the apical position and a linearly bonded NO^+ in the basal plane. The M-N distance for a linear nitrosyl is shorter than that for a bent NO. This is because of greater metal nitrosyl π-bonding in the former unit. The nitrosyl stretching frequencies νNO are 1845 and 1687 cm^{-1} for the linear and bent nitrosyls respectively.

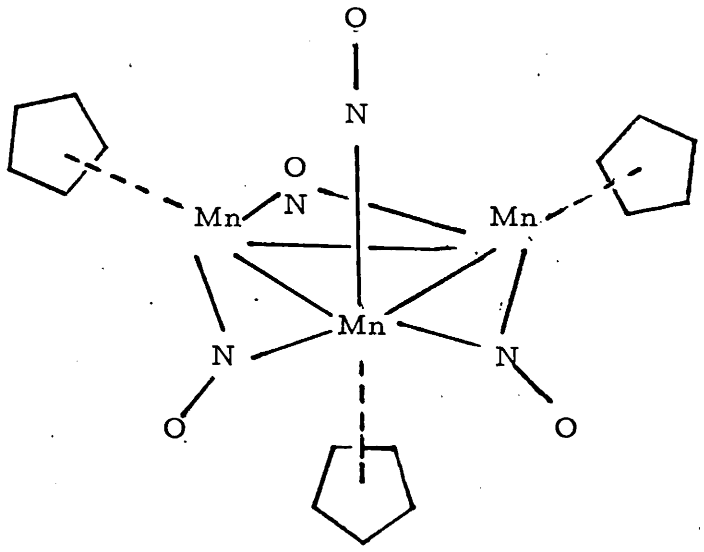


(Fig ii)

The difference between the linear and bent modes of bonding is the electron pair on the nitrosyl ligand, the interconversion would be easily achieved by withdrawing or donating an electron pair to the metal course. This was first postulated by Collman and his co-workers in 1969.[40] When the nitrosyl bends, an electron pair withdraws from the metal, this in fact will cause the creation of a vacant coordination site on it which facilitates many catalytic processes.[41] This agrees with the point of view suggesting that NO can activate a metal centre more than the corresponding carbonyl which exhibits no tendency to bend.

Bridging NO groups:

Bridging nitrosyl groups, like the linear ones, are considered to act as three-electron donors. They are less common than bridging carbonyl groups. Both doubly and triply bridging nitrosyls can occur. The NO stretching frequencies decrease with the extent of the bridging. For example in the complex $[Mn_3(\eta^5\text{-}C_5H_5)_3(NO)_4]$ there are two bands due to the doubly bridging NO groups at 1543 and 1481 cm^{-1} and one from the triply bridging group at 1320 cm^{-1}.



In $[Cr(\eta^5C_5H_5)(NO)(\mu\text{-}NO)(\mu\text{-}NH_2)(NO)(\eta^5\text{-}C_5H_5)Cr]$, the terminal NO groups absorb at 1644 cm^{-1}, while the bridging group has a frequency of 1505 cm^{-1}.

Bottomley[42] studied the electrophilicity of coordinated nitric oxide and he declared that NO must have as low an electron density as possible to act as an electrophile. This could be achieved in nitrosyl complexes which show very high ν NO frequencies. This argument is similar to that used by Angelici[43] in his work on carbonyls. The nitrosyls, which Bottomley studied and which behave as electrophiles have ν NO in the range 1886 to 1945 cm^{-1}. Generally complexes with ν NO 1890cm^{-1} react with at least one nucleophile. One example of the reactions studied in this field was the nucleophilic attack by OH^- on $[Fe(CN)_5(NO)]^{2-}$ as follows:

$$[Fe(CN)_5(NO)]^{2-} + 2OH^- \rightleftarrows [Fe(CN)_5(NO_2)]^{4-} + H_2O$$

This reaction has an equilibrium constant of $1.5 \times 10^6\ dm^6\ mol^{-2}$ which is lower than the value 2.3×10^{31} for the parent reaction

$$NO^+ + 2OH^- \rightleftarrows NO_2^- + H_2O$$

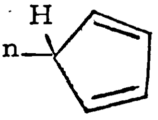
This showed clearly that coordinated NO^+ in $[Fe(CN)_5(NO)]^{2-}$ is a much weaker electrophile than "free" NO^+

Two methods are available for indicating the presence of a linear MNO group, a) the study of ν NO frequencies and b) Crystallography, which shows MNO angles between 170.3 and 180° i.e. linear.

2.4 Cyclopentadienyl complexes.[44]

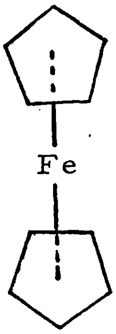
The cyclopentadienyl group can bond in several ways to metals. The most important are

i) Ionic cyclopentadienides which contain the $C_5H_5^-$ ion, e. g. sodium cyclopentadienide.

ii) η^1-cyclopentadienyls, e. g. Me_3 Sn 

iii) η^5-cyclopentadienyls.

All the elements of the first transition series from vanadium to nickel inclusive form bis-cyclopentadienyls, $M(\eta^5\text{-}C_5H_5)_2$, which possess the sandwich structure like ferrocene.



In these molecules the metal atom is equidistant between two planes regular C_5 rings.

η^5-Cyclopentadienyl-carbonyl complexes.

Many stable η^5-cyclopentadienylcarbonyl complexes are known. In all these complexes the η^5-cyclopentadienyl metal bonding is covalent. Most of these compounds are stable at room temperature. Since the η^5-cyclopentadienyl system is a better donor and a weaker acceptor than carbon monoxide ligand, the η^5-C_5H_5 group stabilizes the M-C≡O bonding.Both the metal carbonyls themselves and cyclopentadienyl carbonyls obey the 18-electron rule with few exceptions and also give stable anions when treated with alkali metals, e. g.

$$[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2 \xrightarrow{Na/Hg} Na^+[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$$

Representative compounds formed by elements of the first transition series are listed. (Table 2).

The cyclopentadienylnitrosyl complexes having the general formula $[M(\eta^5\text{-}C_5H_5)(NO)]$, where M = Ni[45], Pd,[46] Pt[47] were prepared several years ago. In such compounds the nitric oxide acts formally as a three electron ligand. The microwave spectrum of the nickel complex shows the symmetric structure as follows:

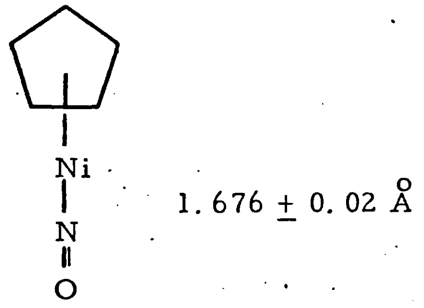


TABLE 2

Metal	Number of d electrons	Formula
Ti	4	$TiCp_2(CO)_2$
V	5	$VCp(CO)_4$
Cr	6	$[CrCp(CO)_3]_2$
Mn	7	$MnCp(CO)_3$
Fe	8	$[FeCp(CO)_2]_2$
Co	9	$CoCp(CO)_2$
Ni	10	$[NiCp(CO)]_2$

2.5. Reactions of cyclopentadienyldicarbonylnitrosyl manganese (I) salts with nucleophiles

Reactions of substituted cyclopentadienyl nitrosyl manganese complex cations $[\mathrm{Mn}\eta^5\text{-}(C_5H_4R)(CO)_2(NO)]^+$, R = H or Me with some phosphines and nitrogen donor ligands have been investigated by many authors.[48,49] When L=triphenylphosphine, triphenyl phosphite and pyridine crystalline complexes in which one or two carbonyl groups have been displaced were isolated from the reaction mixture. The reactions were carried out in acetone solution. Slow evolution of a gas was observed when the complex $[\mathrm{Mn}\text{-}(\eta^5\text{-}C_5H_4R)(CO)_2(NO)]^+[PF_6]^-$ was dissolved in this solvent. The gas probably is carbon monoxide. Also it was noticed that the colour of the solution changes from orange to brown. This did not happen if ethanol was used instead of acetone. This behaviour suggests possible substitution of a carbonyl group by an acetone molecule may take place. The reaction between $[\mathrm{Mn}(\eta^5\text{-}C_5H_4R)(CO)_2(NO)]^+$ and ligands such as dimethyl phenyl phosphine, pyridines and the bipyridyl occurred smoothly in cold acetone. Brunner and Schindler[49] found that substitutions occurred in refluxing ethanol during periods greater than 1 hr. James and McCleverty[50] reported that the substitution of carbonyl ligands by the rather weakly basic triphenyl phosphine and triphenyl phosphite did not happen smoothly without a catalyst such as trimethylamine. The compounds were identified by their infrared and n.m.r. spectra, which are consistent with the asymmetry of the molecules, the manganese atom being a prochiral centre. The compounds may be regarded as having a pseudotetrahedral structure with the C_5 ring occupying one co-ordinate site.

King et al.[48,51] also studied the reaction between the manganese salt $[\mathrm{Mn}\,(\eta^5\text{-}(C_5H_5)(CO)_2(NO)]^+[PF_6]^-$ and some tertiary phosphines and related ligands upon heating in methanol. Yellow to orange products are formed without ultraviolet irradiation having the formula $[\mathrm{Mn}\,(\eta^5\text{-}(C_5H_5)(CO)(NO)\,L\,]^+$, $L = PPh_3$, $AsPh_3$, $SbPh_3$, but not $BiPh_3$ or $P(OPh)_3$. These reactions could be effected thermally in contrast to the corresponding reactions of the isoelectronic $[\mathrm{Mn}\,(C_5H_5)(CO)_3]$ with tertiary phosphines which require ultaviolet irradiation.[52] The products here were purified by separation from any unreacted manganese salt by dissolving in dichloromethane, then filtering. The presence of hexafluorophosphate anion was proved by an infrared band in the region 860 - 820 cm^{-1}.

The reaction of $[\mathrm{Mn}(RC_5H_4)(CO)(NO)\,L\,]^+$ with primary amines, where $R = H$ or CH_3, $L = CO$, PPh_3 was studied by Busetto et al.[53] They suggested a nucleophilic attack at the carbon atom of the coordinated carbonyl group. The nature of the carboxamido products was established from their infrared spectra and, where possible, by elemental analysis. The similarities of their infrared spectra to those of the well characterized methylamine complexes in the C-O and N-O stretching regions confirm that the structure of these compounds is of the type shown below:

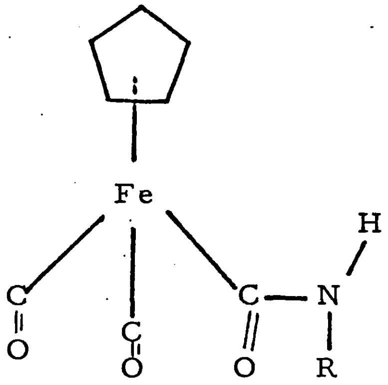
$$[\mathrm{Mn}(XC_5H_4)(CO)(NO)\,L\,]^+ + 2NH_2R \longrightarrow [\mathrm{Mn}(XC_5H_4)(NO)(L)(CONHR)\,] + RNH_3^+$$

Reactions of cyclopentadienylironcarbonyl cations with amines were investigated by Angelici and Busetto.[54] Complexes such as $[\mathrm{Mn}(CO)_4(NH_2R)(CONHR)]$, have been prepared by reaction of $\mathrm{Mn}(CO)_5Br$ with primary aliphatic amines.[55] Angelici showed that, when the iron compound, $[\mathrm{Fe}\,(\eta^5\text{-}C_5H_5)(CO)_2L\,]^+$, $L = CO$ or PPh_3 reacts with the primary aliphatic amines, RNH_2 the carboxamide complex forms as follows:

$$[\mathrm{Fe}(\eta^5\text{-}C_5H_5)(CO)_2L]^+ + 2RNH_2 \rightarrow [\mathrm{Fe}(\eta^5\text{-}C_5H_5)(CO)(L)(CONHR)] + RNH_3^+$$

The nature of these complexes was established from elemental analysis and their infrared spectra. N.m.r. spectroscopic data also help in elucidating the structure of such compounds. Under the same conditions where $[\mathrm{Fe}(\eta^5\text{-}C_5H_5)(CO)_3]^+$ reacted with amines, the neutral manganese compound $[\mathrm{Mn}(\eta^5\text{-}C_5H_5)(CO)_3]$ did not.

The results obtained from the infrared spectra of these compounds are in accord with:



The [Fe(η^5-C_5H_5)$(CO)_2$($CONHCH_3$) complex shows two strong bands at 1972 and 2015 cm^{-1} in methylcyclohexane solvent which are assigned to the $>C=O$ stretching frequencies of the terminal carbonyl groups and medium intensity band at 1625 cm^{-1} due to $>C=O$ stretching frequency of the carboxamide group, this is in agreement with what was found in previous work on similar systems.[56-60]

It is notable that $>C=O$ stretching frequency in the -CONHR group is lower than in HCONHR (~ 1700), and that these stretching frequencies in the compounds [Fe(η^5-C_5H_5)(CO)(PPh_3)(CONHR)] are lower than those in the parent dicarbonyl compounds

[Fe(η^5-$C_5H_5$$(CO)_2$CONHR].

This could be interpreted because of the π-electron donation from the metal to the CONHR group causing a reduction in the $>C=O$ bond order.

2.6 Results and Discussion

The reactions of $[Mn(MeC_5H_4)(CO)_2(NO)]^+$ with some phosphine ligands were studied in acetonitrile at several temperatures. The range of the phosphine ligand concentration was chosen between 5×10^{-2} M* and 1.5×10^{-1} M according to the solubility limitation in acetonitrile. The concentration of the manganese compound was 5×10^{-3} M. The reaction could be represented as follows:

$$[Mn(MeC_5H_4)(CO)_2(NO)]^+ + L \xrightarrow{CH_3CN} [Mn(MeC_5H_4)(CO)(NO)L]+CO \qquad (1)$$

$$L = PPh_3,\ P(p\text{-}F\text{-}C_6H_4)_3\ ,\ P(OPh)_3.$$

An infrared spectrometer of the type Perkin-Elmer 177 was used for the kinetic study. The absorbance was measured by following the disappearance of the peak corresponding to the highest carbonyl stretching frequency of the starting compound, at different time intervals from the equation:

$$D = \log (T_\infty / T)$$

where T is the transmittance of the peak at time t and T_∞ is the transmittance of the blank solution.

Good linear plots were obtained from the data shown by plotting – lnD versus time (Fig. 1). The pseudo-first order rate constants obtained from duplicate runs of the same reaction were reproducible to 5% or better. The second order rate constants obtained from reactions with the same reagent but at different concentrations were reproducible within the experimental error.

Before making any run, a decomposition study was carried out qualitatively in a test tube to choose the most convenient solvent for the investigated reaction. It was noticed that the manganese compound decomposes faster in acetone than in acetonitrile. The stability in nitromethane and in methanol solvents was good, but the reaction with phosphines was very slow in these solvents. It was found that the manganese cation

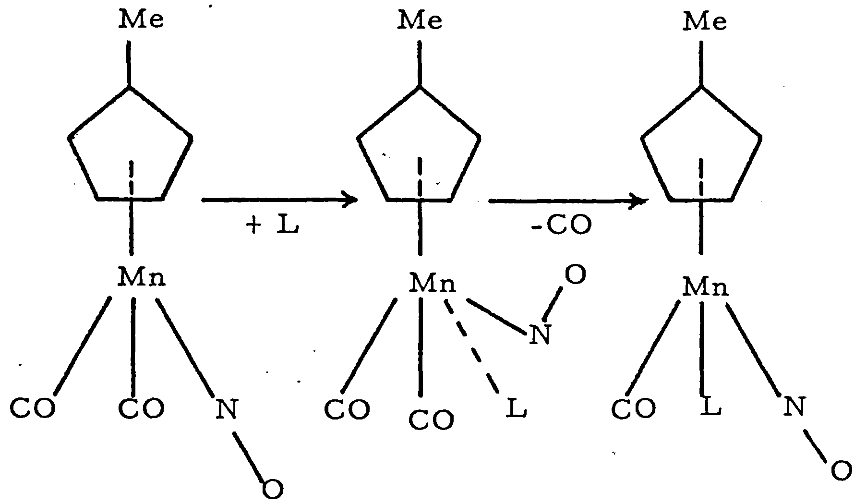
*M = mol dm^{-3}

tends to decompose in acetonitrile solution within a short period (about 150 min). This explains why the range of temperature used for Arrhenius plot study is limited (10, 15, 20, 25 ± 0.1°C).

The data collected from kinetic studies of reaction (1) where L is triphenylphosphine are shown in Table 3. From these data a definite dependence of the observed rate constants on the concentration of the reagent used can be discerned. This is illustrated by (Fig. 2) which shows a plot of k_{obs} versus the reagent concentration in acetonitrile. The figure shows a zero intercept which agrees with the rate law give by the following equation.

$$\text{Rate} = k_2\,[L]\,[\text{Complex}]$$

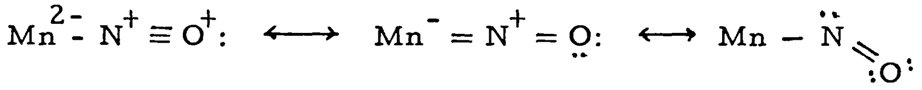
This is in agreement with observations for some metal carbonylnitrosyl complexes such as $[Co(CO)_3(NO)]$ and $[Mn(CO)(NO)_3]$. These results suggest that substitution involves a bimolecular displacement mechanism, which could be of the type represented as follows:



The rate determining step of this mechanism involves not only the ion $[Mn(MeC_5H_4)(CO)_2(NO)]^+$, but also the reagent L.

This mechanism is exactly like that proposed for the CO substitution reaction of $[Co(CO)_3(NO)]$ and it is similar for the S_N2 mechanism proposed in organic chemistry for reactions at a tetrahedral carbon. The configuration of the five coordinated intermediate is not known, however it is quite possibly either a square pyramid or trigonal bipyramid. The latter is favoured here since there are many examples of such structures in systems containing π-bonding ligands.

The reason why metal nitrosyl carbonyls undergo bimolecular displacement reactions may be due to the ease with which nitric oxide can occur in metal complexes in the forms NO^+, NO, NO^- compared with carbon monoxide which can act only as a two electron donor in these systems. As mentioned above nitric acid is normally a three electron ligand, but can behave as a one electron donor ligand in some complexes. It is thought that the nitrosonium ion NO^+ is the better approximation of the ground state existence of this ligand.



$$Mn^{2-} - N^+ \equiv O^+: \longleftrightarrow Mn^- = N^+ = \underset{\cdot\cdot}{O}: \longleftrightarrow Mn - \overset{\cdot\cdot}{N} \searrow :O:$$

III I II

1e donor

A major contribution from structure I is found in most of the M - NO bonding. Structure II shows that nitric oxide behaves as a one-electron donor and is present in the form NO^-. Structure II is not significantly important for the ground state of the manganese complex. In the transition state, its formation would be of great value, the reason is because a vacant orbital of low energy on the metal can then be ready to accept a pair of electrons from an entering reagent. By this, a bimolecular displacement process could be approached.

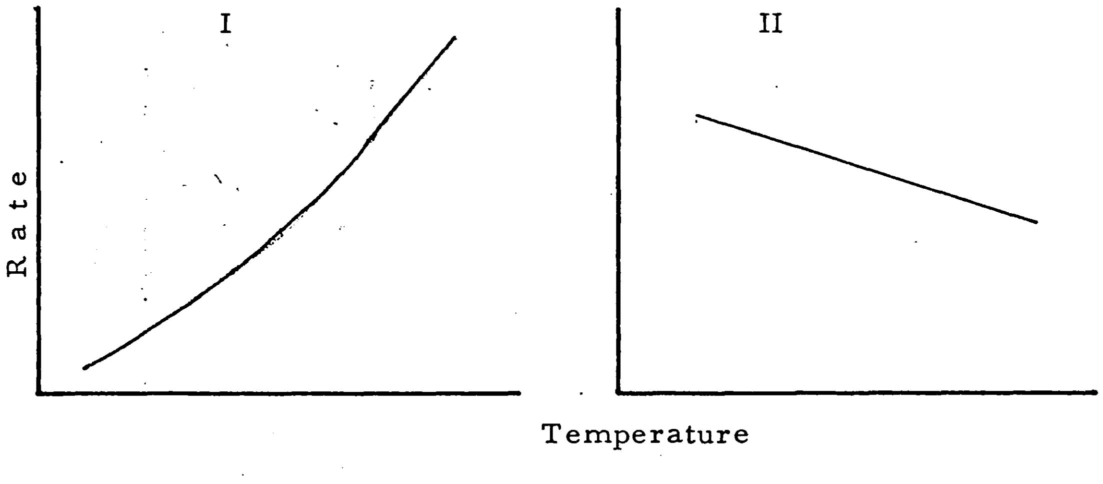
This type of mechanism is not available to binary carbonyl systems such as $[Ni(CO)_4]$ when they react with different nucleophiles. The first step of the reaction involves the slow dissociation of nickel tetracarbonyl to give a tri-coordinate intermediate as shown below.

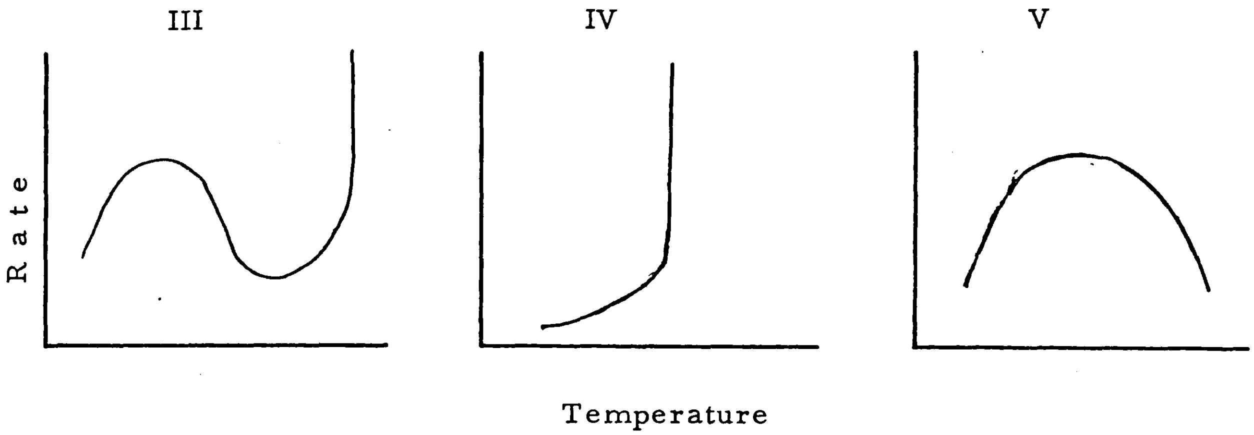
$$[Ni(CO)_4] \xrightarrow{slow} Ni(CO)_3 + CO \xrightarrow[+ L]{fast} [Ni(CO)_3L]$$

The kinetic study of this reaction showed that it is first order and the rate determining step is dependent only on the nickel complex concentration. Nickel tetracarbonyl is tetrahedral and diamagnetic. The activated complex formed in the transition state is likely to be a tri-coordinated species. Spectroscopic evidence for such species have been found at very low temperatures by matrix isolation. The fourth coordination position of the nickel may be occupied subsequently by the attacking ligand.

Measurements of activation parameters can give an indication about the type of mechanism followed. For instance a positive activation entropy is to be expected for a dissociative process, because in the transition state some degrees of freedom are gained. But in case of bimolecular reaction mechanism, the activation entropy is negative, because some degrees of freedom are lost.

Observed rate constants depend on temperature. Plots showing different forms of this dependency are given below.[61]





Case 1 is common and called Arrhenius temperature dependence, but cases from II to V may be called anti-Arrhenius. When Arrhenius' equation holds, it is found that a plot of $\log_e k$ versus $1/T$ is nearly linear with negative slope. This is in agreement with the relationship

$$d \ln k / dT = E_a / RT^2 \quad ,$$

E_a is known as Arrhenius activation energy, which is independent of temperature. Integration results in

$$\ln k = -E_a/RT + \text{constant, or}$$

$$k = Z\, e^{-E_a/RT} \quad ; \text{ k is the rate constant,}$$

T is the absolute temperature, R is the gas constant.
By plotting lnk against $1/T$, a straight line is obtained from which the slope could be calculated

slope = $-E/R$, and from this relationship
E could be determined.

The enthalpy of activation, $\Delta H^{\ddagger}$, could also be determined from the equation

$$\Delta H^{\ddagger} = E - RT$$

Subsequently the entropy of activation $\Delta S^{\ddagger}$ can be derived using the following equation:

$$\ln k = \frac{\ln k'}{h} + \ln T - \frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}$$

k' = Boltzmann's constant

h = Planck's constant.

The values of the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reaction of manganese compound with PPh_3 were recorded in Table 5.

The negative value of $\Delta S^{\ddagger}$ indicates that the reaction proceeds by a bimolecular mechanism. Many workers have found similar results for such bimolecular substitution reactions, for example for the reaction of $[Co(CO)_3(NO)]$ with PPh_3, Basolo found $\Delta H^{\ddagger} = 64$ k J mol^{-1} and $\Delta S^{\ddagger} = -103$ J. K.$^{-1}$ mol^{-1}.

The reaction of the manganese compound with $P(p\text{-}F\text{-}C_6H_4)_3$ was tried at 25±0.1°C. Under the same conditions at which the triphenylphosphine ligand was studied, this reaction was found to be too slow to follow kinetically even by using 20 or 50 times excess of the ligand concentration.

At 35 ± 0.1°C, however, a reasonable rate of change in the intensity of the infrared peaks was observed. The decomposition of the manganese compound at such a high temperature, however, caused difficulty.

The kinetic procedure is described below in the experimental section. The reaction was followed by measuring the change in absorbance at 2125 cm^{-1}. The peak which is gradually formed at 2075 cm^{-1} is assigned to the product.

By plotting -lnA against time a straight line was obtained, from which values of the initial rate constants could be calculated (Fig. 4). The relationship between k_{obs} and the phosphine ligand concentration gave a good linear plot passing very near to the origin (Fig. 5). This indicates that the observed rate constants are proportional to the tri-para-fluorophenylphosphine concentration. The slope of this plot gives the value of a second order rate constant.

Unfortunately, because of the tendency of the manganese compound to decompose faster at higher temperatures, it will be unsatisfactory to extend the study to determine the activation parameters for this reaction. Table 6 shows the values obtained for observed rate constants with different ligand concentrations.

The reaction between the manganese compound and $P(OPh)_3$ was investigated by using the same reactant concentrations as for PPh_3 ligand. Even at 60°C, however, only traces of product were formed after 1 hr. This agrees with the reported sequence of reactivity of the phosphine ligands for substitution of metal carbonyl complexes. The rates lie in the order[15]

$$P(Et_3) \sim P(n\text{-}Pr)_3 > P(Et)_2Ph > P(Et)Ph_2 > P(OMe)_3 > PPh_3 > P(OPh)_3$$

The reaction between the manganese compound and diphenyl-p-methoxyphenylphosphine was also attempted. The reaction went smoothly at first but after about 70 min, it started to accelerate suddenly. This behaviour which was also observed with the ligand $P(p\text{-}F\text{-}C_6H_4)_3$ is not understood, but may be due to traces of impurities in the solvent which catalyse the reaction.

TABLE 3

Values of k_{obs} and k_2 for the reaction between $[Mn(MeC_5H_4)(CO)_2(NO)]^+ PF_6^-$ and PPh_3 in acetonitrile at different temperatures.

T/°C	[L] / mol dm^{-3}	$10^4 k_{obs}$ / s^{-1}	$10^3 k_2$ / $dm^3 mol^{-1} s^{-1}$
10.0	0.05	0.28	0.56
10.0	0.075	0.59	0.78
15.0	0.05	0.64	1.28
15.0	0.075	1.09	1.45
15.0	0.10	1.24	1.24
15.0	0.12	1.60	1.33
20.0	0.05	1.05	2.10
20.0	0.075	1.41	1.88
20.0	0.10	1.91	1.91
20.0	0.12	2.30	1.91
25.0	0.05	1.70	3.40
25.0	0.075	2.61	3.48
25.0	0.10	3.03	3.00
25.0	0.12	4.30	3.58

TABLE 4

Values of ln k_2 and 1/T for the reaction between [Mn(MeC$_5$H$_4$)(CO)$_2$(NO)]$^+$PF$_6^-$ and triphenylphosphine in acetonitrile at the chosen temperatures.

T/K	1/T/K^{-1}	k_2/dm^3 mol^{-1} s^{-1}	ln k
283.4	0.00350	0.67×10^{-3}	-7.30
288.2	0.00347	1.28×10^{-3}	-6.66
293.4	0.00340	1.95×10^{-3}	-6.24
298.2	0.00335	3.48×10^{-3}	-5.66

TABLE 5

Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of the reaction between [Mn(MeC$_5$H$_4$)(CO)$_2$(NO)]$^+$PF$_6^-$ and PPh$_3$ in acetonitrile at different temperatures.

T/K	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/JK mol^{-1}
283.4	78.3	-29.4
288.2	78.2	-28.7
293.4	78.2	-30.1
298.2	78.2	-29.9

TABLE 6

Values of k_{obs} for the reaction between $[Mn(MeC_5H_4)(CO)_2(NO)]^+PF_6^-$ and P (p - $F(C_6H_4)_3$) at 35. 0 ± 0. 1 °C.

[L] / mol dm^{-3}	k_{obs} / s^{-1}
0. 156	2.1×10^{-5}
0. 20	3.0×10^{-5}
0. 225	3.3×10^{-5}
0. 25	3.7×10^{-5}

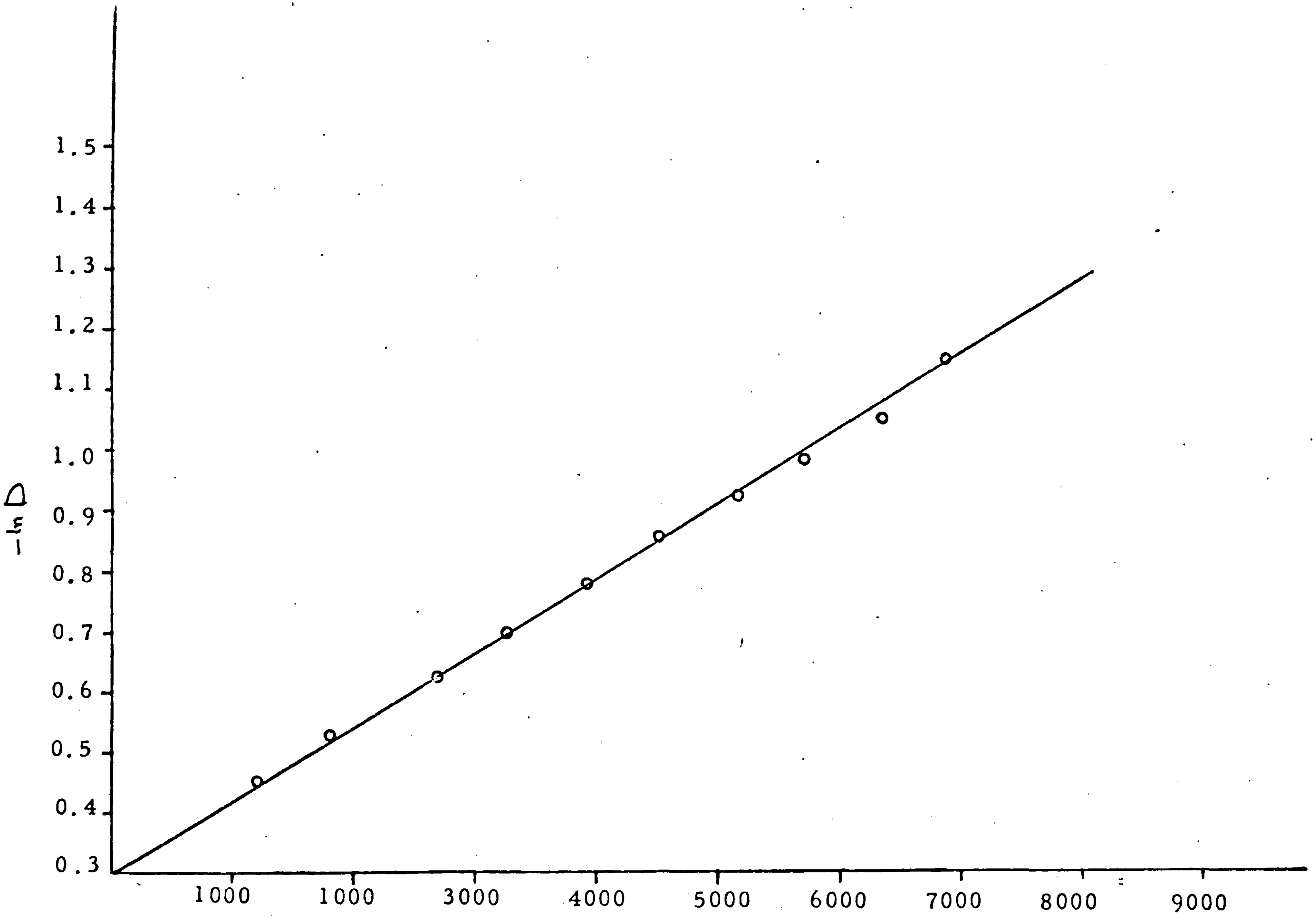


Fig. 1. Pseudo first order kinetic plot for the reaction between $[Mn(MeC_5H_4)(CO)_2(NO)]PF_6^-$ and PPh_3 in CH_3CN at 15°C

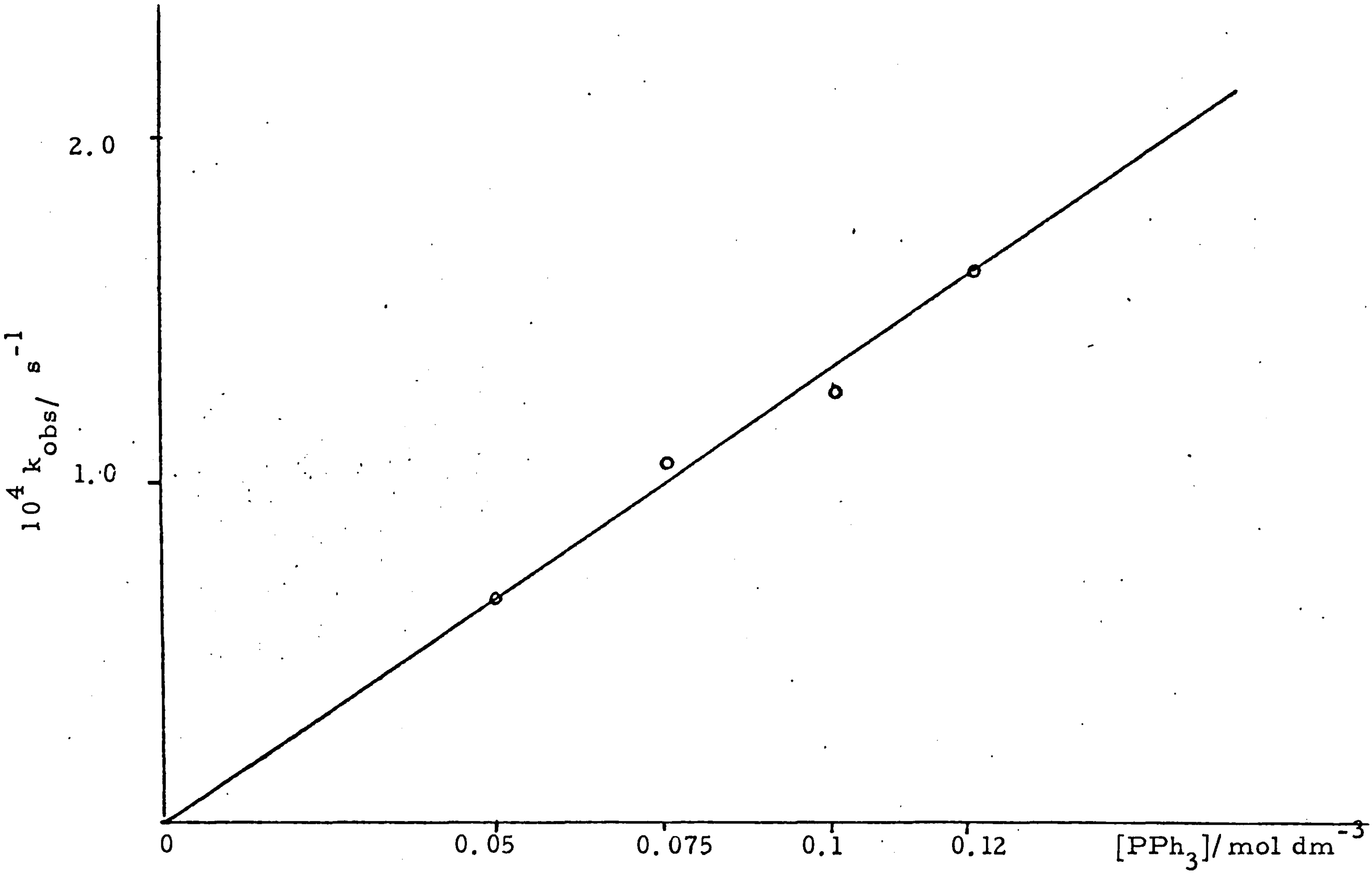


Fig. Plot of k_{obs} v. PPh_3 concentration for the reaction between $[Mn(MeC_5H_4)(CO)_2(NO)]^+ PF_6$ and PPh_3 in CH_3CN at 25°C

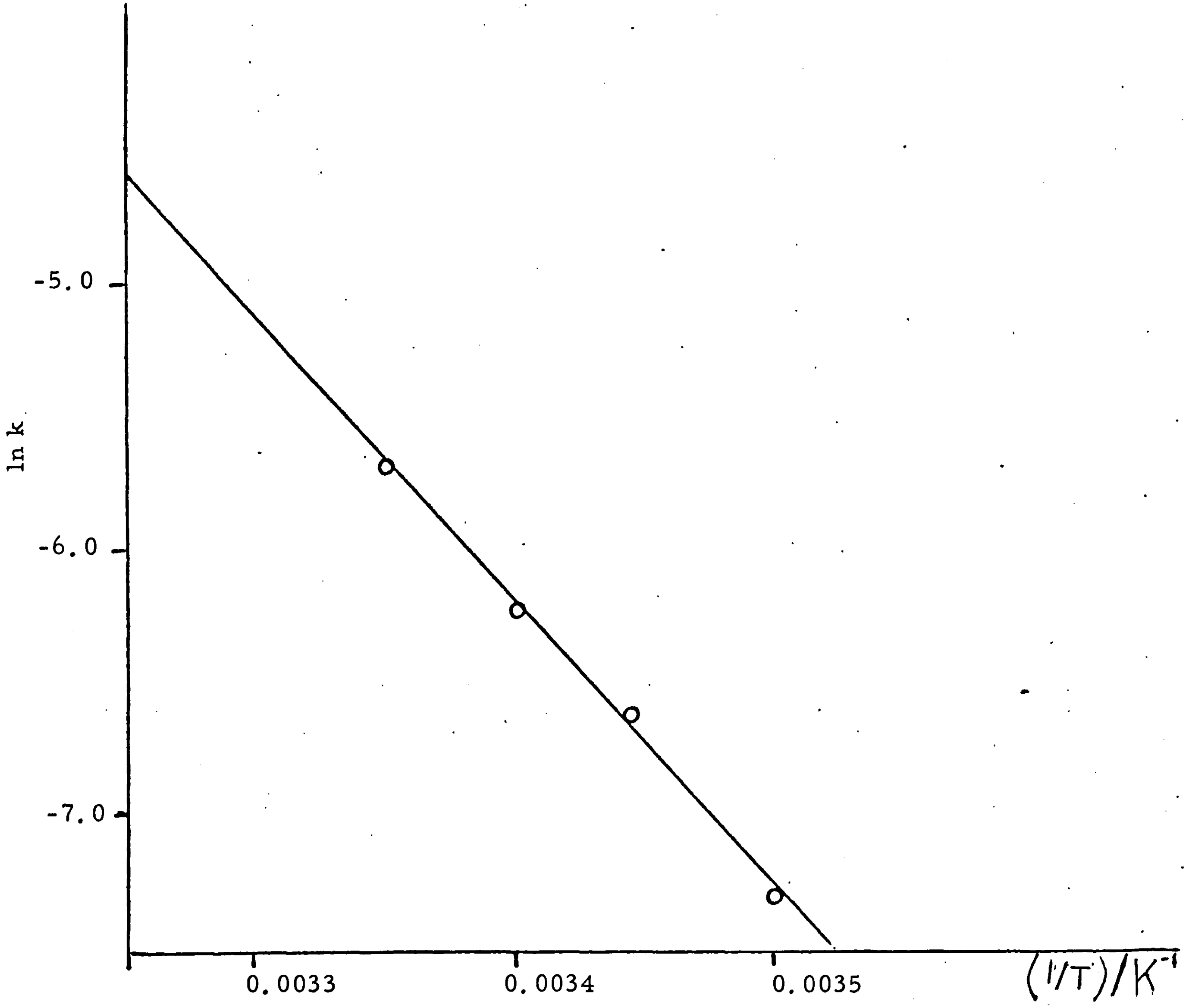


Fig. 3. Arrhenius plot of the reaction between $[Mn(MeC_5H_4)(CO)_2(NO)]^+PF_6^-$ and PPh_3 in CH_3CN

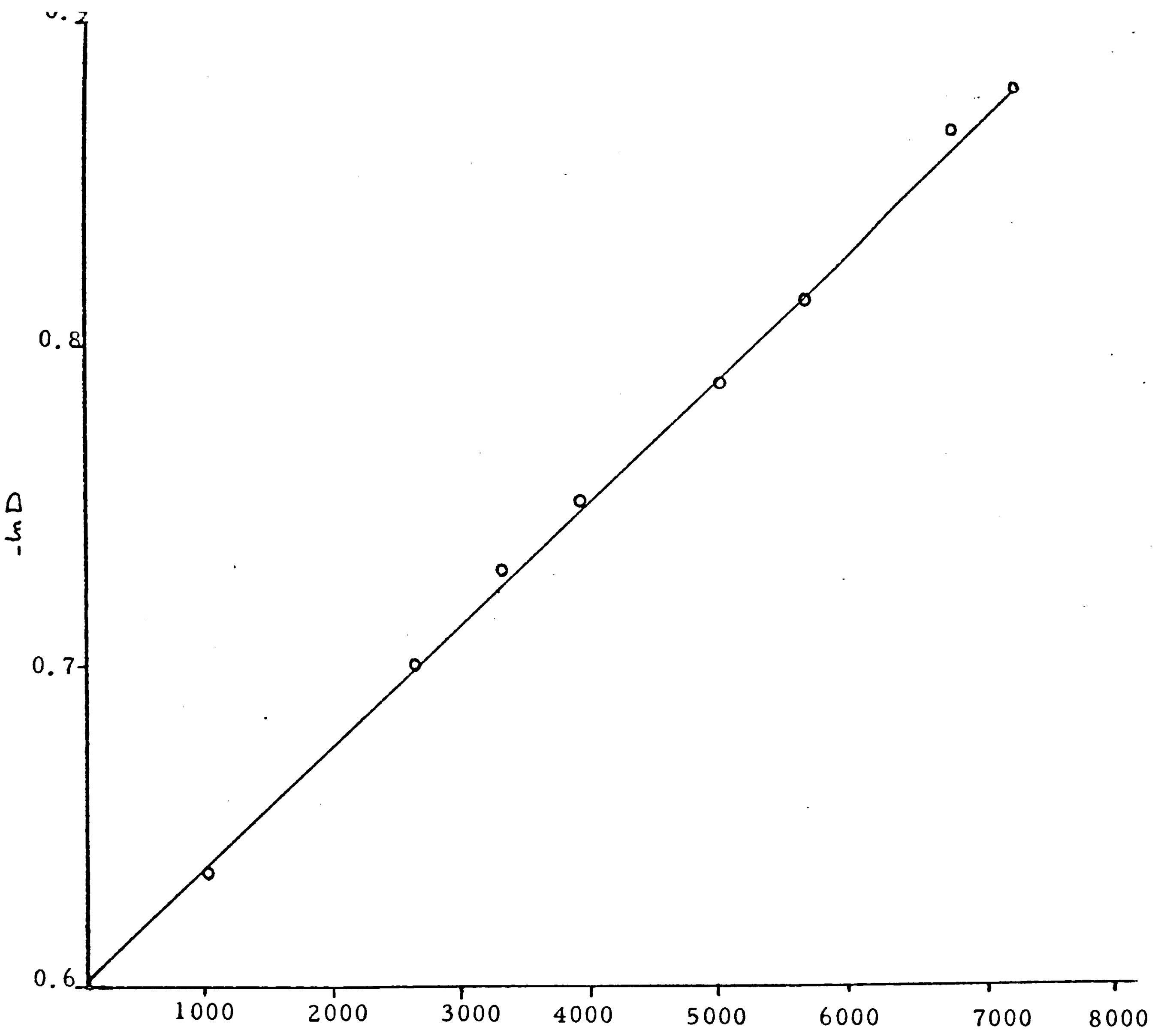


Fig.4 Pseudo first order kinetic plot for the reaction between $[Mn(MeC_5H_4(CO)_2(NO)]^+PF_6$ and $P(p\text{-}F(C_6H_4)_3)$ in CH_3CN at 35°C

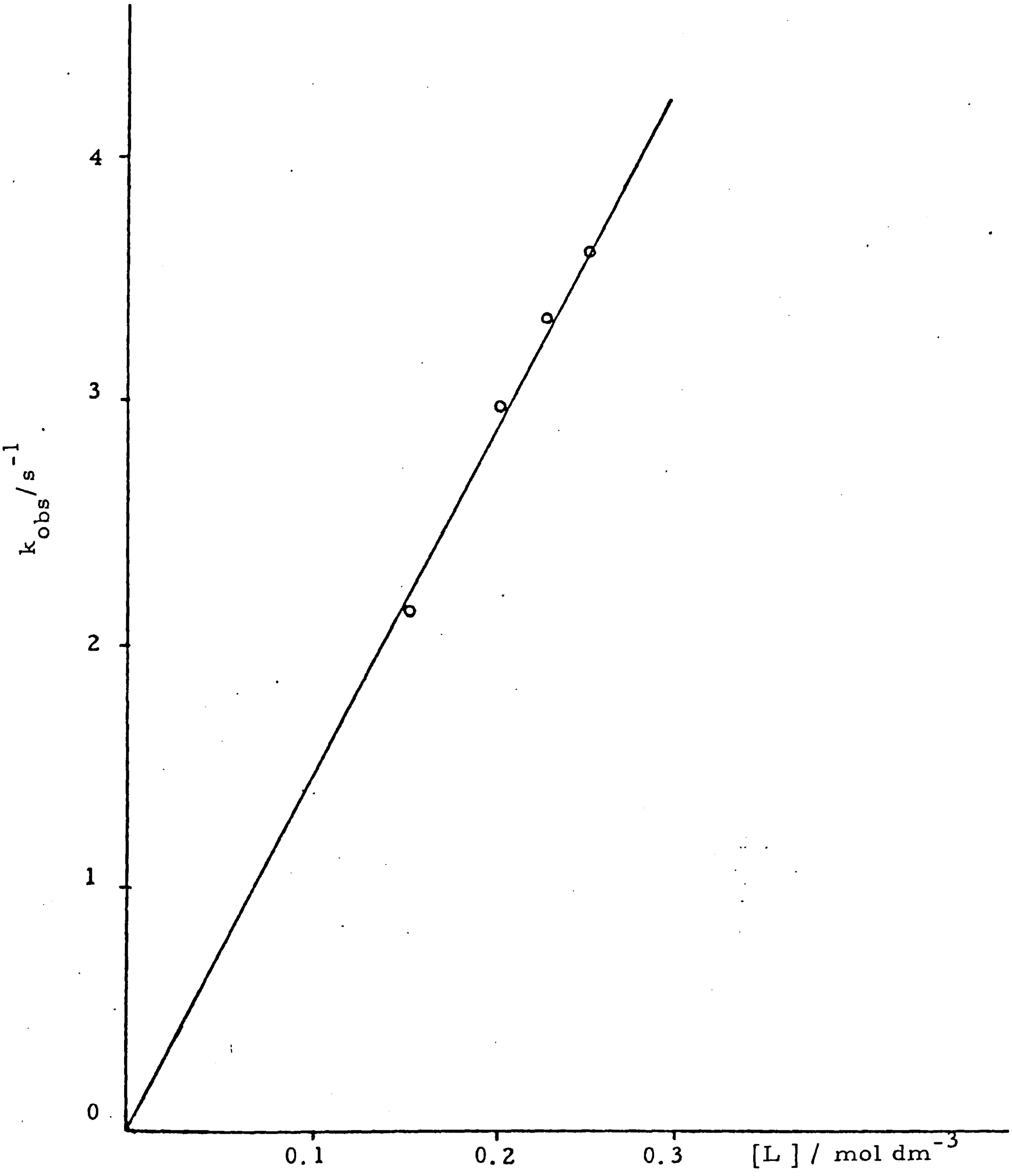


Fig.5 Plot of k_{obs} v. [P(p-F(C_6H_4)$_3$)] for the reaction between [Mn(MeC_5H_4)(CO)$_2$(NO)] and in CH_3CN at 35°C.

2. 7 Experimental Section

Reagents and Solvents:

Triphenylphosphine: was obtained commercially and used without any further purification.

Tri(4-fluorophenylphosphine): used as the commercial product.

Triphenylphosphite: was obtained commercially, but, before use it was dissolved in a suspension of sodium in ether, allowed to stand overnight and then fractionally distilled under nitrogen.

Acetone: this was purified by adding type Linde (4Å) molecular sieves, and then distilled afterwards.

Tetrahydrofuran: this was refluxed over and distilled from sodium and benzophenone. This solvent had to be used directly after distillation.

Acetonitrile: was purified by the method of Perrin. Shaking with dried Linde 4Å molecular sieves removed most of the water content in acetonitrile. Then stirring with calcium hydride until no further hydrogen was evolved, removed acetic acid, but left traces of water. The solvent was distilled by fractional distillation at high reflux under nitrogen. Phosphorus pentoxide was added to remove any remaining water. Any excess of P_2O_5 should be avoided, because it forms an orange polymer. Traces of P_2O_5 could be removed by distilling from anhydrous K_2CO_3. However this method of purification was convenient for some reactions while for others it was not. This was explained by running the infrared spectrum of different samples of the solvent. When the spectrum of the purified solvent by Perrin's method was compared to that of the standard one a strong new peak appeared at 1230 cm^{-1} which can be assigned to P = O.

Preparation of methylcyclopentadienylcarbonylnitrosylmanganesehexafluorophosphate

The complex was prepared according to King's[30] method. The reactants, methylcyclopentadienyltricarbonylmanganese (30 g.) in 95% ethanol (450 cm^3) and concentrated hydrochloric acid (90 cm^2) were mixed under nitrogen. The mixture was heated to boiling point, and a solution of sodium nitrite (10.5 g.) in water (25 cm^3) was added dropwise. The reaction mixture was filtered to remove sodium chloride. The filtrate was treated immediately with a solution of ammonium hexafluorophosphate (30 g.) in water (50 cm^3), then allowed to cool. The product was precipitated as yellow crystals which were filtered and purified by recrystallization from dry diethylether after dissolving in dry acetonitrile. Yield was 80%.

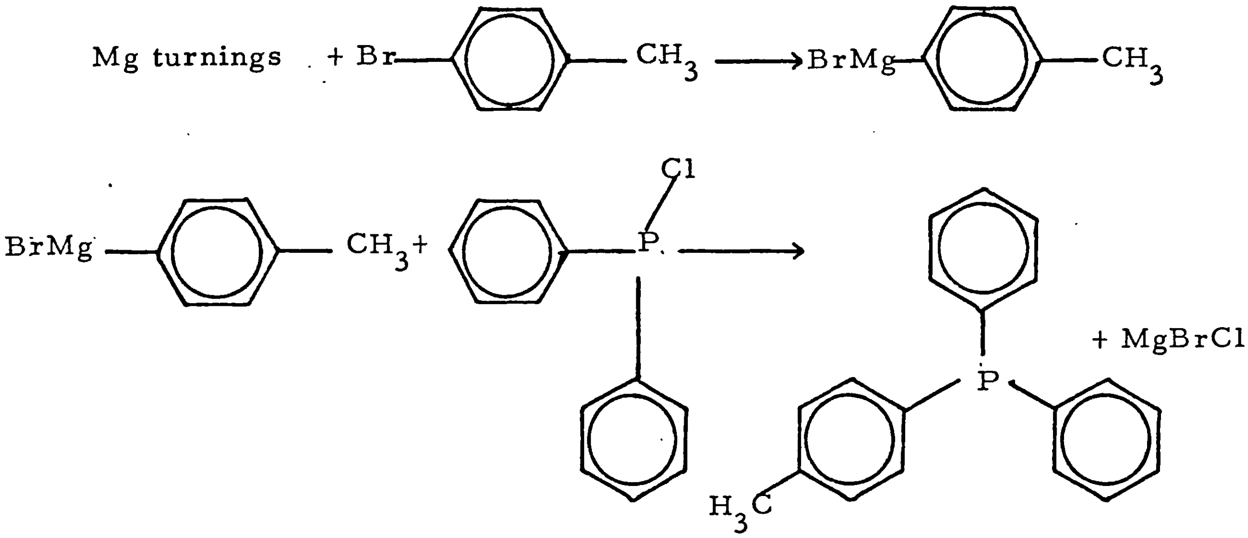
Preparation of methylcyclopentadienylcarbonylnitrosyltriphenylphosphitemanganese hexafluorophosphate.[49]

A solution of $[Mn(MeC_5H_4)(CO)_2(NO)]^+[PF_6]^-$ (1.3 g.) in anhydrous acetone(10 cm^3) was mixed with triphenylphosphite (1 g.) with good stirring under nitrogen. Complete evolution of carbon monoxide gas ceased after about 2 hr. - the solvent was removed under reduced pressure. The residue was taken up several times in small quantities of methylene chloride. The solution was filtered, and hexane was added to the filtrate to precipitate the product. The orange phosphite derivative is air stable in the solid state, but decomposes slowly in solution through oxidation. Yield is about 72%.

Preparation of diphenyl-p-tolylphosphine from a Grignard reagent and chlorodiphenylphosphine.[63]

The method followed was that of Valient et al.

The magnesium (turnings) (5.6 g) was placed in the reaction vessel, to which a solution of para-bromotoluene (37.6 g) in tetrahydrofuran (75 cm^3) was added in drops very slowly. The reaction is exothermic. After adding the whole quantity of p-bromotoluene, the reaction mixture was treated with a solution of chlorodiphenylphosphine (33 g.) in tetrahydrofuran (25 cm^3). Then it was left under reflux for about 24 hr. to obtain good yield 75% (m.p.78.8, Lit 79 °C). The method could be represented by the equations



diphenyl-p-tolylphosphine

Preparation of diphenyl-p-methoxyphenylphosphine

The procedure followed is similar to the preceding one except in the first step p-bromoanisole was used instead of p-bromotoluene to prepare the Grignard reagent (Yield 70%, m.p. 78.7°C, Lit. 79°C).

Kinetic procedure

The rates of the reactions

$$[\mathrm{Mn(MeC_5H_4)(CO)_2(NO)}]^+[\mathrm{PF_6}]^- + \mathrm{L} \longrightarrow$$

$$[\mathrm{Mn(MeC_5H_4)(CO)(NO)\,L}] + \mathrm{CO}\uparrow \quad , \qquad (1)$$

$$\mathrm{L} = \mathrm{PPh_3},\ \mathrm{P(OPh)_3}, \mathrm{P(p\text{-}FC_6H_4)_3}$$

were followed by monitoring changes in the infrared spectrum of the reaction mixture by using an infrared spectrometer of the type Perkin-Elmer 177. All the kinetic studies were carried out under pseudo-first order conditions using at least a tenfold excess of reagent. A preliminary study showed that $[\mathrm{Mn(MeC_5H_4)(CO)_2(NO)}]^+[\mathrm{PF_6}]^-$ obeyed the Beer-Lambert law in the C-O stretching region.

The reactions were carried out under nitrogen in an aluminium foil-wrapped vessel (the complex is photosensitive), fitted with a serum cap. The reagent solutions were prepared and thermostatted for about 20 min. They were then transferred into the reaction vessel by means of a syringe equipped with a six inch needle. A sample of the mixture was then injected into the infrared cell. The concentration of the $[\mathrm{Mn(MeC_5H_4)(CO)_2(NO)}]^+[\mathrm{PF_6}]^-$ had to be between 5×10^{-3} M and 2×10^{-2} M. At appropriate time intervals small portions were withdrawn from the reaction vessel with the syringe, transferred into the infrared cell and their infrared spectra measured against a reference containing the reagent solution only. About fifteen measurements were made during a period of 115 min.

A few reactions were too fast to follow by the preceding method. In such cases the reactants were prepared, thermostatted, and mixed together in the normal manner. However, as soon as they were mixed a small volume was transferred into a thermostatted infrared cell. Repeated scans over the frequency range 2400 cm^{-1} to 2000 cm^{-1} were made at suitable time intervals. The change in absorbance due to the highest energy C-O stretching band of $[Mn(MeC_5H_4)(CO)_2(NO)]^+]PF_6]^-$ was followed continuously by means of a recording pen. It was found that the bath temperature which supplied the cooling water for the cell needed to be at 23.2 °C in order to give a temperature of 25.0°C within the thermostatted cell when it was in the infrared beam.

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CHAPTER THREE

KINETIC STUDY OF THE REACTION OF (6-PHENYLHEXA-3, 5-DIEN-2-OL) TRICARBONYLIRON AND TRIFLUOROACETIC ACID

CHAPTER 3.

Kinetic study of the reaction of (6-phenylhexa-3, 5-dien-2-ol) tricarbonyliron and trifluoroacetic acid.

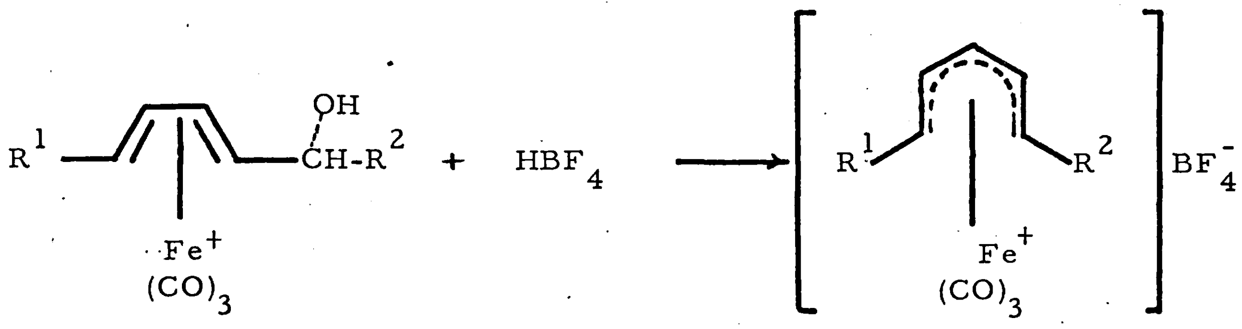
3.1. Introduction.

Several cationic complexes in which a tricarbonyliron species is π-bonded to a pentadienyl group have been prepared. Fischer and Fischer[1] in 1960 succeeded in isolating stable salts of the cyclohexadienyltricarbonyl cation from the reaction of cyclohexadienetricarbonyliron with triphenylmethyl fluoroborate. Dauben and Honnen[2] had previously used a similar method for preparing the salts of the tropyliumtricarbonylmolybdenum cation. The same principle was utilised to obtain salts of cycloheptadienyltricarbonyliron cation by hydride ion abstraction from cycloheptadienetricarbonyliron.[3]

Study of the structure and spectroscopic properties of substituted pentadienyltricarbonyl cations has been carried out by many workers. For instance the investigation made by Mahler et al[4, 5], covered many important aspects of the chemistry of such tricarbonyliron cations. The structural properties have been studied in detail by n.m.r. spectroscopy.

Mechanistic studies and kinetic measurements usually make use of infrared spectroscopy for following the decrease in the intensity of the characteristic bands of the carbonyl groups in the parent cation.

Mahler and Pettit[4] showed that the pentadienyltricarbonyl iron cations can be prepared by treatment of a series of pentadienoltricarbonyliron complexes with fluoroboric acid. Addition of ether to the reaction mixture caused precipitation of the cation salts as bright yellow crystals. In all cases n.m.r. analysis of the salts indicated that they possessed the cisoid structure illustrated below.



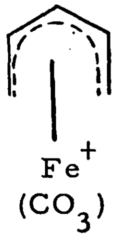
a - $R_1 = R_2 = H$

b - $R^1 = H$, $R^2 = CH_3$

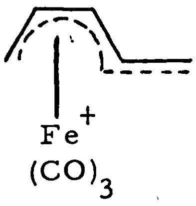
c - $R^1 = R^2 = CH_3$

The salts were found to be thermally stable; however, they were found to react with a variety of nucleophiles such as water, alcohols, amines, hydride ions, and electron-rich aromatic compounds.

Before going any further, it is worth mentioning that acyclic cations might exist in two forms, a cis and a trans form as shown below.



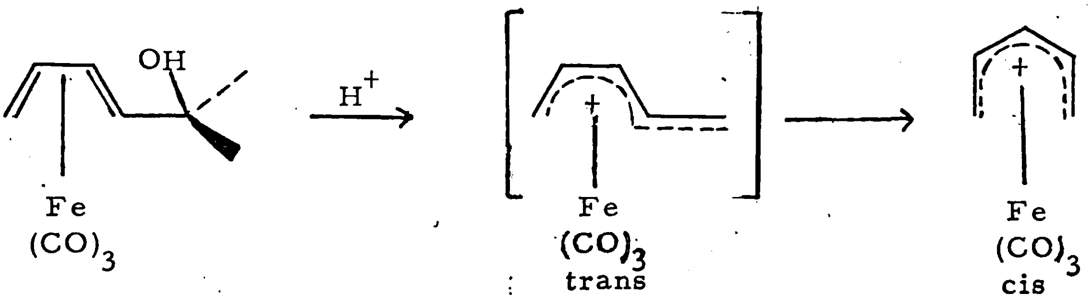
cis



trans

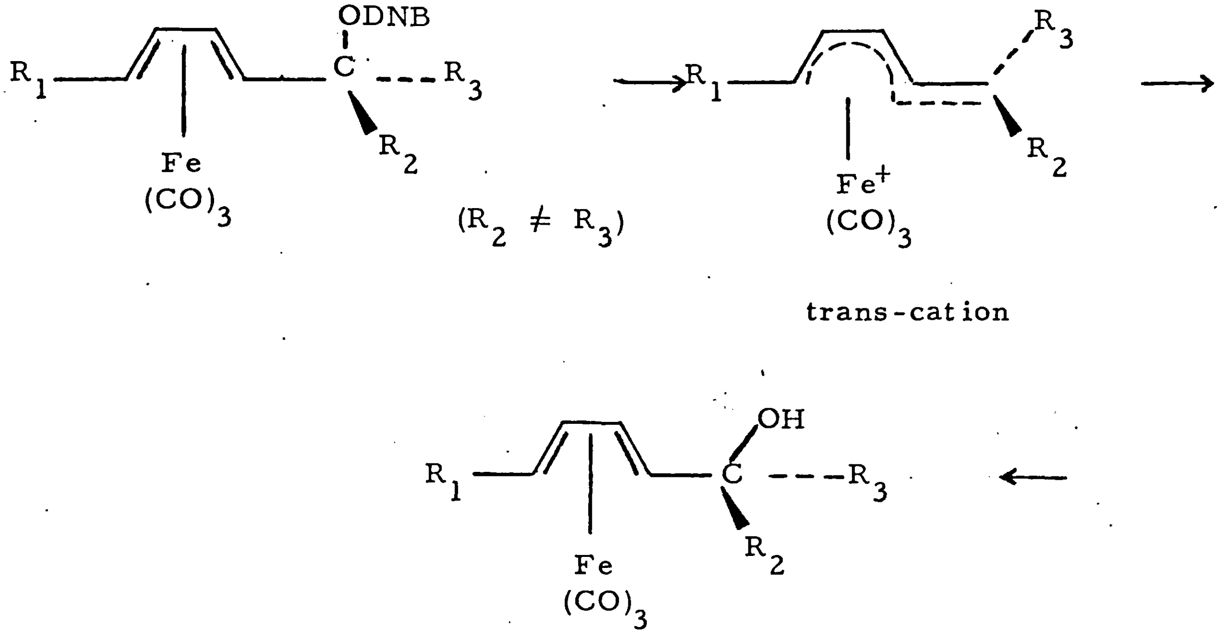
Further evidence for the symmetrical nature of the parent cis-π pentadienyltricarbonyliron cation was obtained from ^{13}C n.m.r. spectroscopy.

The trans-pentadienyltricarbonyliron cations were proposed first by Mahler and Pettit[4, 5] as intermediates in the formation of the geometrically inverted cis-pentadienyl tricarbonyliron cations, from the alcohol complexes.



The rearrangement of acylic trans pentadienyltricarbonyl iron cation to the cis isomer might indicate the greater thermodynamic stability of the latter.

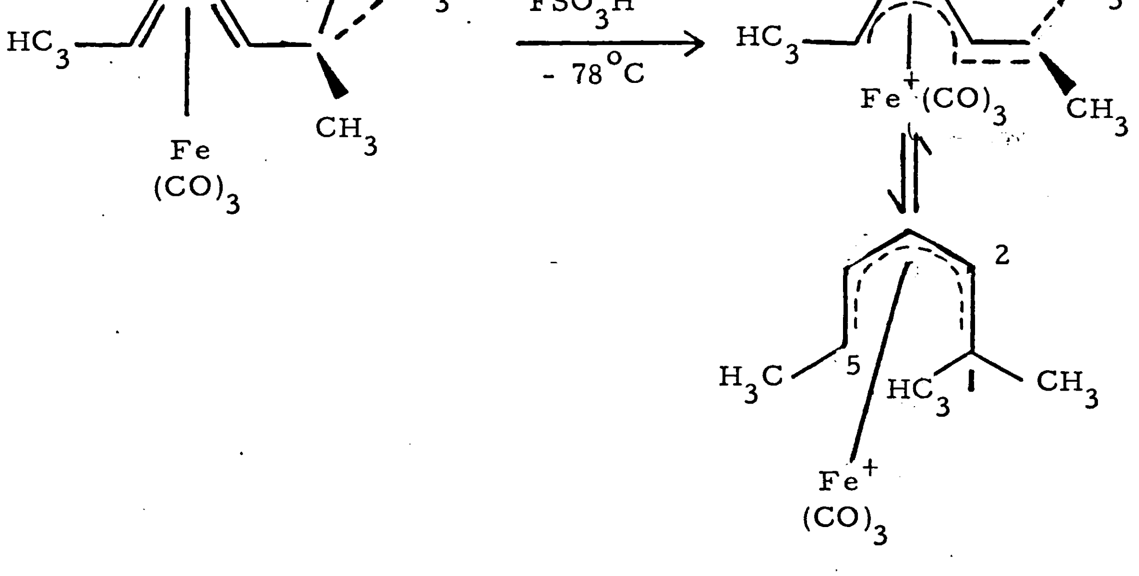
Clinton and Lillya[6] have offered more direct evidence for the presence of trans ions from a kinetic study of the hydrolysis reaction of the 2, 4-dinitro-benzoate esters of the diastereomeric alcohols shown below. It was found that the ψ-exo ester solvolyses about 90 times faster than the ψ-endo isomer. The mechanism proposed for this reaction is consistent with S_N1 type. With the bulky leaving group departing exo to iron, a trans-pentadienyl-tricarbonyliron cation is suggested in the intermediate step. Retention of configuration for the solvolysis of several pentadienyl ester complexes was observed.



trans-cation

DNB = dinitro-benzoate

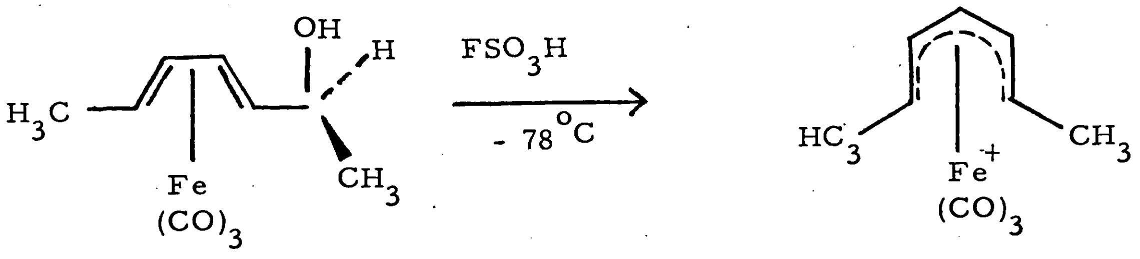
Some results in favour of an equilibrium between the trans and cis cation have been obtained. Sorensen and Jablonski[7] observed such trans species by n.m.r. spectroscopy together with some interconversions of the cis ions. Protonation of the ψ-endo alcohol shown below with fluorosulphonic acid at low temperature gave a deep red solution containing a mixture of the trans-pentadienyltricarbonyliron cation and the cis form.



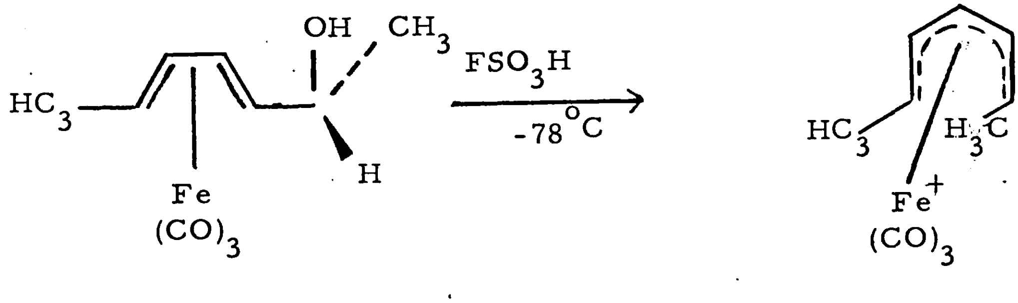
The equilibrium constant for the cis ⇌ trans interconversion which presumably involves rotation about the C_2-C_3 bond is 3.0 ± 0.3 at -50°C favouring the trans form.

A study of the rate of trans ⇌ cis interconversion using a modification of the nuclear magnetic double resonance method of Forsen and Hoffman[8] has verified that an equilibrium situation exists and leads to a rate constant of 0.75 sec^{-1} at -32.5°C and an energy barrier (E_a) for trans → cis in the order of 54 kJ.

In contrast to Mahler and Pettit[5] who isolated only the cis, syn, syn ion from either of the diastereomeric alcohol complexes of the pentadientyltricarbonyliron, the authors found that the alcohols clearly showed stereospecific conversion into the cis ions in strong acid solutions at low temperature:



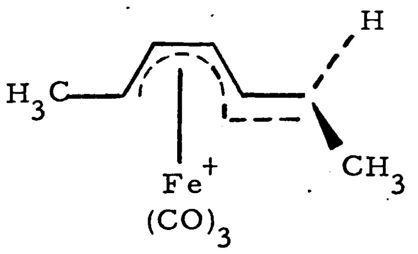
ψ-exo

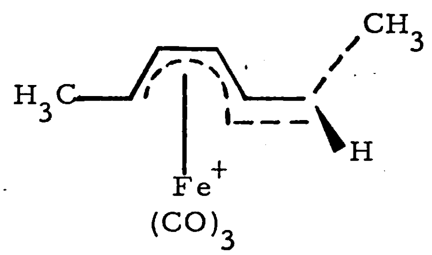


ψ-endo

N.m.r. studies indicated that the conversion of cis, syn, anti ion to cis, syn, syn ion becomes possible at temperatures above 0°C.

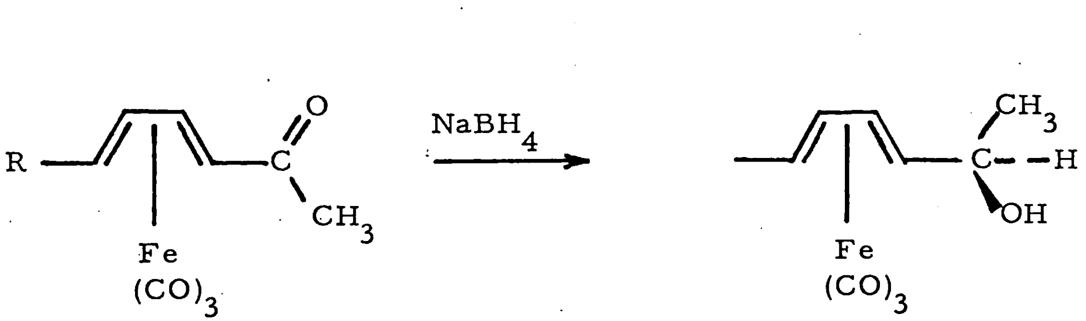
Also it could be assumed according to the preceding observations that both diastereomeric alcohols initially give the following trans cations.





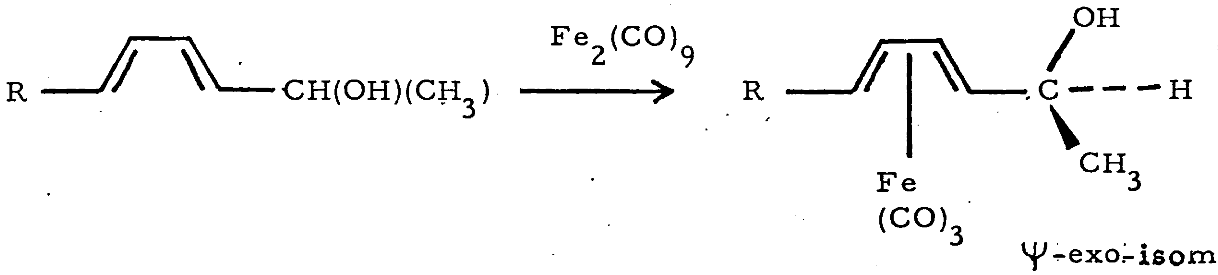
The rearrangement to the cis ion occurs at low temperature, probably because the carbonium lifetimes are extended. Under solvolytic conditions where the product is formed with retention of configuration, the trans ions must be trapped before rearrangement happens.

Clinton and Lillya[9] prepared the two pairs of diastereomeric dienol complexes as shown below. The ψ-endo diastereomer is formed preferentially from the attack of sodium borohydride on the dienone.



ψ- endo-isomer

The other isomer can be prepared by direct coordination of the dienol with $Fe_2(CO)_9$.



Ψ-exo-isomer

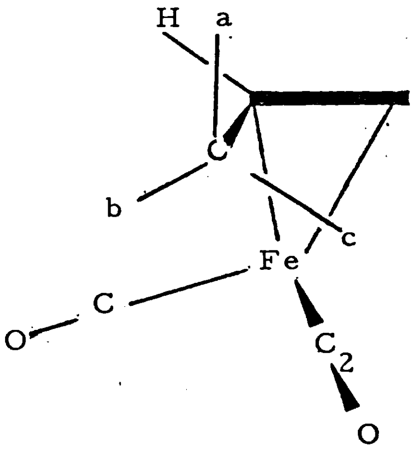
It was found that the dienoltricarbonyl iron compounds exhibit no intramolecular hydrogen bonding between the hydroxy group and iron. Application of conformational analysis to the dienols can give some information about the relative configurations.

Examination of the following model shows that the three distinct positions which substituents on the carbinol carbon occupy in an idealized staggered conformation can be classified according to steric factors as follows.

a - uncrowded

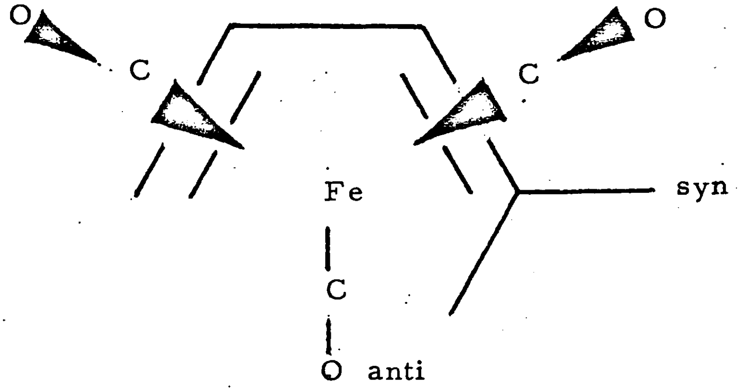
b - slightly crowded

c - severely crowded



The sterically preferred conformations of the two diastereomeric dienol complexes will be those with the largest group in the two relatively least hindered positions. The two diastereomers shown above are assigned Ψ-exo and Ψ-endo configuration according to the favoured positions of the hydroxy group with respect to the iron atom.

However x-ray crystallography has contributed to determining the geometry of the tricarbonyliron complexes of 12 structurally diverse dienes. The 4-carbon diene unit is nearly planar and when the complexes are viewed along the normal dropped from ion to the diene plane, two carbonyl ligands are always eclipsed with the two formal double bonds of the diene.



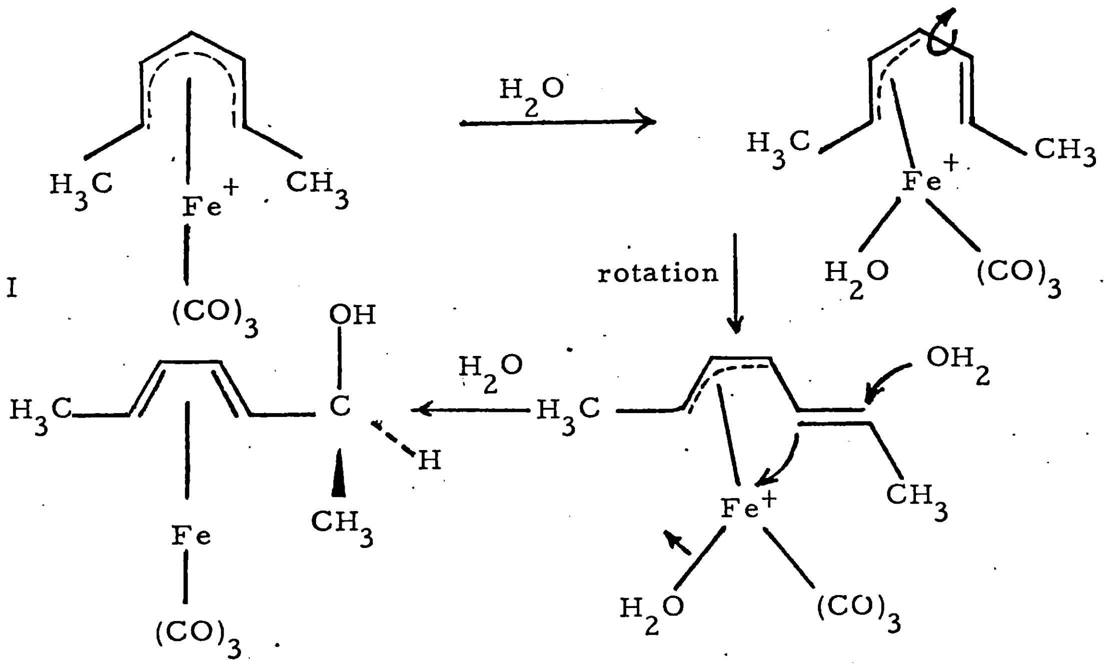
All 12 compounds exhibit this preference. Anti substituents are displaced out of the diene plane away from iron but syn-substituents appear to be bent toward iron.

3.2 Nucleophilic attack on pentadienyltricarbonyliron cations

Investigation of the synthesis and properties of the acyclic cations syn-1-methylpentadienyltricarbonyliron $[C_6H_9Fe(CO)_3^+]$ and syn, syn -1, 5 dimethylpentadienyltricarbonyliron $[C_7H_{11}Fe(CO)_3^+]$ indicated (from n. m. r. data) that these species, like the corresponding cyclic species possess cisoid arrangement of pentadienylcarbon atoms.

These cations can undergo many electrophilic reactions with nucleophiles such as water, alcohols, amines, phosphines, aromatics and hydride ions. The hydrolysis reaction was the most thoroughly studied. This reaction was shown by Mahler and Pettit[5] to be stereospecific. They found that the nucleophilic attack of water on cation I gives only one diastereomer. One mechanism which has been proposed involves an equilibrium between cis I and trans II 1, 5 dimethylpentadienyltricarbonyliron cations. The attack of water occurs through the trans cation as follows

I

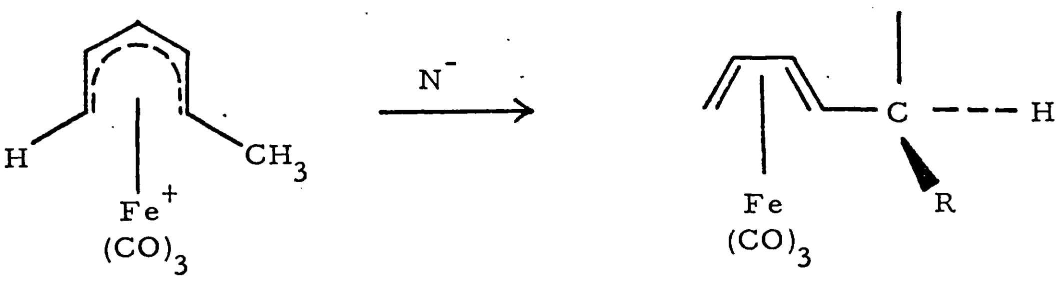


II

The same reaction was studied by Lillya[9] and then later by Willcott[10], and Bayoud[11]. They all came to the same conclusion, that only one of two possible diastereomers with conformations RR and SS was formed. The two diastereomers in these compounds are derived from the presence of two asymmetric centres in the alcohol, one at the C-atom bonded to the hydroxyl functional group and the other resulting from the unsymmetrical diene-iron tricarbonyl group. Foreman[12] who employed the Lanthanide shift reagent technique has questioned the conformation assigned by Pettit[9] and co-workers to the alcohol formed from the hydrolysis of these pentadienyl cations. He declared that the alternative diastereomers i.e. RS and SR rather than enantiomers RR and SS were formed.

This contradiction has been resolved by Riley and Davis[13] in their crystallographic study of the structure of one of these alcohols, (the 1,5-dimethyl species), which proved Lillya's suggestion.[9]

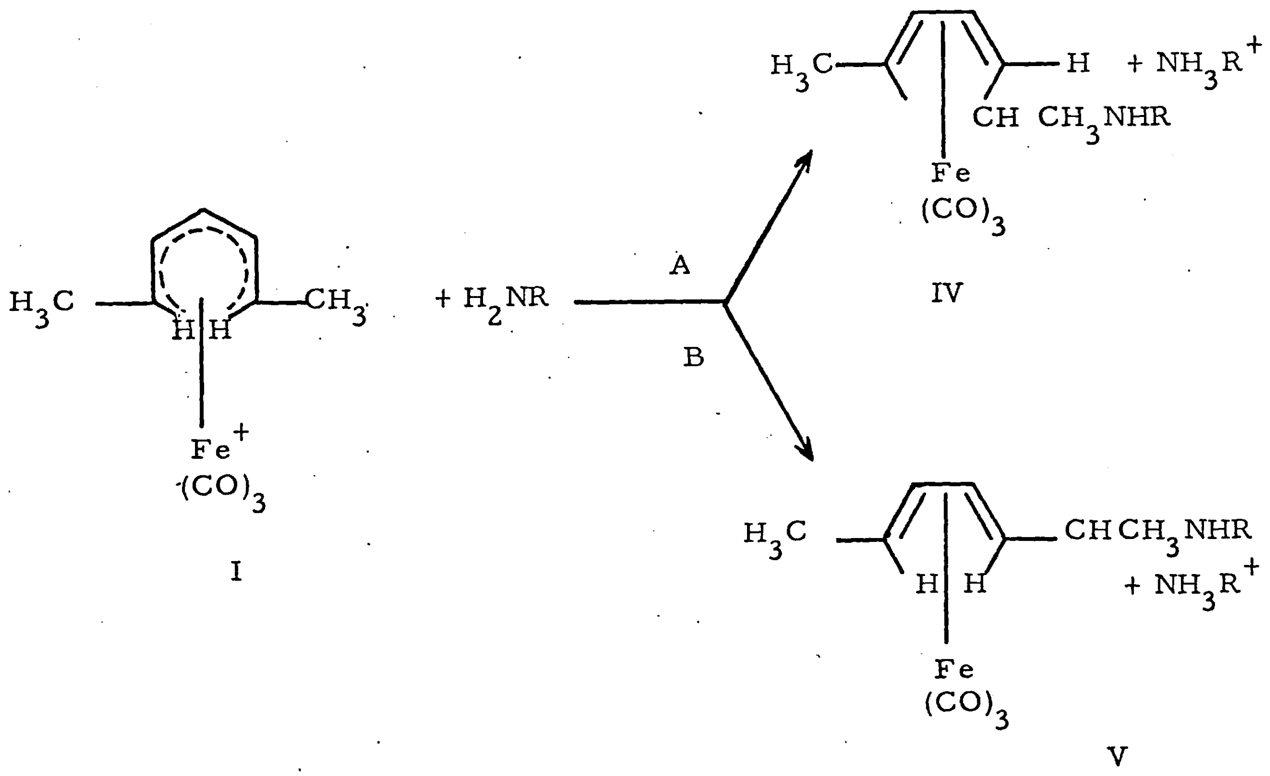
The important features of the preceding mechanism are the hydrated π-allyliron cation, and that the attack by the nucleophile occurs from the least hindered face. In the case of a substituted pentadienyltricarbonyliron cation, water prefers to attack at the carbon atom which bears the smallest substituent. If only one end of the cation is substituted, however, the attack happens at this substituted position because it is thought that the substituent stabilises the reactive intermediate.



Nucleophilic attack favours the terminal carbon which bears a substituent.

On the other hand, the reaction of salts of pentadienyltricarbonyl iron cation with sodium borohydride does seem to be accompanied by geometrical inversion. The reaction product is a mixture of 80% (cis-1, 3-pentadiene)and 20% (trans-1, 3-pentadiene) tricarbonyliron complexes.

Musco et al[14] have investigated the reactions of amines with (syn, syn-1, 5-dimethylpentadienyl)tricarbonyliron (cation I). They found that the reaction pathway is dependent on the basicity of amines; for example, strongly basic amines pK_b 3-6 such as isopropylamine, ethylamine and methylbenzylamine react with I by pathway A, (illustrated below), the product IV was identified from TLC examination of the reaction mixture. Amine having pK_b 10-13 values such as p-bromoaniline, m-nitroaniline and p-nitroaniline give quantitative yields of compounds of type (V). Moderately basic amines react by either A or B, for example p-toluidine pK_b 8-9 showed intermediate behaviour.

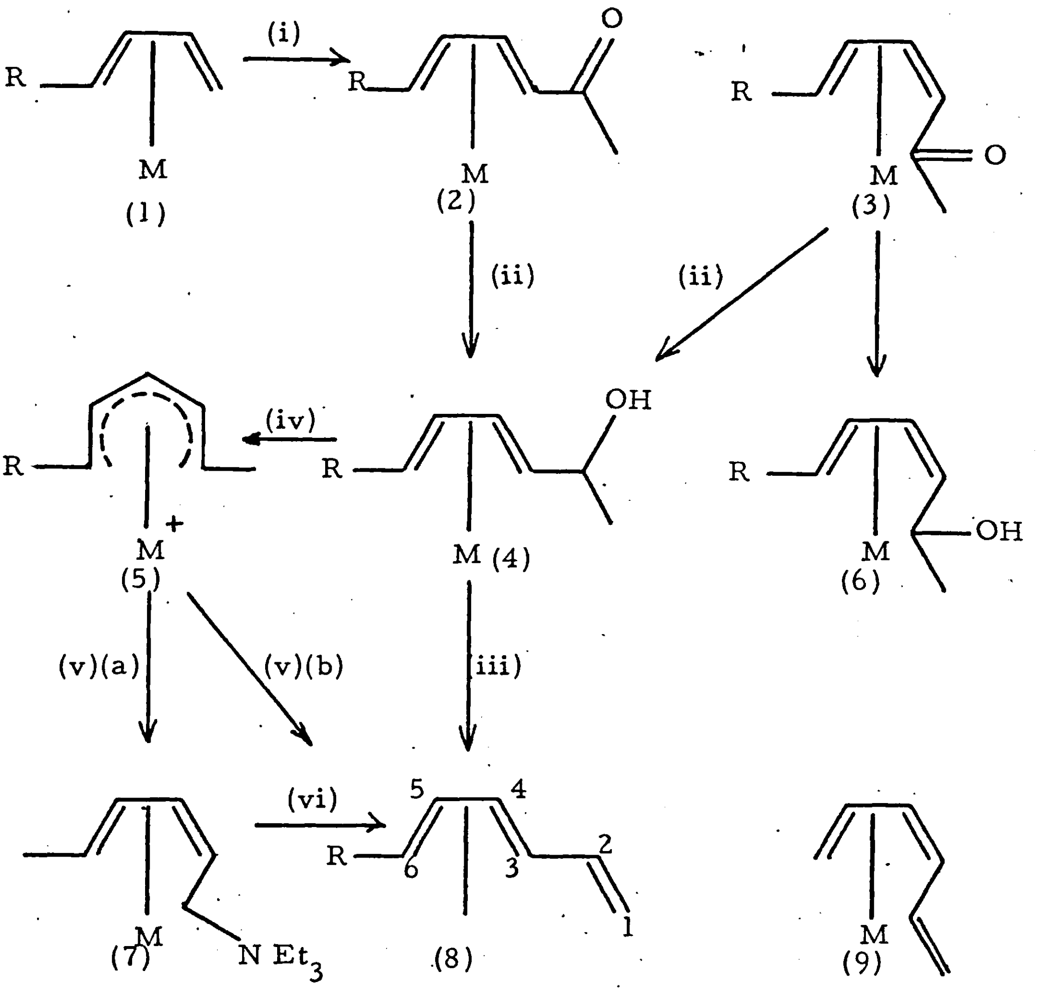


It could be concluded from these results that the strong amines attack the cis ion directly whereas reactions of the weak amines proceed through the the trans ion.

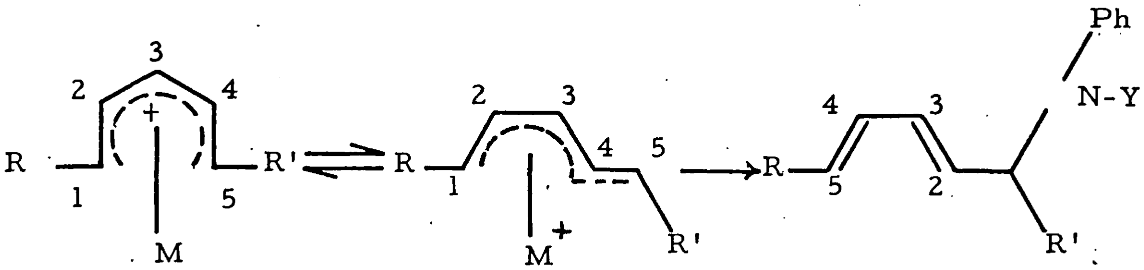
Recently McArdle and Sherlock[15] reported the reactions of the 1-methylpentadienyltricarbonyliron cation with amines, triphenylphosphines and triphenylarsine. They found that aniline and diphenylamine add to the substituted end of the ligand in the 1-methylpentadienyltricarbonyl cation to give dienylamine complexes having syn-geometry. Tertiary amines, PPh_3 and $AsPh_3$ add to the unsubstituted end to give quaternary adducts having anti-geometry. The tertiary amine adducts undergo elimination when heated in vacuo to give the syn-hexatriene complex in good yield. The 1,5-dimethylpentadienyltricarbonyl iron is converted directly into the syn-heptatriene complex on treatment with tertiary amines, but forms anti adducts with PPh_3. Deuterium labelled syn-1-methylpentadienyltricarbonyl iron cation protonates at its uncoordinated double bond.

The authors observed that (5a) formed an adduct (7) with NEt_3 where as (5b) gave the triene (8b), led to the suggestion that steric effects were an important factor in the reaction of cations with tertiary amines.

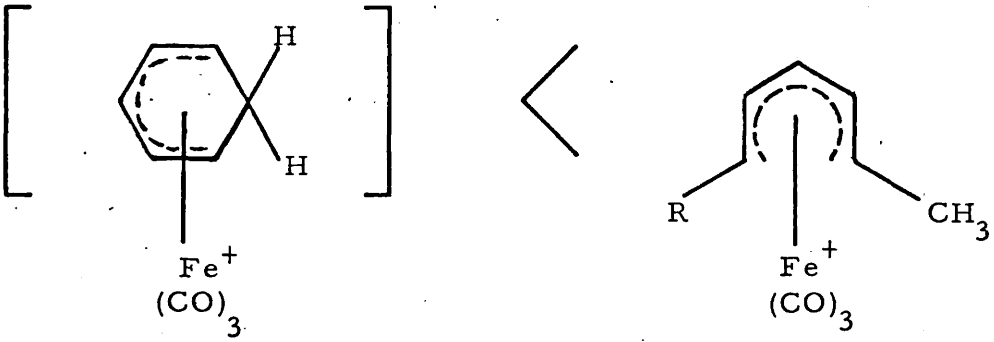
The structure of the phosphine adduct of (5a) could be determined from its n.m.r. spectrum.



M = Fe(CO)$_3$, R = H (a) or Me (b). (i) MeCOCl-AlCl$_3$; (ii) $[BH_4]^-$; (iii) silica gel; (iv) HPF$_6$; (v) NEt$_3$; (vi) heat in vacuo.

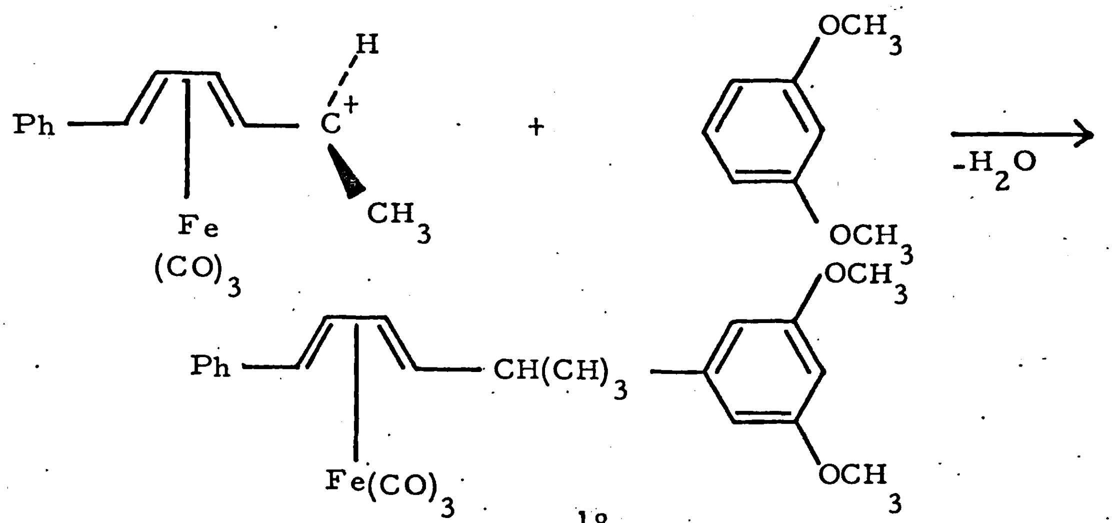


The cyclohexadienyltricarbonyliron cation is also attacked by nucleophiles, but is much less reactive than the corresponding open chain cation. For example, salts of the cyclic cation can be recrystallised from water without change, but the acyclic cation is rapidly attacked by water to give the ψ-exo-dienol.

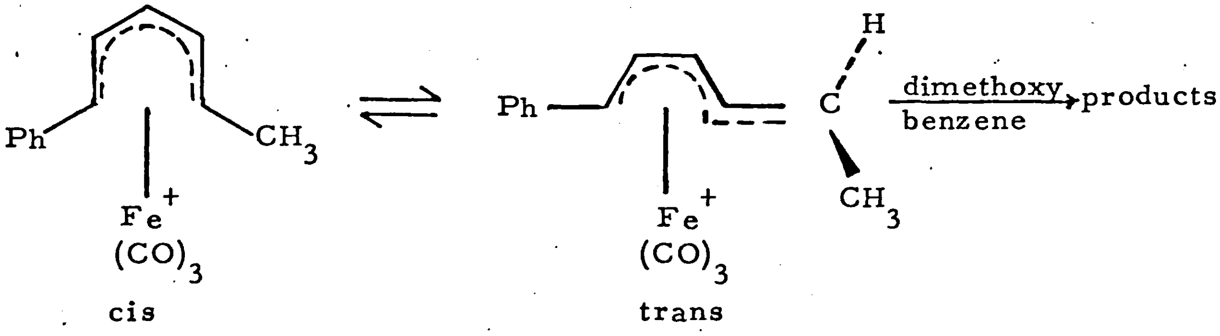


There is some evidence that nucleophilic attack on coordinated ligands occurs exo to the metal.[16] Hydride abstraction from coordinated dienes by triphenylmethyl cation also takes place exo for steric reasons.[17]

Open chain cations can act as electrophiles towards some reactive benzenoid aromatic compounds, as follows:

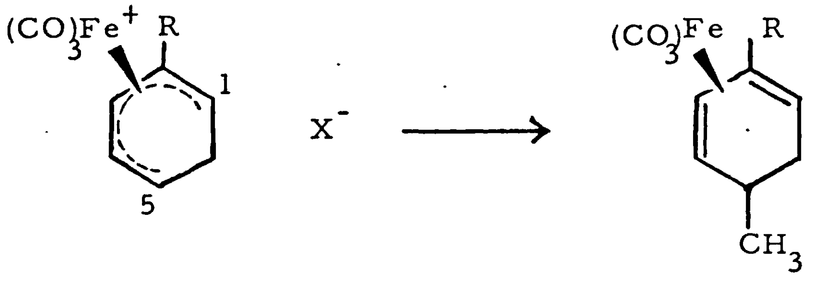


The reaction was studied kinetically[18] in excess of the nucleophile (1,3-dimethoxy benzene) by following the disappearance of a carbonyl stretching band in the infrared spectrum. The product was characterised by analysis and n.m.r. spectroscopy. It was suggested that the reaction proceeds via the trans cation which exists in equilibrium with the cis form.



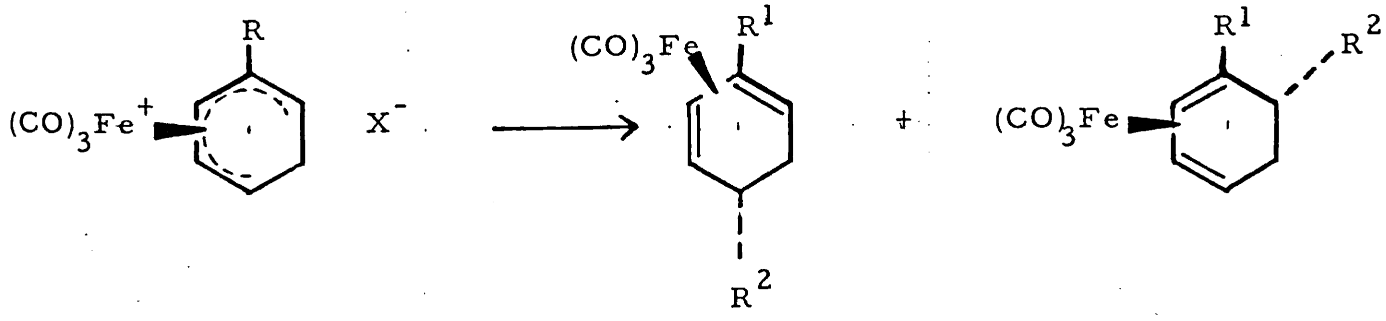
The mechanism is consistent with the observations that the open chain cations are greater in their reactivity compared with the cyclic cations as the latter can exist only in the cis form. Because of the much greater reactivity which open chain cations possess, they could also be attacked by the solvent, thus acetonitrile decomposed salts of open chain cations, whereas, the same solvent was used in a kinetic study[19] for the reaction of β-diketones with cyclohexadienyl and cycloheptadienyliron tricarbonyl tetrafluoroborates.

Pearson[20] has reported that the reaction of cyclohexadienyltricarbonyliron salts with lithium dimethylcuprate gives stereospecific methylation. The products were identified by deuterium labelling, which showed that alkylation occurs at the opposite side of the dienyl system to that occupied by $Fe(CO)_3$.



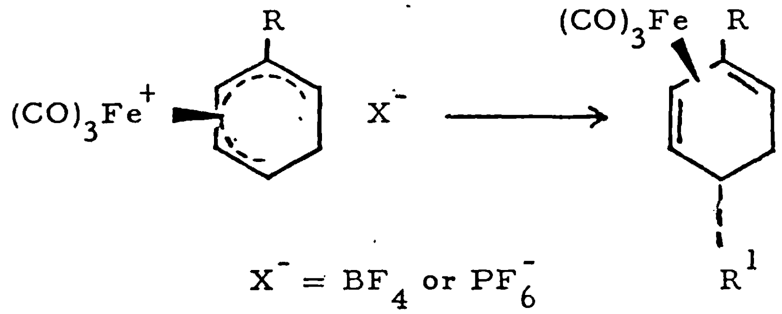
With the asymmetric complexes ($R = CH_3, OCH_3$) attack can take place at either terminus. The n.m.r. spectra of the products indicate exclusive methylation at C_5 (with $R = OCH_3$) and greater than 95% methylation at C_5 for ($R = CH_3$). This could be mainly attributed to steric factors.

The same author also studied the reaction between mixed alkylcuprate reagents (LiR^1R^2Cu) and the cyclohexadienyltricarbonyliron salts:



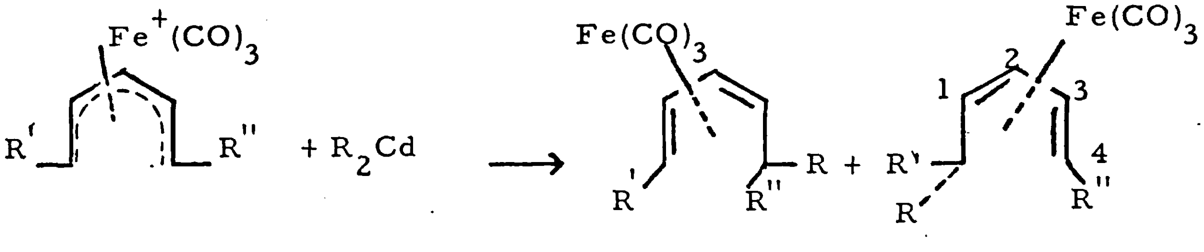
When R^2 = SPh, alkylation of the iron cation may be achieved in moderately good yields, but when $R^1 = Pr^i$, Bu^n and Bu^i, only small yields are obtained. The n.m.r. spectrum of the methylation product in the case where R^1 = H, R^2 = Me, showed that the compound was identical with that produced in the reaction with lithium dimethylcuprate. It follows that alkylation occurs at the face which is opposite to that occupied by $Fe(CO)_3$.

Birch et al[21] have made a comprehensive study of the alkylation of the dienyltricarbonyliron salts with organocadmium reagents. They found that for a series of R_2Cd, (with R =Ph, $PhCH_2$, Me_2CH_2, $CH_2 = CHCH_2$, $MeCH = CH\text{-}CH_2$, or MeCH=CH) at 0°C and under nitrogen atmosphere, the product resulted from attack at the terminal carbon atom of the dienyl system.



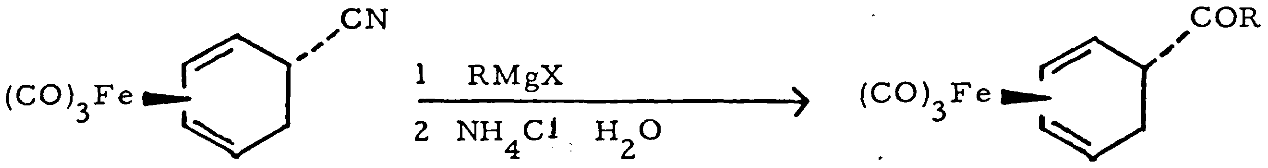
$X^- = BF_4$ or PF_6^-

On the other hand, the acyclic pentadienyltricarbonyliron salts, in their reaction with organo-cadmium reagents under identical conditions, give greater yields. The reaction may proceed through the following scheme:



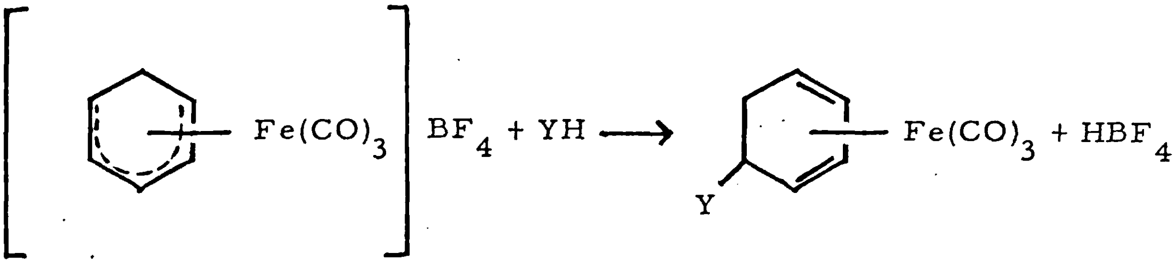
The 'H n.m.r. spectrum of phenylation products indicate that the reaction occurs with retention of the cisoid geometry of the dienyl system, that is, direct attack of the organocadmium reagent on the cis cation is indicated.

Lewis et al[22], recently prepared a series of (5-acyclohexa-1,3-diene) tricarbonyliron complexes from the reaction of the dienyliron cation and Grignard reagents as shown below.



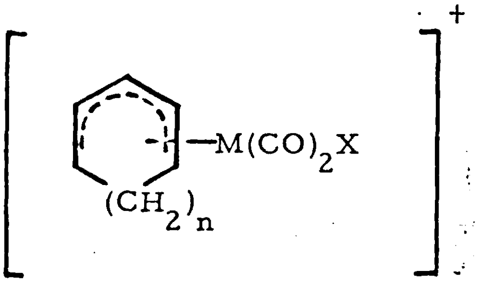
The structure of the product was determined from n.m.r. and X-ray study. The molecules are monomeric and the cyano ligand adopts the exo-stereochemistry, with respect to the metal. The iron atoms are formally four-coordinate, the fourth site being occupied by the butadiene segment of the cyclohexadiene ring. In both molecules the butadiene moiety is planar and the carbon atoms may be considered as sp^2 hybridized. The Fe-C (butadiene) distances are similar. The cyano ligands are approximately linear. The exo-orientation of the cyano group in (5-exo-cyanocyclohexa-1,3-diene) tricarbonyliron has been confirmed by X-ray analysis.

Kane-Maguire et al[23] reported that the cationic dienyl complex $[Fe(C_6H_7)(CO_3)]^+BF_4^-$ can act as an electrophile towards aromatic heterocycles to yield substituted dienes according to

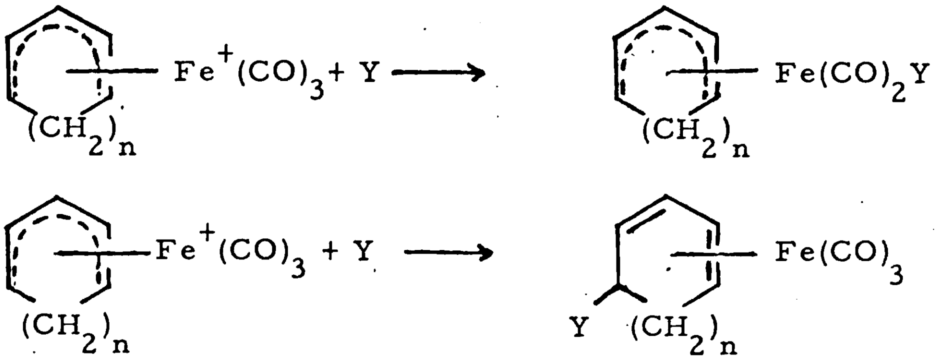


YH = indole, methylindole, pyrrole, furan, thiophene, but no reactions were observed with benzene, alkylbenzene, anisole or phenol. The reactions presumably go to completion as evidenced by the disappearance of the dienyl carbon infrared bands. The products were isolated as pale yellow crystals, by evaporating the reaction mixture to dryness and recrystallization from methanol/water.

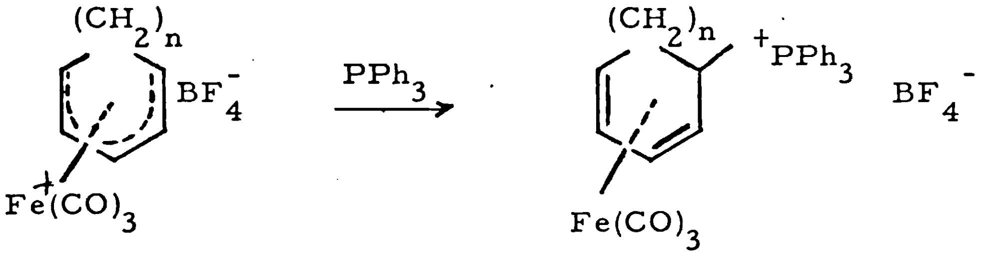
Kane-Maguire[24] has carried out a kinetic study of nucleophilic attack on coordinated cyclic organic complexes of the type:



(where n = 1,2; M = Fe, Ru, Os; X = CO, PPh_3). Two types of substitution have been observed:



However, Evans et al[25] reported the addition reaction of triphenylphosphine and pyridine to cyclohexadienyl and cycloheptadienyl-tricarbonyliron. They found that the addition leads to the formation of phosphonium ions in which attack of the PPh_3 has occurred at the dienyl fragment as follows.



(I) $n = 1$ (III) $n = 1$
(II) $n = 2$ (IV) $n = 2$

The addition of excess of triphenylphosphine to a suspension of either (I) and (II) in dichloromethane rapidly leads to a clear solution. Addition of ether to these solutions precipitates white crystalline products. Identification of these compounds was by analysis and 'H n.m.r. spectra. In all previous studies attack by bases such as tertiary phosphines had been found to occur at the metal atom and replacement of one carbonyl group took place.

3. 3. Results and Discussion

The reaction between ψ-endo-(6-phenylhexa-3, 5-dien-2-ol) tricarbonyliron and an excess of trifluoroacetic acid was studied kinetically at 16. 0 ± 0. 1 °C in nitromethane. This solvent was chosen for several reasons. Firstly non-polar solvents cause precipitation of the complexes. Secondly, other solvents such as acetonitrile and alcohols were found to decompose the iron compound. Trifluoroacetic acid was chosen for the protonation process for the dienyl complex, because it was found that it is soluble in nitromethane and does not decompose the product. Acids which are supplied in aqueous solution, such as tetrafluoroboric acid and hexafluorophosphoric acid are unsuitable as the reactions must be studied under anhydrous conditions.

The reaction was followed by measuring the changes in the carbonyl stretching region (2400 x 2000 cm^{-1}) in the infrared spectrum as a function of time. A preliminary study showed that the iron compound obeys Beer's law.

It was found that the ψ- exo -dienol isomer reacts too fast with acid to follow by a conventional infrared method. It was not suitable therefore for this kind of study, but the reaction of trifluoroacetic acid with the ψ-endo was clear, smooth and readily followed at the chosen temperature. Plots of $\ln \frac{a}{a - x}$ against time gave straight lines in which the slope = k_{obs} as in (Fig. 1). This indicates that the reaction is first order in the iron compound, the trifluoroacetic acid being in excess. To prove that the reaction order is dependent also on the acid concentration, the relationship between k_{obs} and the trifluoroacetic acid concentration was plotted. A good straight line (Fig. 2) was obtained passing close to the origin. This shows that the reaction proceeds according to a simple kinetic expression:

$$\text{Rate} = k_2 \, [\text{Acid}] \, [\text{Complex}]$$

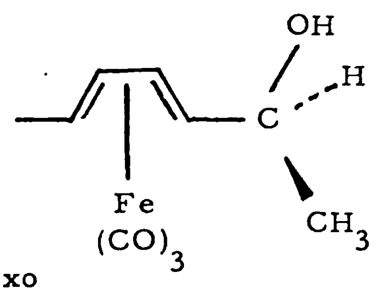
so that the reaction is overall second order.

When the reaction between the iron compound and trifluoroacetic acid was tried at higher temperatures some decomposition occurred, which could be noticed from the darkening of the yellow solution.

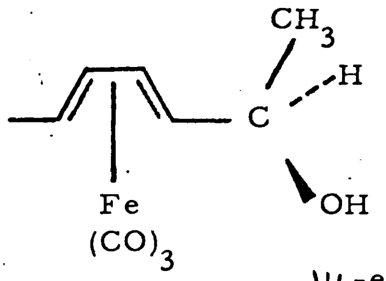
A preliminary study of this reaction was carried out by Holder[26] which showed a more complicated process. He found that the reaction reached an equilibrium state; in our study, however, it clearly went to completion. The difference could be explained by the presence of water in the reactants in the preliminary work.

The mechanism proposed is represented in scheme 1 from which it is clear that the reaction proceeds through several steps. The first one is the protonation of the alcohol oxygen atom. This is followed by elimination of water which leads to the formation of a trans ion. Rearrangement of this cation by rotation give rise to the observation of either of the cis-pentadienyl cations according to the reaction temperature. The protonation process is likely to be fast as for example in acid catalysed ester hydrolysis.[27] Loss of water might be the rate determining step.

There is a similar explanation which is given previously in favour of the preçeding mechanism. This could be discussed in terms of the stereochemistry of the dienol isomers which are reported by Clinton and Lillya.[9] They found that the most stable conformation of each isomer is as below.



ψ-exo



ψ-endo

The existence of a preferred stereochemistry was demonstrated by measuring the rate of solvolysis of the 3,5-dinitrobenzoate esters of both isomers. Clinton and Lillya[6], in their work showed that the ψ-exo complex reacts 100 times faster than the ψ-endo. They suggested that the rate determining step is the alkyl oxygen fission leading to formation of the trans cation. It is likely that the leaving group, the dinitrobenzoate ion in the ester hydrolyses, or water in our reaction, departs exo-to iron. As discussed above, the exo-conformation of the leaving group is favoured in the case of the ψ-exo alcohol and its derivatives, but is less favourable for the ψ-endo.

In the ester hydrolysis, the trans cation is immediately trapped by a water molecule to form the corresponding alcohol with retention of configuration. In the protonation of the alcohols the trans ion can isomerise to give the cis, syn, syn-pentadienyl ion as observed, from the n.m.r. spectrum shown in (Fig.3, 4)

We recorded the n.m.r. spectrum of the iron compound (Fig. 3) and our product from the reaction between ψ-endo-(6-phenylhexa-3,5-dien-2-ol)tricarbonyliron with trifluoroacetic acid at ambient temperature to see if the cis, anti, syn, penta-dienyl cation is formed or whether it rearranges to the cis, syn, syn form. The following resonances were observed (Fig. 3).

i) A sharp singlet peak at 7.55δ is assigned to the phenyl group

ii) A clear doublet resonance at 4.14δ, must be due to the anti-hydrogen H^1

iii) A doublet triplet resonance at 3.6δ is assigned to the anti-hydrogen, H^5 adjacent to the methyl group.

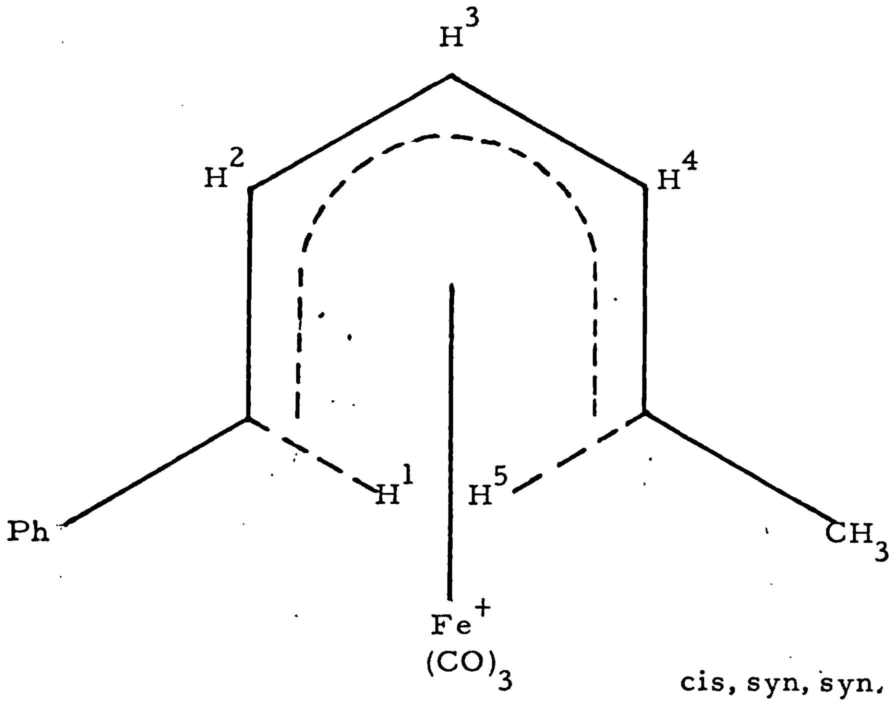
iv) A doublet at 1.85δ is assigned to a syn-methyl group which in comparison to the anti methyl at 1.57δ is slightly shifted to low field.

v) A triplet at 6.94δ could be assigned to H^3 which could be interpreted in terms of a cis coupling between H^2 and H^3 and also between H^3 and H^4.

vi) Doublet of doublets at 5.85δ, J 6.5, 13Hz, assigned to H^4 compared with 6.02δ, J 6, 12.5 Hz, found in ref.[26]

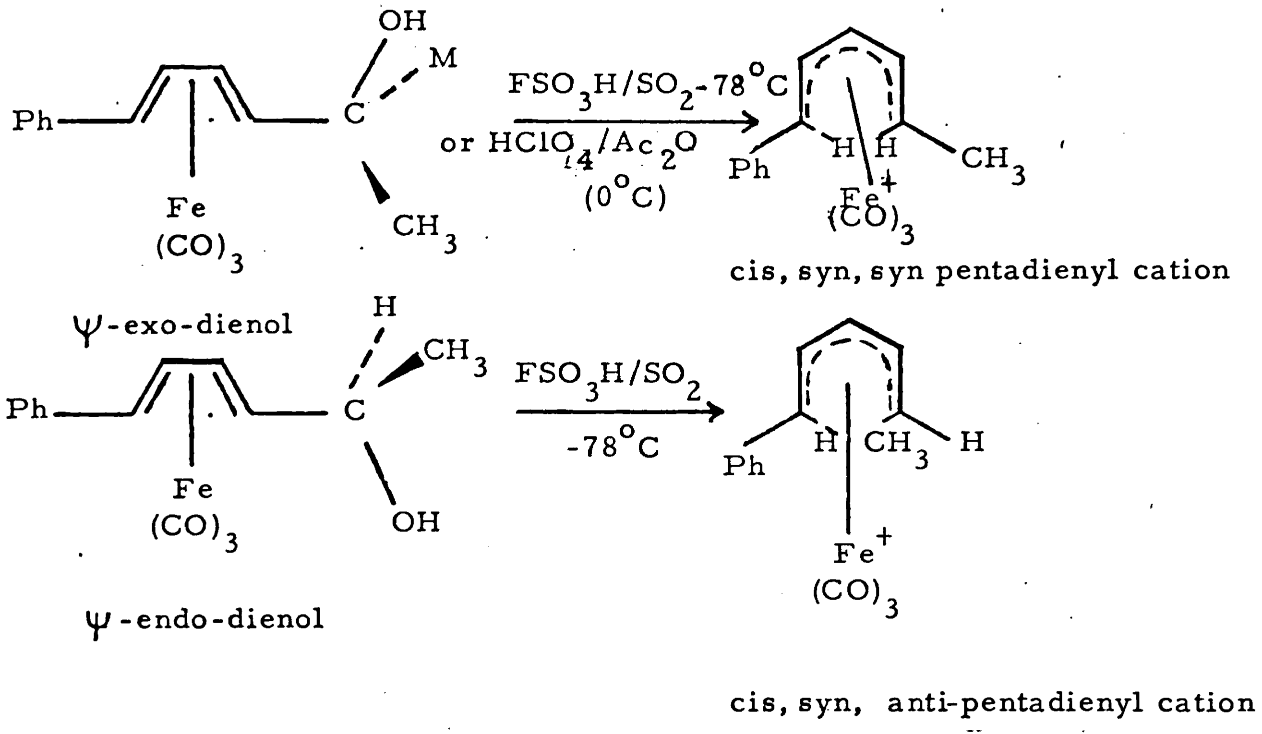
vii) Doublet of doublets at 6.44δ, J 6.5, 13Hz, due to H^2 is consistent with the previous work values at 6.64, J 6, 12.6 Hz.

Assignment could be followed from the structure shown below and from Table 2.



cis, syn, syn.

Holder[26] carried out an n.m.r. study for the reaction of both diastereomers of (6-phenylhexa-3,5-dien-2-ol) tricarbonyliron with fluorosulphonic acid at low temperature (-78°C). It was found that each isomer gave a different cationic species:

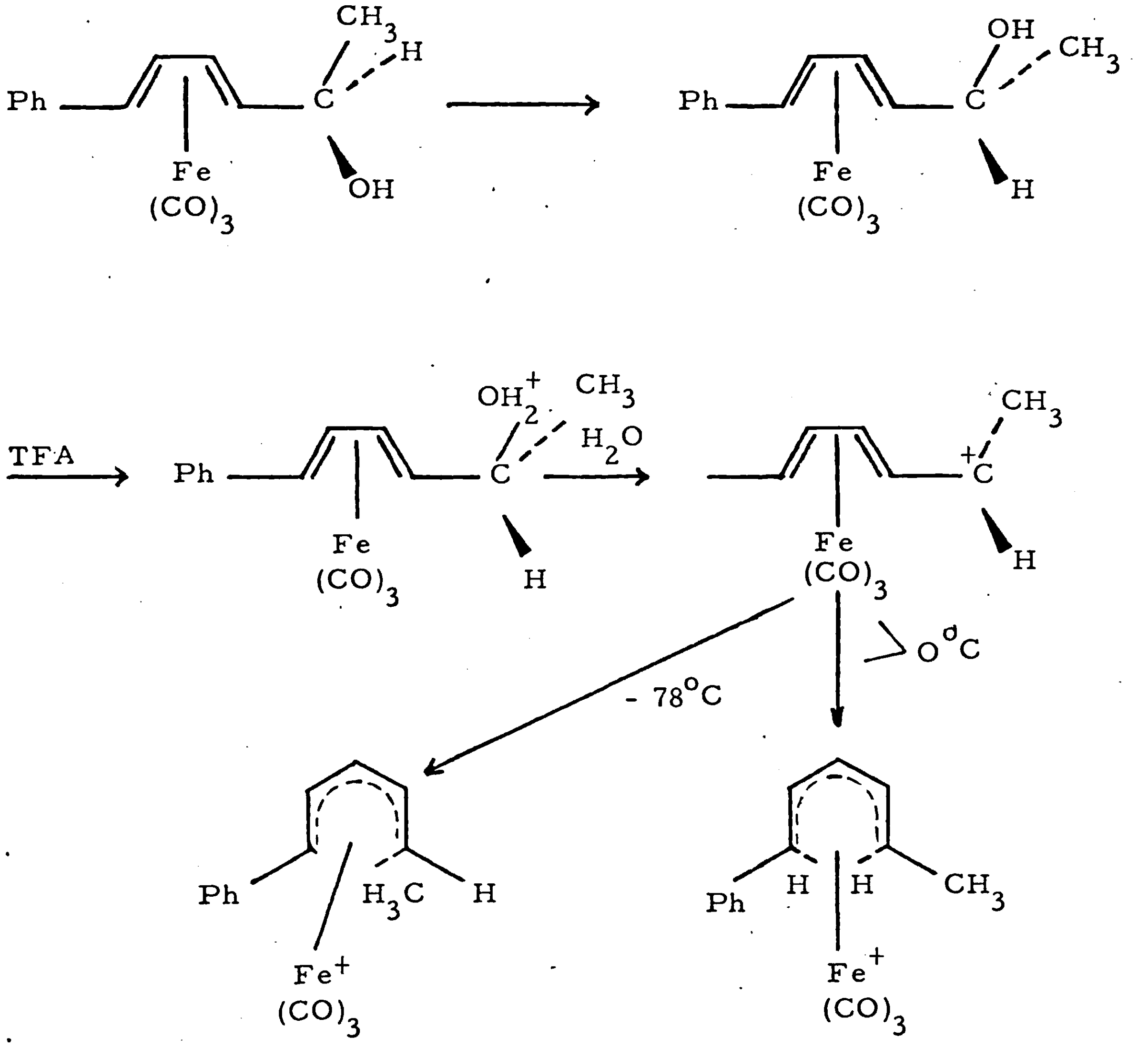


We can conclude that the two different cis pentadienyl cations were formed as a result of the trans ions rotations. On the other hand, from our study at higher temperature, only the thermodynamically more stable cation (cis, syn, syn) could be observed. In other words the formation of this cation from the ψ-endo isomer could be from interconversion of the trans ion.

In conclusion, the kinetic data showed that the reaction of ψ-endo isomer with trifluoroacetic acid is a second order process, first order in the dienol and first order in the acid, Table 1.

The results obtained from n. m. r. study are consistent with initial protonation of hydroxyl group oxygen followed by loss of water exo- to iron to generate trans pentadienyl cations. These trans ions formed two cis pentadienyl cations at (-78°C). Only the more stable cis, syn, syn (1-phenyl, 5-methyl pentadienyltricarbonyliron) was observed at room temperature.

Proposed mechanism for the reaction between (6-phenylhexa-3, 5-dien-2-ol)tricarbonyliron salt and trifluoroacetic acid.



Scheme 1.

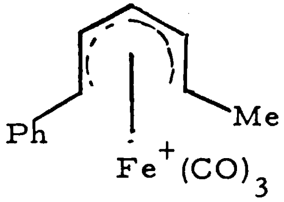
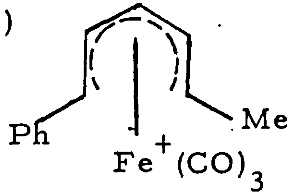
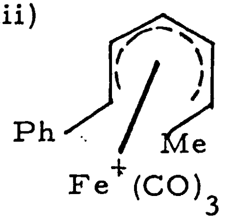
TABLE 1

Values of k_{obs} and k_2 for the reaction between Iron compound and trifluoroacetic acid at 16.5°C.

[Complex] / mol dm^{-3}	[Acid] / mol dm^{-3}	k_{obs} / s^{-1}	$k_2/dm^3 mol^{-1} s^{-1}$
0.005	0.067	2.09×10^{-4}	3.12×10^{-3}
0.01	0.10	3.14×10^{-4}	3.14×10^{-3}
0.01	0.134	4.68×10^{-4}	3.49×10^{-3}
0.005	0.161	5.41×10^{-4}	3.36×10^{-3}
0.01	0.20	6.36×10^{-4}	3.18×10^{-3}
0.01	0.268	9.10×10^{-4}	3.39×10^{-3}

TABLE 2

Proton n.m.r. shifts relative to TMS (δ)

Complex	Ph	H^1	H^2	H^3	H^4	H^5	Me
i) 	7.55 M	4.14 d	6.44 dd	6.94 t	5.83 dd	3.6 dt	1.85 s d
ii) 	7.58 M	4.24 d	6.64 dd	7.02 t	6.02 dd	3.89 dt	1.92 s d
iii) 	7.64 M	4.31 d	6.26 dd	7.23 t	6.06 dd	4.61 M	1.57 a d

i Data refer to solutions in $CDCl_3$ at 100 M Hz

ii Data refer to solutions in CD_3NO_2 at 100 M Hz

iii Data refer to solutions in liquid SO_2 at (- 60°C)[26]

s = syn, a = anti

Fig 1 Pseudo first order kinetic plot for the reaction between ψ-endo-(6-phenylhexa-3,5-dien-2-01) tricarbonyliron and CF_3COOH at 16.0°C.

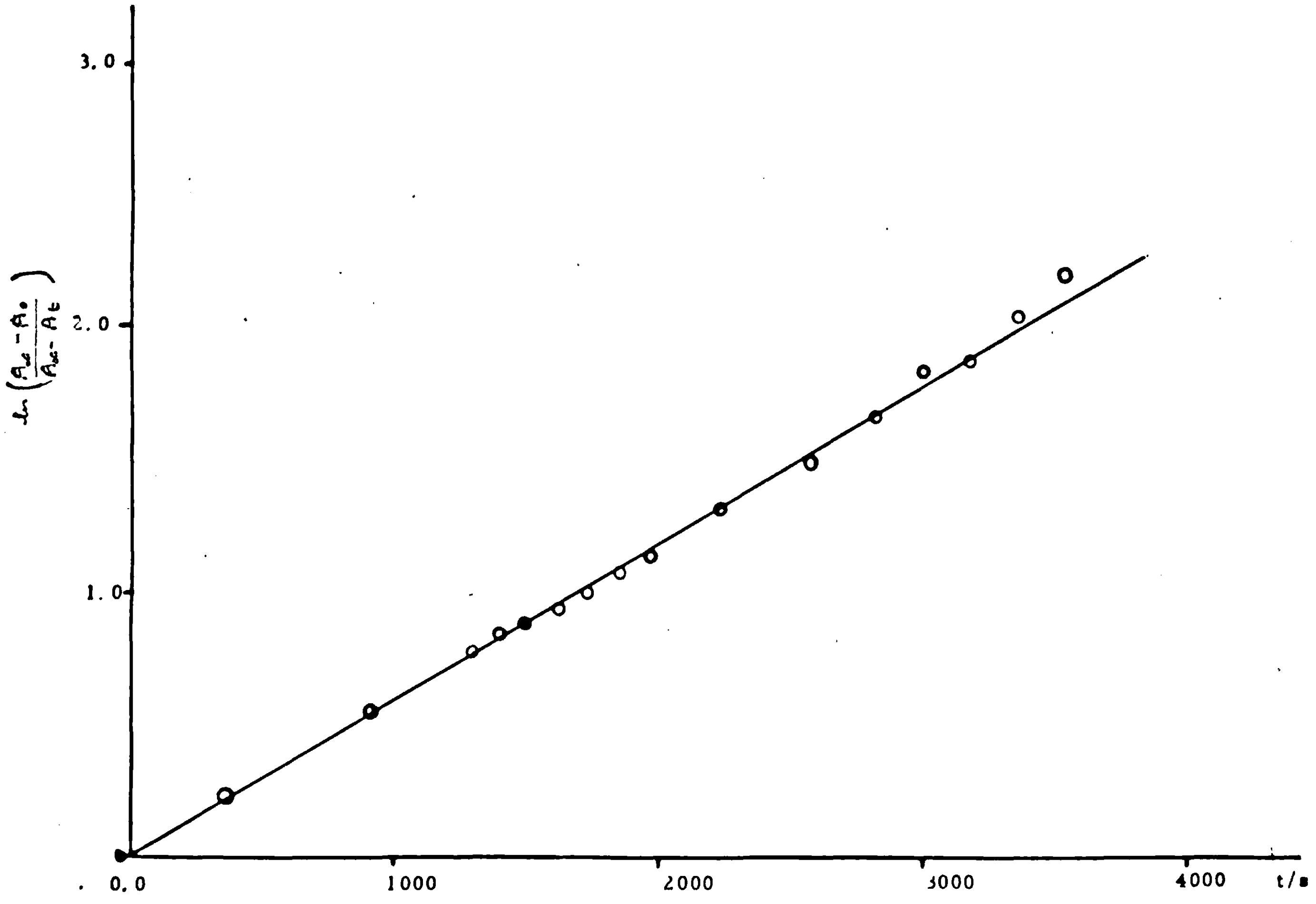
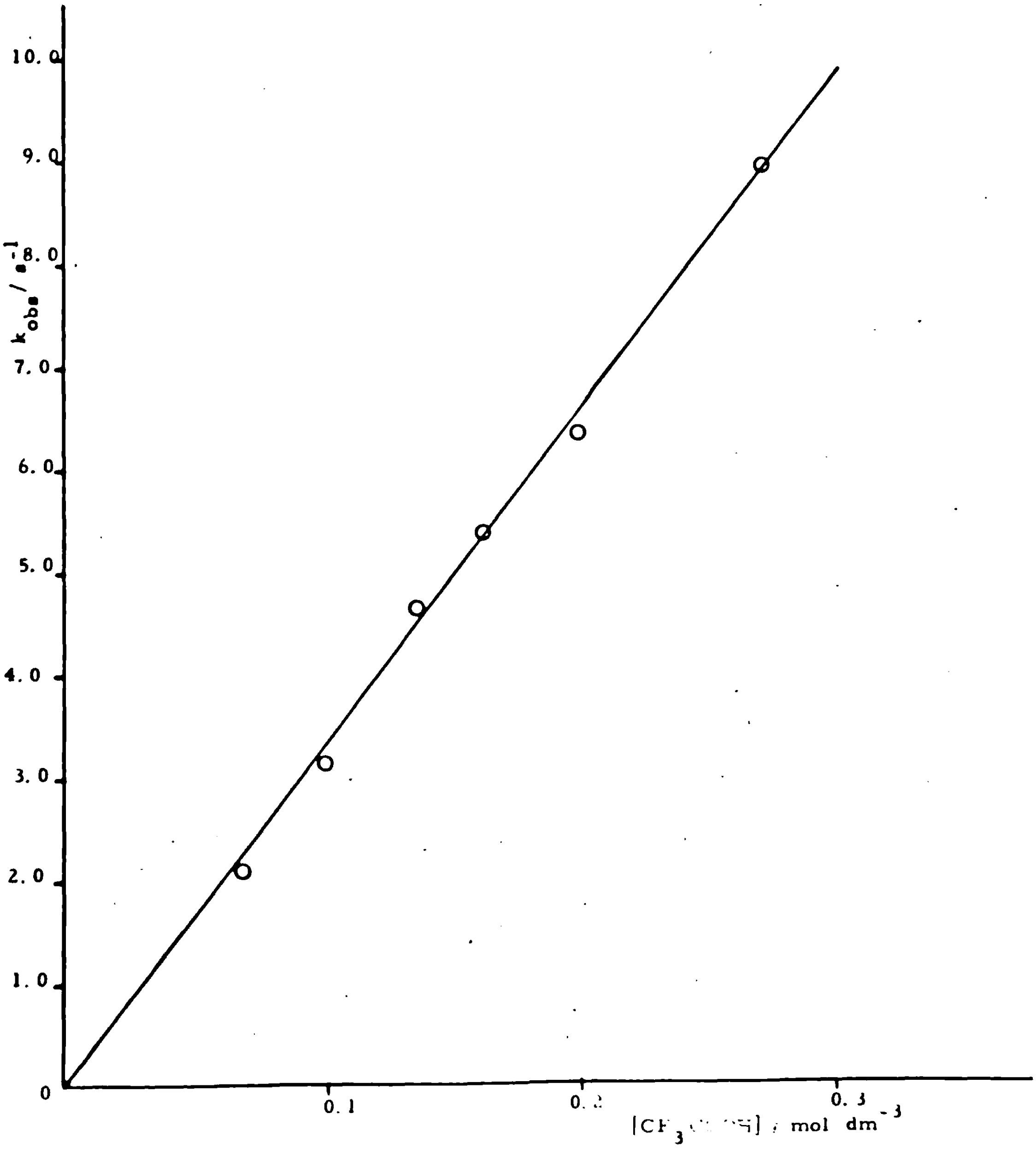


Fig 2 Plot of k_{obs} v. trifluoroacetic acid concentration for the reaction between ψ-endo-(6-phenyl-hexa-3,5-dien-2-ol) tricarbonyliron and trifluoroacetic acid at 16.0°C.



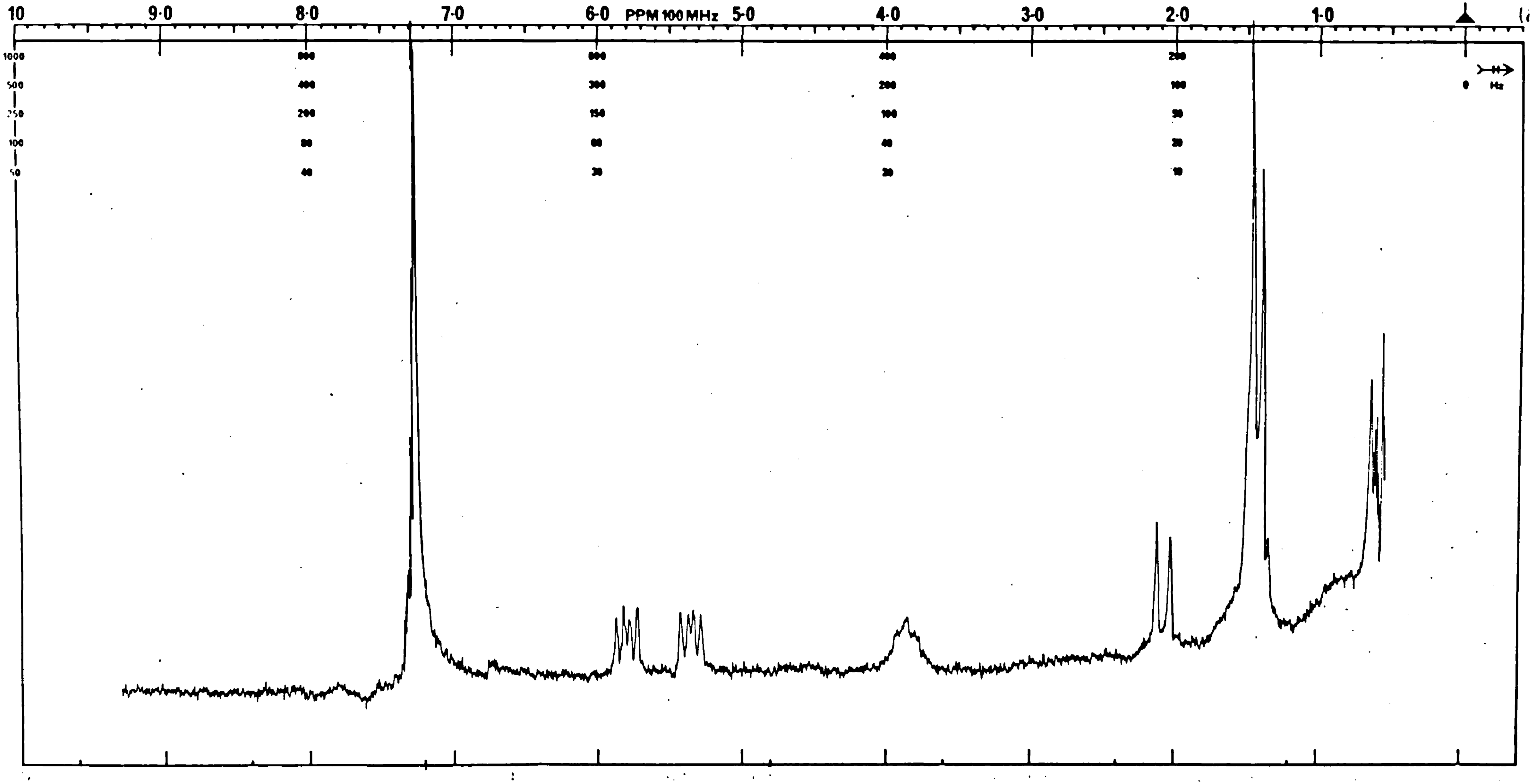


Fig 3. 'H n. m. r. spectrum of γ-endo-(6-phenylhexa-3, 5-dien-2-ol) tricarbonyliron in $CDCl_3$ at ambient temperature (100 MHz).

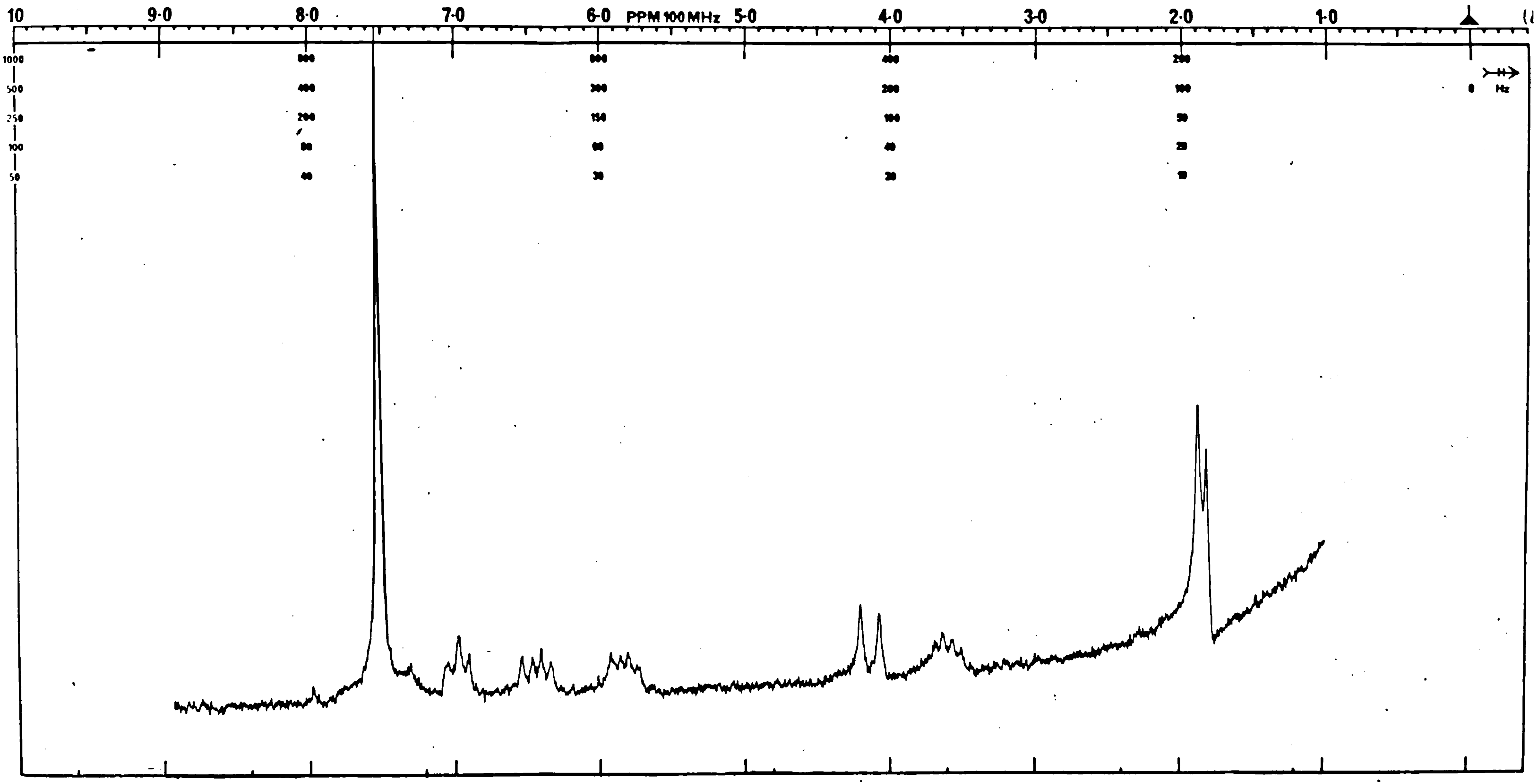


Fig 4. ^{1}H n.m.r. spectrum of ψ-endo-(6-phenylhexa-3,5-dien-2-ol) tricarbonyliron in $CDCl_3$ at ambient temperature after addition of trifluoroacetic acid. (100 MHz).

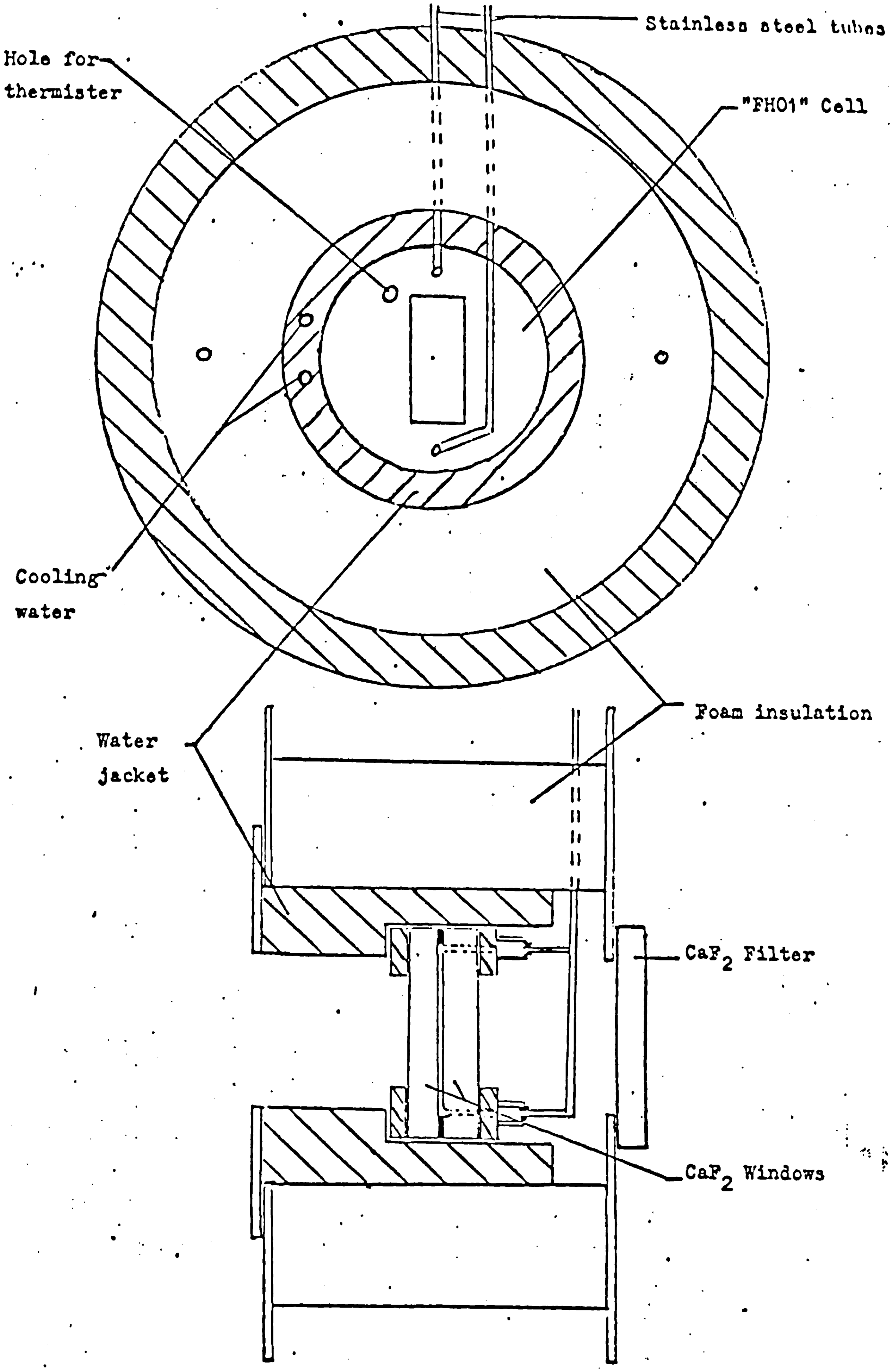


FIG 5 Constant temperature infra-red cell

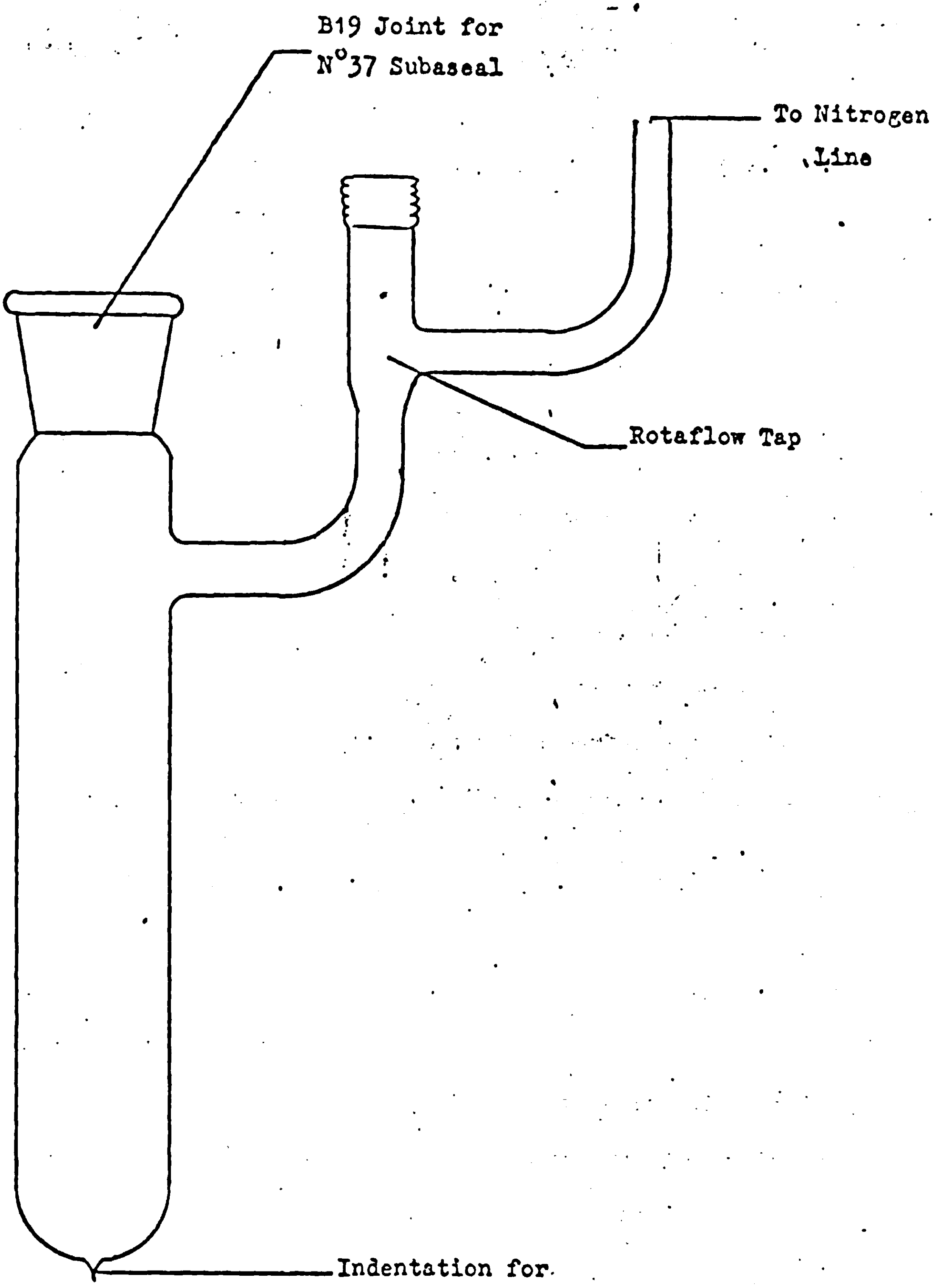


FIG 6 Reaction Vessel

3.4. Experimental

a. Materials.

ψ-endo(6-phenylhexa-3, 5 dien-2-ol) tricarbonyliron was prepared by Miss I Moon and Miss K Smith by the method followed by Clinton and Lillya[9]. The yellow product was purified by repeated recrystallization from petroleum ether. Nitromethane was used as a solvent for the kinetic study. This solvent (BDH) had to be purified before use. The method used was based on that of Olah.[28] The solvent was washed three times with 100 cm^3 aliquots of a solution containing sodium bicarbonate (25 g) and sodium metabisulphite (25 g) in water (1000 cm^3). Following that, it was washed with distilled water (100 cm^3), 5% sulphuric acid (100 cm^3), again with water (100 cm^3) and sodium bicarbonate solution.

The wet nitromethane was dried with anhydrous sodium sulphate followed by dried magnesium sulphate. Final removal of water was with activated "Drierite", then filtration through a 60 cm column of activated molecular sieves (4 Å) type. Distillation was carried out for the dried solvent at reduced pressure, through a 500 cm Vigreux column under nitrogen, b.p. 57°/156 mm Hg.

Trifluoroacetic acid

The acid (Koch Light) was purified by mixing it (100 cm^3) with trifluoroacetic anhydride (20 cm^3) under nitrogen. The mixture was allowed to stand overnight before being fractionally distilled through a 150 cm Vigreux column. The acid fraction was collected at 70.5 - 71.0° and stored under nitrogen in greaseless apparatus.

b. Apparatus

The infrared spectrometer Perkin-Elmer 177 was used for recording the spectrum of the reaction mixture at 2105 cm^{-1}. A jacketed cell of the type shown in Fig. 5 was employed for the kinetic study.

The solutions required for the kinetic work were prepared by dissolving the appropriate amount of reactant in pure nitromethane in a nitrogen flushed dry box. In case of preparing the acid solution, standard accurate pipettes were used. Both solutions were degassed thoroughly by the aid of liquid nitrogen and kinetic tube shown in Fig. 6. The technique of transferring the reacting solutions to the cell was explained on page 50 .

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CHAPTER FOUR

KINETIC AND SPECTROSCOPIC STUDIES ON CYCLOPENTADIENYL (CYCLO-OCTA- 1-2,4-6 DIENYL) COBALT CATION

CHAPTER 4.

Kinetic and Spectroscopic studies on cyclopentadienyl (cyclo-octa-η-1-2, 4-6 dienyl) cobalt cation

4.1. Introduction.

The aim of the work described in this Chapter was to study the kinetics for the reaction between cyclopentadienyl(cycloocta-η-1, 2, 4-6 dienyl) cobalt tetrafluoroborate and methoxide ion. A preliminary qualitative investigation showed that the reaction was very fast, but if the methoxide was buffered at low concentrations (ca 10^{-5} mol. dm^{-3}), it could be followed by a stopped-flow technique. The activation parameters can be obtained by measuring the rate of reaction at different temperatures. In order to calculate the concentration of methoxide in the buffer solutions at temperatures other than 298 K, ancillary thermochemical data are required. The variation in the autoprotolysis constant of methanol with temperature has been reported.[1] The dissociation constant of triethylamine in methanol, however, is known only at 25°C. To be able to calculate values at other temperatures, the enthalpy of neutralization of triethylamine by perchloric acid in methanol was measured by solution calorimetry.

A spectroscopic study of the reaction of triphenylphosphine with the cobalt salt showed the stoicheiometry to be 1:1. Recently, the kinetics[2] of this reaction were reported, so we did not proceed ourselves with this aspect of the work.

The proton n.m.r. spectrum of cyclopentadienyl-(cyclo-octa-η -1-2, 4-6 dienyl) cobalt tetrafluoroborate has been assigned with the aid of double resonance experiments.

4.2. Flow techniques.

The study of rapid reactions is very important because many vital practical processes such as muscle action, cell reproduction, the combustion of rocket fuel and gasolene, and the actions of poisons and nerve gases come into this category. Such reactions at one time were regarded as instantaneous reactions. As it was not possible to follow such reactions by conventional methods, other special techniques had to be developed, of which flow techniques were the first. The most widely used method is the stopped-flow. There are two other methods, continuous flow and accelerated flow.

In 1923, Hartridge and Roughton[6], were the first to use these techniques for studying biochemical processes. They wished to measure the rate of reaction between oxygen and haemoglobin in water. They made a solution of carboxyhaemoglobin flow up a vertical tube illuminated by bright light and then into a dark tube. Under the influence of light, the carbon monoxide in combination with the haemoglobin was photochemically displaced by dissolved oxygen. The reaction in the flowing liquid was monitored at various distances along the tube.

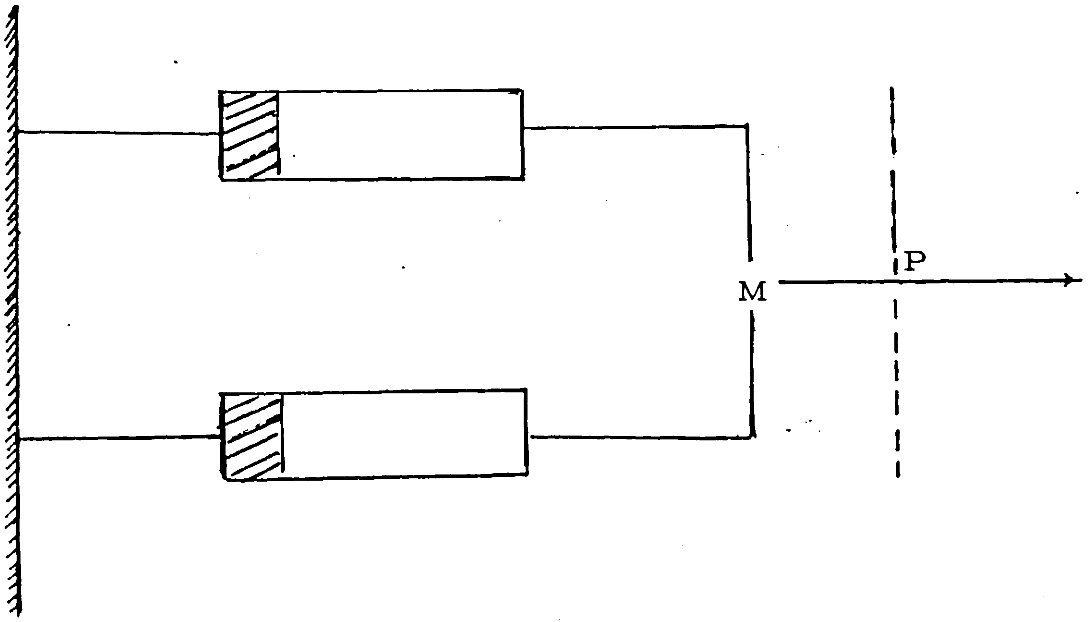


Fig. i

In the continuous flow method, the two reactants are passed from big reservoirs along two capillary tubes which meet at a mixing point (M, Fig. i). The concentration of one or both reactants can be determined at the observation point P. A source of monochromatic light and a photomultiplier connected to an oscilloscope might be used at P for measuring the composition of the solution. The great disadvantage of continuous flow is the requirement that large volumes of reactant solutions are consumed. This tends to be very serious with biochemical reactions in particular, where the quantities available may be very small.

In all flow techniques, it is necessary that the flow should be very fast to reduce as much as possible the mixing time. Moreover, it is assumed that all the fluid elements move with the same velocity.

In the accelerated flow method, the reactants are driven from syringes of equal volume. The change in reactant concentrations can be followed at P from the beginning of the drive, until maximum flow velocity is achieved. The flow rate increases steadily as the plungers accelerate so that, at the detection point, the overall reaction time decreases. That means the time between mixing and observation is inversely proportional to the flow rate.

The stopped flow technique has now become quite standardized. The reagents are kept in two hypodermic syringes of equal volume, usually between 2 and 50 cm^3. The plungers are pushed together to deliver equal amounts of the two reactants to the mixing cell. The solutions are made to flow, then stopped suddenly. This is done by passing the mixing solution into a third syringe arranged, so that the plunger is forced against a stop and at the same time operates a microswitch. By the time the mixed liquid has reached the observation point a certain fraction of the reaction will be over. The range of reaction half lives, which can be measured by flow technique is from a few milliseconds to a few minutes. The stopped-flow apparatus which is used in our study is described in detail.

4.3 Cyclopentadienyl (cyclo-octa-1, 5-diene)cobalt I

This compound was prepared by King et al[3] by direct interaction of dicarbonyl (cyclopentadienyl) cobalt and (cyclo-octa-1, 5-diene). In Japan, it was obtained by the hydrogenation of the corresponding cyclo-octa-1, 3, 5-triene and cyclo-octatetraene complexes. Lewis and Parkins[4] treated a mixture of anhydrous cobalt bromide, cyclopentadiene, and cyclo-octa-1, 5-diene with isopropylmagnesium bromide in diethylether for preparing this compound.

The salt $[Co(C_5H_5)(C_8H_{11})]^+[BF_4^-].H_2O$ was prepared by dissolving the appropriate amount of cyclopentadienyl(cyclo-octa-1, 5-diene) cobalt in dichloromethane, followed by treatment with $Ph_3C^+.BF_4^-$. After five minutes, the solution was extracted with water, and washed with diethylether. Evaporation of the aqueous layer in vacuo gave the crimson product.

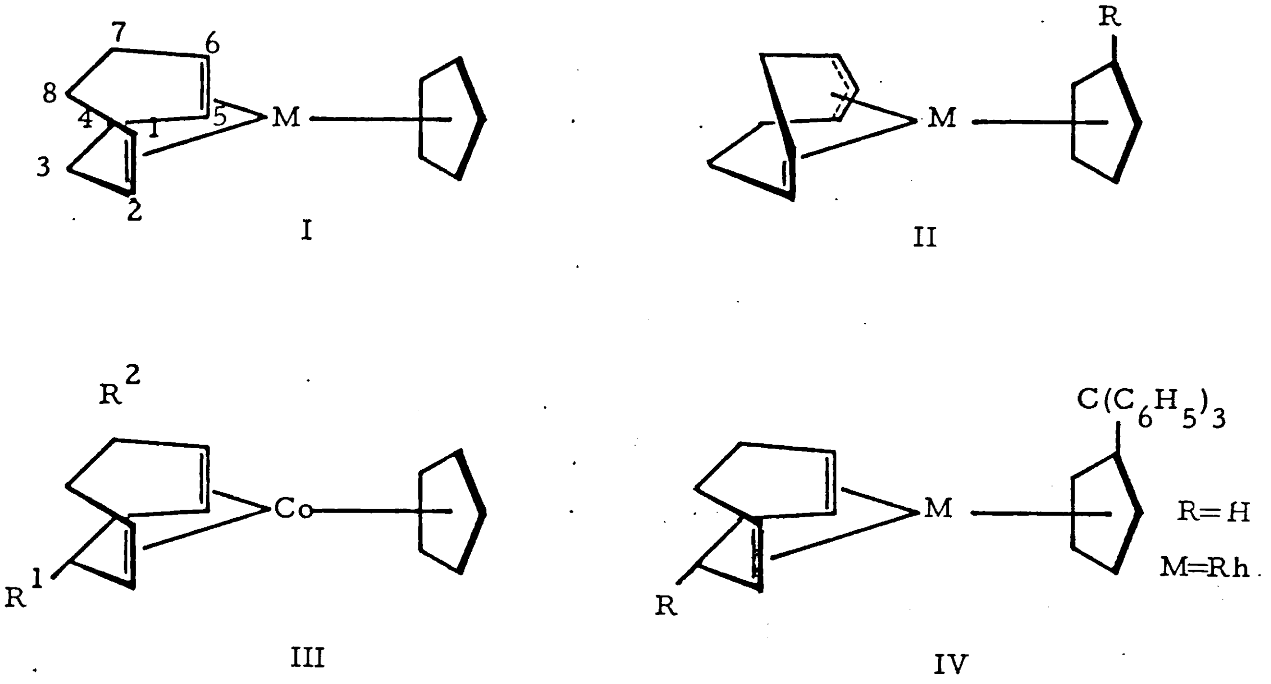
The salt is air-stable and soluble in acetone, liquid sulphur dioxide and water to give red solutions. The cation is precipitated from water by using a saturated aqueous solution of potassium hexafluorophosphate or by picric acid.

The nuclear magnetic resonance spectrum of the $[Co(C_5H_5)(C_8H_{11})]^+$ was measured in liquid sulphur dioxide Lewis and Parkins[4] assigned a sharp peak at δ 5.4 to the protons of the cyclopentadienyl group. In a different solvent, carbon disulphide, the cyclopentadienyl protons were observed at δ4.5. The remainder of the spectrum, however, indicated that the symmetry of the cyclo-octa-1, 5-diene ring has been destroyed. An infrared study was also carried out by the same authors who noticed a broad absorption band at 1060 cm^{-1}, which is due to the asymmetric stretching mode of the fluoroborate anion in the salt $[Co\eta^5(C_5H_5)(C_8H_{11})]^+[BF_4^-]$

On the other hand, the reaction of cyclopentadienylcycloocta-1, 5-diene rhodium with 1 mol. of trityl fluoroborate in dichloromethane leads to some decomposition, but tritylcyclopentadienyl(cyclo-octa-1, 5-diene) rhodium is isolated in 50% yield by chromatography of the solution on silica, with the rhodium compound electrophilic substitution of the cyclopentadienyl ring occurring before hydride ion abstraction.

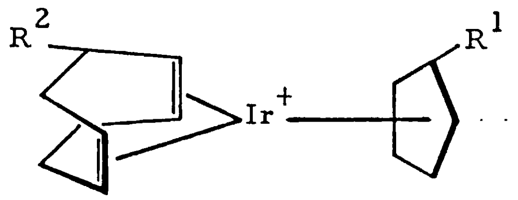
The n.m.r. spectrum of $[Rh(C_5H_5)(C_8H_{12})]$, Scheme 1, in deutero-chloroform gives resonances of relative intensities 5:4:8 at δ 5.2, 3.9 and 2.0 assigned to the cyclopentadienyl, coordinated olefinic and saturated methylene protons respectively. The spectrum of the trityl derivatives $[Rh(Ph_3.C.C_5H_4)(C_8H_{12})]$ shows fine distinct resonances in the ratio 15:2:2:4:8 at δ7.4, 5.3, 4.7, 3.6 and 1.9 respectively. The band at δ7.4 is a multiplet assigned to the phenyl protons. The triplets at 5.3 and 4.7 are assigned to the protons of the cyclopentadienyl ring.

Cyclopentadienyl (cycloocta-1, 5-diene) iridium reacts in the same way as the Rh analogue. With 1 mol. of the reagent trityl fluoroborate, the neutral compound tritylcyclopentadienyl (cyclo-octa-1, 5-diene)iridium (I, R, $=Ph_3C$, $R^2= H$) is obtained. Its n.m.r. spectrum[5] in $CDCl_3$ shows peaks at δ7.3, 5.2, 4.7, 3.4 and 1.8. The resonance at 7.3 is due to the phenyl protons and those at 3.4 and 1.8 are due, respectively, to the coordinated olefinic and saturated protons of the cyclo-octa-1,5-diene ligand. These are at slightly lower field than the corresponding resonances at 3.8 and 1.9 in the unsubstituted complex. The cyclopentadienyl resonances at δ 5.2 and 4.7 appear as triplets owing to coupling in the cyclopentadienyl ring.



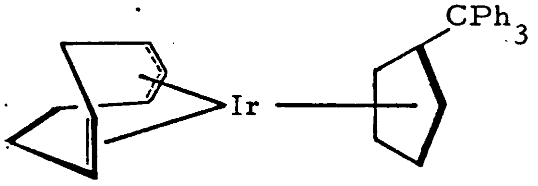
Scheme 1

If 2 mol. of trityl fluoroborate reacts with $[M(C_5H_5)$-(C_8H_{12}), M = Rh or Ir, the cationic cyclo-octa-2,5-dienyl complex can be obtained, $[Ir(Ph_3C^{J}C_5H_4)(C_8H_{11})]^+$ (I) which can be isolated as the hexafluorophosphate salt. The n.m.r. spectrum of this ion in liquid sulphur dioxide is very complicated. The cyclopentadienyl protons appear at δ 5.9 and 5.6 showing the high field shift expected for cations when compared with their neutral compounds.



I

$R_1 = Ph_3C$, $R_2 = H$



II

4.4 Results and Discussion

The reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-.H_2O$ and methoxide ion was studied at 395 nm by the stopped-flow technique over the range of temperature between 25 and 45°C. The cobalt compound was found to be stable for a few days in acidic methanol. The methoxide was generated from a methanolic buffer mixture of perchloric acid and triethylamine as explained in the experimental section. A preliminary study showed that the reaction of the cobalt cation with 10^{-2} mol. dm^{-3} methoxide ion was too fast to follow even by stopped-flow techniques. By mixing appropriate volumes of the acid (0.05 mol. dm^{-3}) in methanol and the amine solution (0.5 mol. dm^{-3}) in methanol, a range of methoxide concentration from 3.8×10^{-6} to 2.2×10^{-5} mol. dm^{-3} was obtained.

For each concentration of the methoxide six runs were done. The results given below show a typical example with all the settings indicated.

Temp.	29.0 ± 0.1°C
$[Co^+]$	5×10^{-4} mol. dm^{-3}
$[OMe^-]$	7.3×10^{-6} mol. dm^{-3}
Sweep time	20 s
Blank	2400
Sensitivity	0.2 V

No. of runs	k_{obs} (s^{-1})
1	0.312 ± 0.002*
2	0.301 ± 0.002
3	0.302 ± 0.002
4	0.304 ± 0.002
5	0.304 ± 0.002
6	0.303 ± 0.003

*Errors refer to twice the standard deviation in the least squares calculations.

The sweep time was altered according to the reaction conditions. and how fast the reaction proceeded. The range of sweep time available in the stopped-flow apparatus was from 5 ms to 200 s.

The reaction was found to be first order with respect to cobalt compound concentration. This was indicated from plotting ln $(\frac{a}{a-x})$ vs t., which gave a straight line Fig. 9 By finding the relationship between k_{obs} and methoxide ion concentration the order of the overall reaction can be determined. The straight lines obtained when k_{obs} was plotted against $[OMe^-]$, showed a linear dependence of the observed rate constants on the methoxide concentration Fig. e.g. 1. At every temperature over the range used, six runs were done for each of six chosen methoxide concentrations. The calculations of the methoxide ion concentration required values of the autoprotolysis constant of methanol and of the dissociation constant of triethyl-amine in methanol at each temperature. Literature values of the former were used, while the latter were obtained from the enthalpy of neutralisation of triethylamine by perchloric acid, determined calorimetrically (section 4. 5). Table 1 shows the variation of pK_{ap} and pK_a with temperature.

The graphs showing the relationship between k_{obs} and the methoxide concentration at each temperature can be seen in (Figs. 1, 2, 3, 4, 5, 6). Straight lines were obtained in each case with a positive intercept. The slopes of these lines represent k_2 values which vary according to the temperature used. The positive intercept could arise because of some direct attack by the solvent, methanol, therefore the following rate equation is suggested.

$$\text{Rate} = k'_{MeOH} + k_2 [OMe^-][Co^+]$$

The study of the reaction of the cobalt cation with the methoxide ion at different temperatures enables us to calculate the activation parameters of the reaction of cobalt compound with both the solvent and the methoxide ion, by making use of Arrhenius plots. Since the relationship between ln k and (1/T) gives a straight line (Fig. 7, 8) with a slope which is equal to E/R, E, the energy of activation can be calculated. Consequently $\Delta H^{\ddagger}$ can be obtained from the following equation:

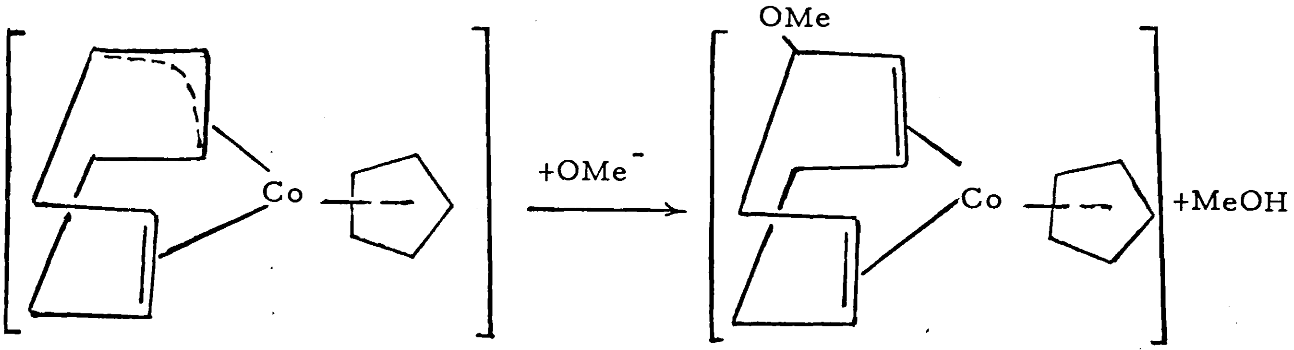
$$\Delta H^{\ddagger} = E - RT$$

The enthalpy of activation, $\Delta H^{\ddagger}$ for attack of methoxide ion was found to be 35.24 ± 0.12 kJ mol^{-1}. The entropy of activation, $\Delta S^{\ddagger} = -43.03 \pm 0.82$ JK^{-1} mol^{-1}, was calculated according to the equation:

$$\ln k = \frac{K}{h} + \ln T - \frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}$$

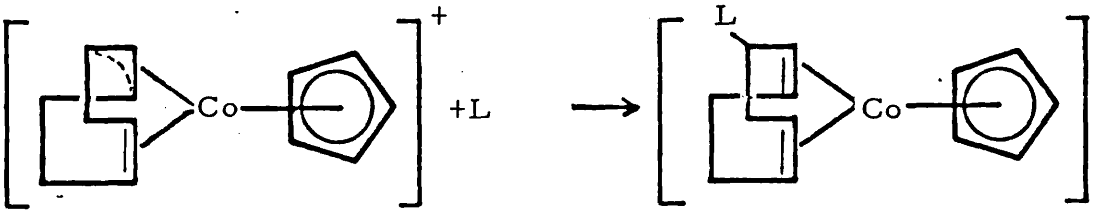
The activation parameters for the reaction with methoxide are listed in Table 5. The negative value of $\Delta S^{\ddagger}$ is expected for this kind of reaction proceeding by an associative mechanism.

However it is worth mentioning that the reaction between the cobalt compound and methanol occurred parallel to that with the methoxide, but at a much slower rate. Table 6 shows the values of k_2 for the methanol reaction which by comparing with the corresponding k_2 values for the methoxide reaction, indicates that the latter is faster by a factor of 10^7 (Table 4). Also, the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated for the solvent reaction. The results in Table 7 show that the enthalpy of activation is greater ($\Delta H^{\ddagger} = 53.33 \pm 0.12$ kJ mol^{-1}) than for the methoxide reaction. The large negative value of the entropy of activation ($\Delta S^{\ddagger} = -115.4 \pm 1.0$ JK^{-1}mol^{-1}) is expected for an associative reaction in which a solvated proton is produced. The following equation is suggested for the reaction:



$[Co(C_5H_5)(C_8H_{11})]^+ + MeOH \longrightarrow [Co(C_5H_5)(C_8H_{11}OMe)] + H^+$

Recently a kinetic study was carried out by Kane-Maguire et al[2] for the reaction between $[Co(C_5H_5)(C_8H_{11}]^+$ and PPh_3 in acetone. The reaction was investigated also by stopped-flow technique at 490 nm. Attack occurred at the terminal carbon of the coordinated allyl group as shown below.



(1)

Reaction (1), L = PPh_3 is rapid in acetone solvent and is accompanied by a large decrease in absorbance at 490 nm. The results observed were consistent with the following rate law

$k_{obs} = k_1[PPh_3] + k_{-1}$

$[Co(C_5H_5)(C_8H_{11})]^+ + PPh_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(C_5H_5)(C_8H_{11}PPh_3)]^+.$

The activation parameters associated with k_1 are $\Delta H_1^{\ddagger} = 21.0 \pm 1.2$ kJ mol^{-1} and $\Delta S^{\ddagger}$, $= - 114 \pm 5$ JK^{-1} mol^{-1}, confirming that the reaction proceeds by bimolecular mechanism. On the other hand, the larger $\Delta H_{-1}^{\ddagger}$ value of 86.2 ± 5.1 KJ mol^{-1} is in agreement with bond cleavage in dissociation k_{-1}, as is the positive $\Delta S_{-1}^{\ddagger}$ of 60 ± 17 JK^{-1} mol^{-1}.

We studied the reaction between $[Co(C_5H_5)(C_8H_{11})]^+$ and PPh_3 using Job's method. The results shown in Fig. 10 indicated that a 1:1 adduct is formed in this reaction, which agrees with Kane-Maguire's work. Our study was made before Kane-Maguire's publication appeared.

4.5 Calorimetry

Calorimetry is a very large topic and hence this introduction is restricted to that branch of experimental thermochemistry that is reaction calorimetry which was used in the work described in this thesis.

All chemical and physical processes are accompanied by energy changes. Calorimetry is employed for the measurement of the changes in energy content which are associated with changing the system from one state to another under specified conditions. The greatest care therefore should be exercised in defining precisely the initial and final states.

The use of calorimetric methods for direct measurement of the heat changes of chemical reactions in solution has been reviewed.[7] Reaction calorimetry in solution is relatively straightforward if the reaction is well defined, complete within a few minutes at the chosen temperature and there is no interference from side reactions.

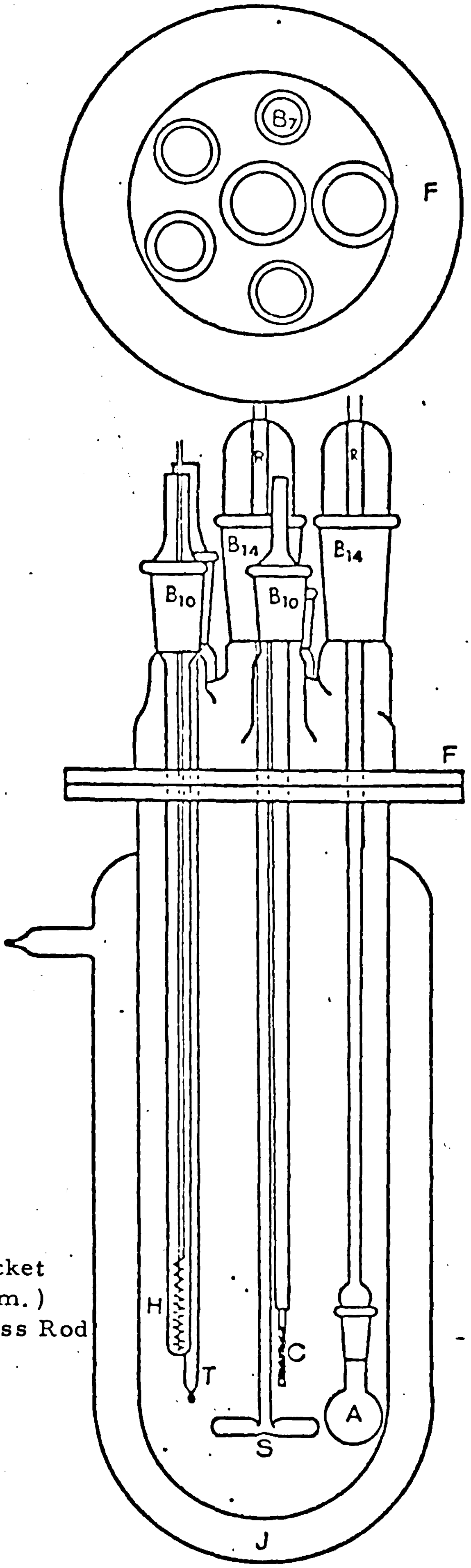
The calorimeters used in this work operate at around 25°C and the compounds of the reaction are normally handled in predominantly aqueous solution. Hence the experiment yields an enthalpy change for a studied reaction at 25°C.

It is convenient to describe briefly the calorimeters used in the course of this work. Two types were used.

a) A purpose built all glass Dewar type calorimeter (Fig. ii)

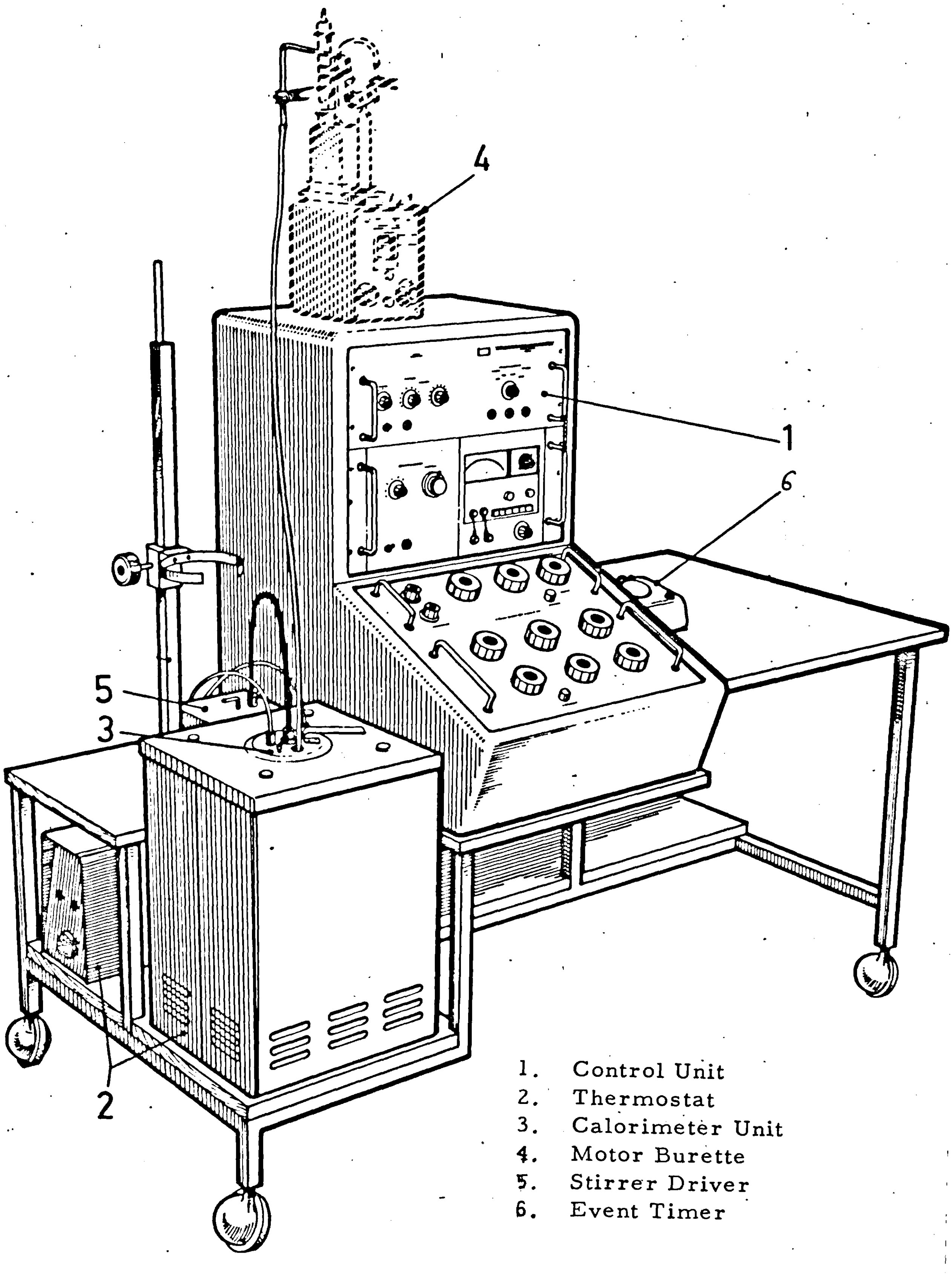
b) A commercial LKB 8700 Reaction Calorimetry System (Fig.iii).

The first consists of a Pyrex Dewar vessel with the vacuum jackets evacuated and sealed at 10^{-6} mm of Hg. The glass lids of the vessels were lubricated with silicone grease to prevent any leakage, as the complete calorimeter is immersed in water during operation. The introduction of components into the calorimeter cell was achieved through



H = Heater
T = Thermistor
S = Stirrer
A = Ampoule
C = Cooling Well
J = Evacuated Jacket
F = Flange (1.5 cm.)
R = Precision Glass Rod

Fig - Longitudinal Section through Calorimeter

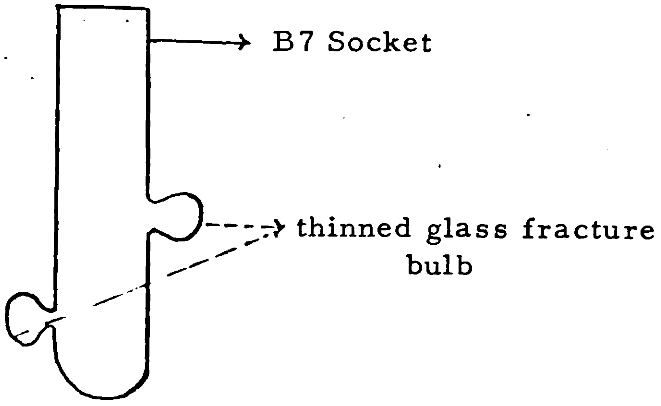


1. Control Unit
2. Thermostat
3. Calorimeter Unit
4. Motor Burette
5. Stirrer Driver
6. Event Timer

Fig iii

sockets in the lids. During the experiment the cell must be immersed to the base of the "quickfit" sockets in a constant temperature water bath maintained at 25.0 ± 0.01 °C. The vessels were equilibrated before the reaction for at least one hour. Cooling of the calorimeter vessels after the reaction step was complete and was achieved by pouring a small amount of liquid nitrogen into the cooling tube.

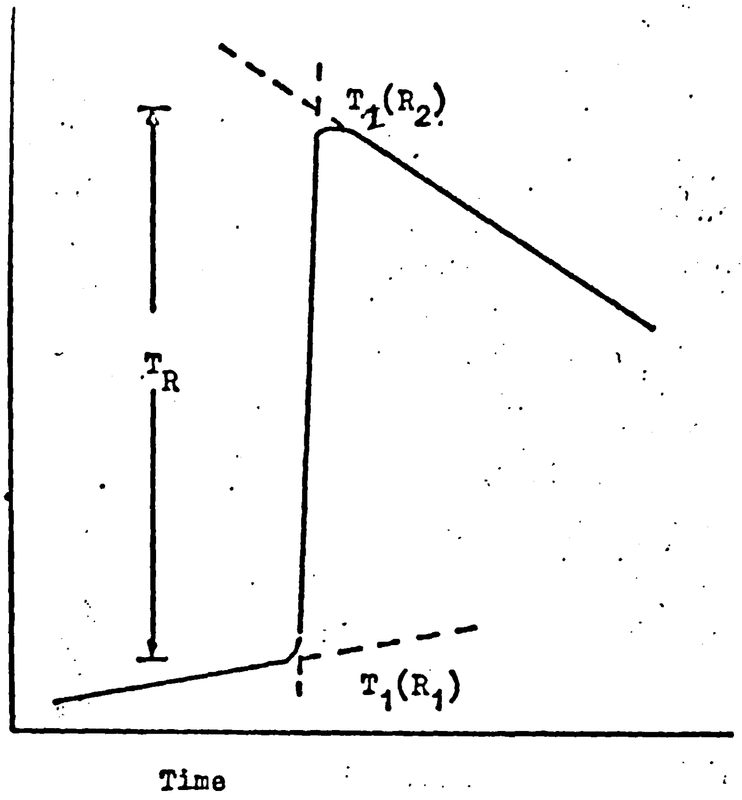
The calorimeters are calibrated by electrical substitution. The temperature sensory device was a thermistor (approx. 5000Ω at 20 °C and about 100ΩK^{-1}.) The thermistor formed one arm of a DC Wheatstone bridge and the out-of-balance bridge potential was displayed on a pen recorder. The ampoule used for the solid compounds is sketched below.



The heat due to ampoule breaking was shown to be negligible from blank calorimetry runs. Because of the nature of the sensing device, the reaction is followed in terms of resistance change, not temperature.

Typical temperature time traces for a reaction and calibration are shown in Fig. iv where, T_1, the temperature at the time of ampoule breaking and, T_2, give the represented corrected final temperature. Correction for thermal leakage is obtained by back extrapolation. The resistance values R_1

(a) Reaction.



(b) Calibration.

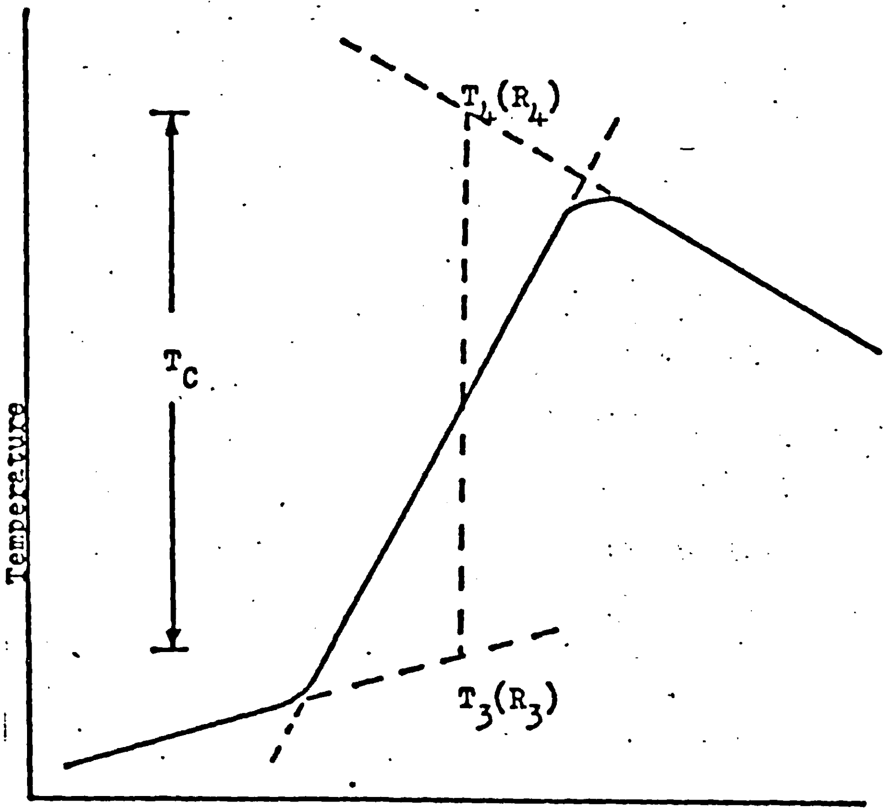


Fig. iv

and R_2 are recorded at T_1 and T_2; ΔT is calculated from the following characteristic equations for a thermistor

$$R = A \exp B/T$$

R = resistance in ohms, T = absolute temperature and A, B are thermistor constants.

$$T = B/\ln(R/A)$$

$$\text{So} \quad \Delta T = T_2 - T_1 = B \Bigg/ \left[\frac{1}{\ln(R_1/A)} - \frac{1}{\ln(R_2/A)} \right]$$

$$= B \ln(R_2/R_1) / [\ln \frac{R_1}{A} \times \ln \frac{R_2}{A}]$$

If ΔT_R is the reaction temperature change and ΔT_C the corresponding calibration temperature change then

$$\frac{\Delta T_R}{\Delta T_C} = \frac{\ln(R_2/R_1)}{\ln(R_4/R_3)}$$

This approximation is justified only when $R_1 \approx R_3$ and $R_2 \approx R_4$ where the terms involving A cancel.

The equation used to determine the enthalpy change during the reaction is

$$\Delta H_R \Big/ \text{K cal mol}^{-1} = f \times p \times t \times \frac{M}{w} \times \frac{\ln R_1/R_2}{\ln R_3/R_4}$$

f = factor to account the heat dissipated in the heater leads
p = power of the heater (in watts)
t = time (in secs)
M= molecular weight (g mol^{-1})
W= weight used (g)

P is obtained by measuring the current in the heater circuit and the potential drop across the heater while the heater is on.

A test reaction was carried out to check the apparatus before doing any calorimetry. This reaction was the neutralization of tris(hydroxy-methylaminomethane), THAM, in excess of 0.1 mol dm^{-3} hydrochloric acid.

$$(CH_2OH)_3C.\ NH_2(c) + n\ HCl\ (aq) \longrightarrow$$
$$\overset{+}{[(CH_2OH)_3C.\ NH_3 + Cl^-]}\ (n - 1)\ HCl\ (aq)$$

Thermochemical data for this reaction are well-documented.[8]

Our results from THAM reaction can be seen in the following table:

Enthalpies of neutralization (ΔH_R) of tris-(hydroxymethyl) amino-methane (THAM) in excess 0.1 $mol^{-1} dm^{-3}$ HCl at 298.15K

Run	m(THAM)/g.	dilution*	$-\Delta H_R$/kJ mol^{-1}
1	0.7044	954.8	29.94
2	0.7306	920.6	29.66
3	0.6825	985.4	29.68
4	0.6939	969.3	29.69
5	0.6847	982.2	29.80
6	0.6948	968.0	29.74

$$\Delta H_R \quad = \quad (-29.75 \pm 0.09)\ kJ\ mol^{-1}$$

*Dilution is calculated from[No of moles of H_2O/No. of moles of THAM]

Determination of enthalpy of neutralisation for the reaction between perchloric acid and triethylamine in methanol.

The value of the heat of neutralisation of the reaction between perchloric acid and triethylamine at 25 ± 0.1°C can be used to determine the dissociation constant of triethylamine (pK_a) over the range of temperature of the kinetic measurements, taking Ritchie's value at 25°C and applying the Van't Hoff isochore.

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H}{RT^2}$$

These results are shown in Table 1

The autoprotolysis constant pK_{ap} for methanol also changes with temperature. The data we used in this work are from a paper by Koskikallio.[1] Both values pK_a and pK_{ap} were needed to find out the correct methoxide ion concentration generated from the methanolic buffer mixture (perchloric acid + triethylamine) at different temperatures.

The reaction was studied at 25.0 ± 0.1°C. The LKB-8700 solution calorimeter (Fig.iii) was used for this work. A known weight of triethylamine liquid was contained in a special ampoule which was suspended inside the calorimeter. The calorimeter was charged with the acid solution (100 cm^3 of 0.05 mol dm^{-3}) and left in the water bath to achieve thermal equilibrium. When the ampoule was broken remotely, an evolution of heat was observed through the resistance change of the thermistor. The calorimeter is calibrated by electrical substitution.

The reaction can be represented by the following equation:

$$Et_3N(l) + [HClO_4 + MeOH]\ \text{soln.} \xrightarrow{\Delta H_1} [\,Et_3N + HClO_4 + MeOH]\ \text{soln.}$$

Alternatively, the reaction may be written:

$$Et_3N(l) + [2HClO_4 + MeOH]\ soln \xrightarrow{\Delta H_1} [Et_3NH^+ + MeOH_2^+ + 2ClO_4^-]soln.$$

The heat of solution of triethylamine in methanol was required as an ancillary measurement.

$$Et_3N(l) + MeOH\ (l) \xrightarrow{\Delta H_2} [Et_3N + MeOH]\ soln.$$

Therefore the enthalpy of neutralisation (ΔH_n) is given by

$\Delta H_n = \Delta H_1 - \Delta H_2$

from 4 experiments, $\Delta H_1 = -53.52$ kJ mol^{-1}

and from 3 experiments, $\Delta H_2 = -9.21$ kJ mol^{-1}, hence

$\Delta H_n = -44.31$ kJ mol^{-1}

This is close to the value obtained from previous work by Grunwald[9] ($\Delta H_n = -44.45$ kJ mol^{-1} at 25°C. In his experiment however, he studied the neutralisation of hydrochloric acid by sodium methoxide in methanol.

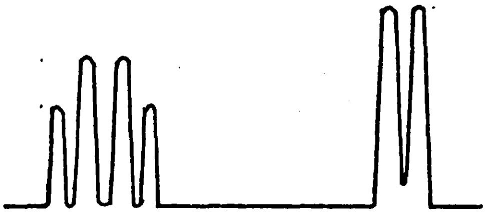
4.6 N.m.r. study for the compound $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-.H_2O$

Double resonance or spin decoupling can often provide an effective means of simplification of complex spectra and of determining which nuclei are coupled in such spectra. To apply this method it is necessary that the nuclei to be decoupled should be separated in chemical shift by at least 20 - 30 Hz. Suppose we have a system (AX) with two doublets only, and that while observing the resonance of A with the usual weak rf field, H_1, a much stronger rf field, H_2, is provided at the resonance frequency of X. In this case the A doublet collapses to a singlet. The reason is because the field H_2 has caused the nucleus to jump back and forth so rapidly between its possible spin states and that it no longer perturbs the spin states of A. Difficulty may arise sometimes owing to the fact that at levels of the field H_2 below that required for complete collapse of a multiplet, additional lines appear.

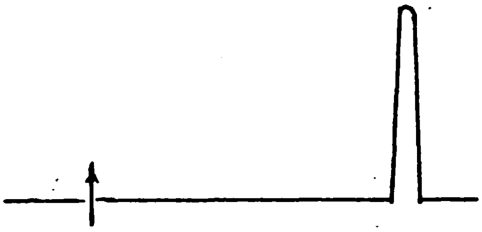
By reversing the experiment, one can see also the collapse of the doublet of X upon irradiating A. Double irradiation may be carried out either by keeping the field H_2 constant on the chosen resonance while sweeping H_1 through the spectrum (frequency sweep) or by sweeping H_0, which is equivalent to sweeping H_1 and H_2 together while maintaining a fixed frequency difference between them, $\Delta\nu$, equal to $\nu_A - \nu_X$ '(field sweep).

The spectrum of acetaldehyde is a simple case with which to illustrate the idea of double resonance. Field sweep irradiation of the aldehyde proton with $\Delta\nu = 454$ Hz collapses the CH_3 doublet to a singlet, while irradiation of the CH_3 protons collapses the aldehyde quartet to a singlet.

n.m.r. spectrum for CH_3CHO



irradiation at CHO



irradiation at CH_3

By the use of the double resonance technique it was possible to obtain further information to aid assingment of the spectrum of $[Co(C_5H_5)(C_8H_{11})]BF_4$ (Fig.11-17) The proton spectrum of the compound at 90 MHz without any irradiation shows seven different groups of resonances which could be interpreted as follows:

i) A quartet at 6.14 δ should be assigned to H^1, which may couple with three adjacent protons ($H^8, H^{8'}, H^2$).

ii) Two quartets at 5.65 δ obscured by C_5H_5, which could be assigned to H^3 and H^6 protons. (H^3 resonance due to coupling with $H^2, H^4, H^{4'}$) and H^6 which is adjacent to $H^5, H^7, H^{7'}$).

iii) Triplet at 4.46 δ which must be due to H^2 because of coupling with H^3, H^1.

iv) A quartet resonance at 3.66 δ which is due to H^5 (which can couple with $H^6, H^4, H^{4'}$).

v) A complex multiplet at ca. 3 δ is attributed to $H^{4'}$ and $H^{7'}$.

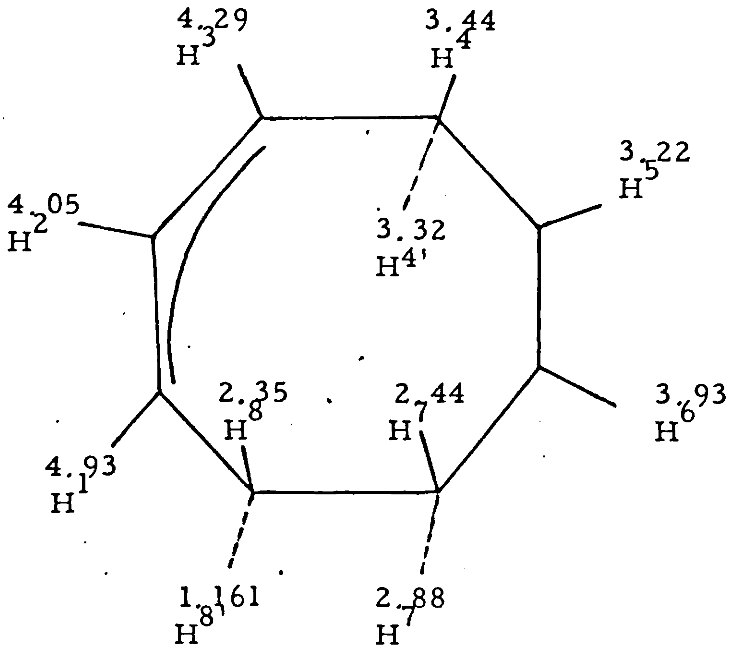
vi) Multiplet at 2.1 δ which could be assigned to $H^{8'}$, H^4, H^7.

vii) Finally, a multiplet at 1.22 δ which is assigned to H^8.

The intensity ratio showed that the compound has 16 protons including a sharp singlet (5H) of the cyclopentadienyl group. On irradiation at different frequencies, one can deduce which protons are adjacent to which by noticing the changes in specified resonances. The following scheme might be useful, the changes are given in terms of positive and negative depending on whether there is any change or not in the original spectrum respectively.

Intensity Ratio	1	5 + 2	1	1	2		3	1
Assignment	H^1	H^3, H^6	H^2	H^5	$H^{4'}$	$H^{7'}$	$H^4H^{8'}H^7$	H^8
	+	-	-	-	-	+	+	↑
	+	-	-	+	+	+	↑	+
	-	+	-	↑	+	-	-	-
	+	+	↑	-	-	-	-	-
	-	↑	+	+	+	+	+	-
	↑	-	+	-	-	-	+	+

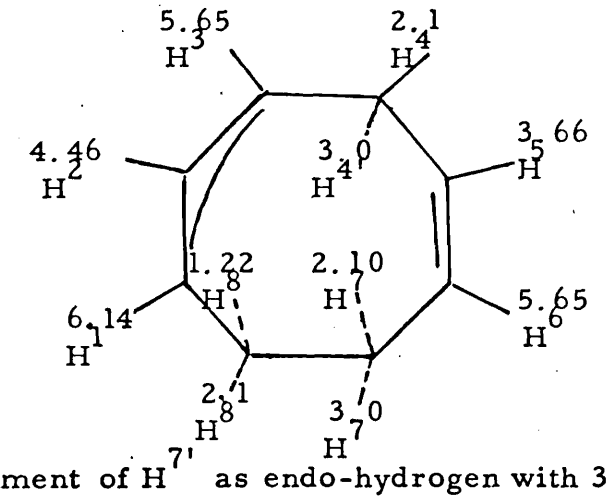
Assignment could be clarified as follows, see Table 8:



Assignments given by Maitlis[10] for the compound

$[Ir(C_5Me_5)(C_8H_{11})]PF_6$

However, for the cobalt compound from this work assignments given by Dr P Powell are consistent with the n.m.r. data.



Assignment of $H^{7'}$ as endo-hydrogen with 3.0 δ shifted to lower field relative to exo-hydrogen H^7 at 2.1 δ is in accord with Pauson's work.[11] The same assumption is made in the assignments of H^4 and $H^{4'}$ and of H^8 and $H^{8'}$.

TABLE 1.

Variation of the dissociation constant (pK_a) of triethylamine and the autoprotolysis constant (pK_{ap}) of methanol with temperature.

T/°C	pK_a	pK_{ap}
25.0	10.88	16.73
29.0	10.78	16.63
33.0	10.68	16.56
37.0	10.58	16.48
41.0	10.48	16.38
45.0	10.39	16.27

TABLE 2

Values of k_{obs} and $[OMe^-]$ for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and methoxide at 25.0, 29.0 and 33.0°C

$T/^oC$	$[OMe^-]$ / mol dm^{-3}	k_{obs} / s^{-1}	$T/^oC$	$[OMe^-]$ / mol dm^{-3}	$T/^oC$	$[OMe^-]$ / mol dm^{-3}	k_{obs} / s^{-1}
25.0	3.8×10^{-6}	0.16	29.0	3.5×10^{-6}	33.0	3.3×10^{-6}	0.26
25.0	5.1×10^{-6}	0.19	29.0	4.7×10^{-6}	33.0	4.4×10^{-6}	0.29
25.0	7.2×10^{-6}	0.25	29.0	6.6×10^{-6}	33.0	6.2×10^{-6}	0.35
25.0	11.2×10^{-6}	0.32	29.0	10.3×10^{-6}	33.0	9.6×10^{-6}	0.51
25.0	16.7×10^{-6}	0.43	29.0	15.4×10^{-6}	33.0	14.4×10^{-6}	0.68
25.0	21.9×10^{-6}	0.54	29.0	20.1×10^{-6}	33.0	18.6×10^{-6}	0.81

TABLE 3

Values of k_{obs} and $[OMe^-]$ for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and methoxide at 37.0, 41.0, and 45.0°C

T/°C	$[OMe^-]$/mol dm^{-3}	k_{obs}/s^{-1}	T/°C	$[OMe^-]$/ mol dm^{-3}	k_{obs}/s^{-1}	T/°C	$[OMe^-]$/mol dm^{-3}	k_{obs} / s^{-1}
37.0	3.1×10^{-6}	0.31	41.0	3.2×10^{-6}	0.41	45.0	3.3×10^{-6}	0.52
37.0	4.2×10^{-6}	0.37	41.0	4.3×10^{-6}	0.49	45.0	4.5×10^{-6}	0.68
37.0	5.9×10^{-6}	0.45	41.0	6.0×10^{-6}	0.57	45.0	6.3×10^{-6}	0.77
37.0	9.2×10^{-6}	0.61	41.0	9.3×10^{-6}	0.73	45.0	9.7×10^{-6}	0.91
37.0	13.8×10^{-6}	0.80	41.0	14.0×10^{-6}	0.98	45.0	14.6×10^{-6}	1.26
37.0	18.0×10^{-6}	0.95	41.0	18.3×10^{-6}	1.15	45.0	19.1×10^{-6}	1.48

TABLE 4

Values of k_2 and ln k of the reaction of $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and methoxide at different temperatures.

T/K	$k_2/dm^3\ mol^{-1}\ s^{-1}$	$1/T\ /\ K^{-1}$	$\ln k_2$
298.2	2.29×10^4	0.00335	10.04
302.2	3.00×10^4	0.00331	10.30
306.2	3.71×10^4	0.00326	10.52
310.2	4.23×10^4	0.00322	10.65
314.2	4.89×10^4	0.00318	10.80
318.2	6.20×10^4	0.00314	11.03

TABLE 5

Activation parameters for the reaction of $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ with methoxide at different temperatures.

T/K	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger\ /JK^{-1}mol^{-1}$
298.2	35.32	-43.1
302.2	35.30	-42.6
306.2	35.26	-42.5
310.2	35.23	-43.1
314.2	35.20	-43.6
318.2	35.16	-43.3

TABLE 6

k_{obs} and k_2 values of the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and methanol at different temperatures

T/K	k_{obs}/s^{-1}	k_2/ $dm^3\ mol^{-1}s^{-1}$	1/T / K^{-1}	ln k_2
298.2	0.09	2.9×10^{-3}	0.00335	-5.84
302.2	0.12	3.8×10^{-3}	0.00331	-5.57
306.2	0.14	4.5×10^{-3}	0.00326	-5.40
310.2	0.19	6.1×10^{-3}	0.00322	-5.10
314.2	0.27	8.6×10^{-3}	0.00318	-4.76
318.2	0.37	11.8×10^{-3}	0.00314	-4.43

TABLE 7

Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and methanol.

T / K	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J$K^{-1}mol^{-1}$
298.2	53.41	-114.5
302.2	53.38	-115.1
306.2	53.34	-115.8
310.2	53.31	-115.8
314.2	53.30	-115.4
318.2	53.24	-115.3

TABLE 8

Chemical shifts related to TMS (δ scale), coupling constants in Hz.

	H^1	H^2	H^3	H^4	H^5	H^6	$H^{4'}$	H^7	$H^{7'}$	H^8	$H^{8'}$
I	6.14 J(12), (18) (18') 7.6Hz	4.46 J(12), (13)= 8.6Hz	5.65	2.1 J(45), (56)(54') = 8.5Hz	3.66	5.65	3.0	2.10	3.0	1.22 J(87)(81) = 6.8Hz	2.1 J(88') = 19
II	4.93 J(12)=7 J(18) ≈ J(18') = 7.5Hz	4.05 J(23) = 7	4.29	3.44 J(44') = 15	3.22 J(56)=6 = 6	3.93 J(67) =6	3.32	2.44	2.88	2.35	1.61

I - 'H n.m.r. data for $[Co(C_5H_5)(C_8H_{11})]^+$, data refers to solutions in CD_3NO_2 at 90 MHz.

II - " " " " $[Ir(C_5Me_5)(C_8H_{11})]^+$, data refers to solutions in $CDCl_3$

Fig. 1. Plot of k_{obs} v. methoxide ion concentration for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and OMe^- at 25.0°C

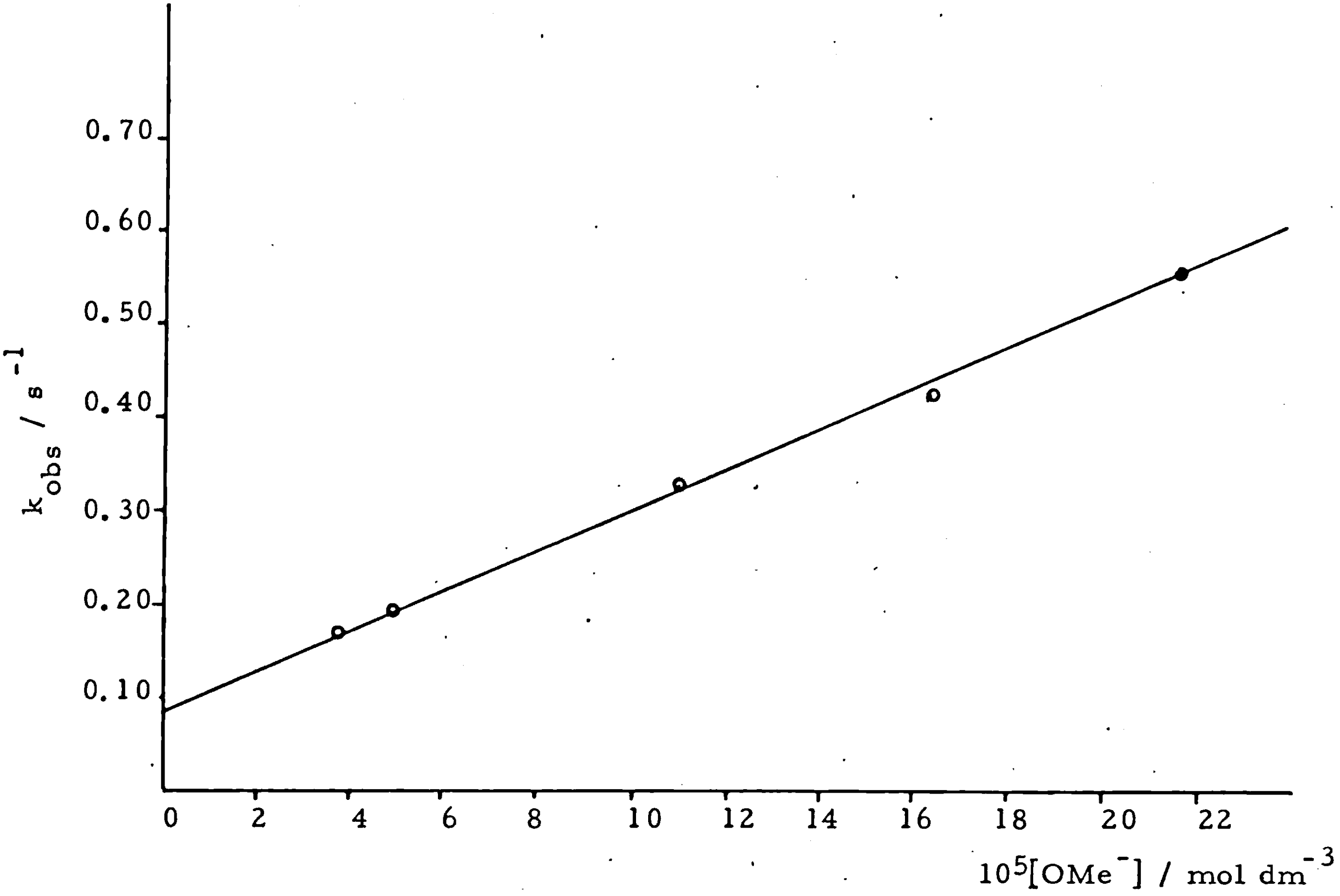


Fig. 2. Plot of k_{obs} v. methoxide ion concentration for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and OMe^- at 29.0°C

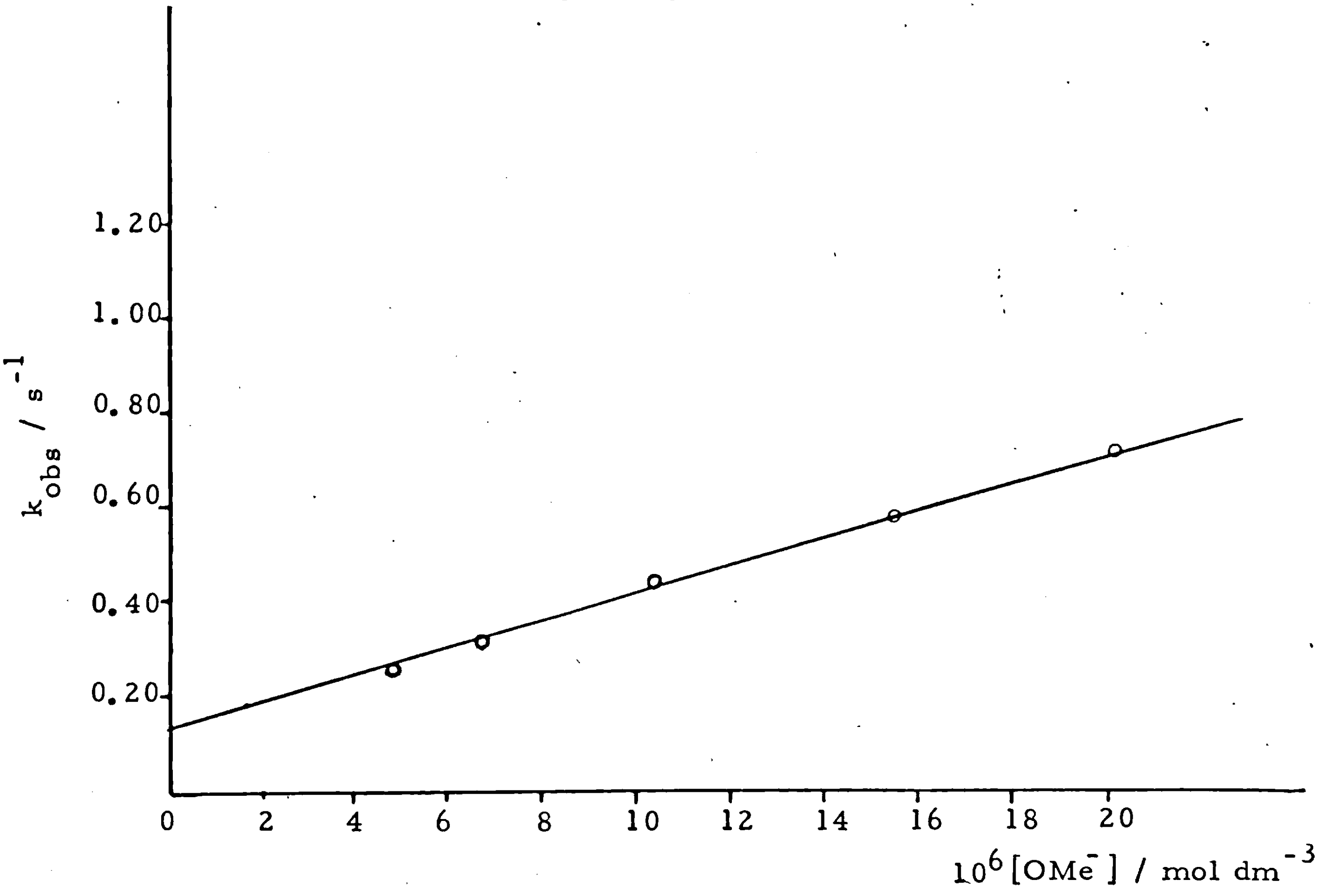


Fig. 3 - Plot of k_{obs} v. methoxide ion concentration for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and OMe^- at 33.0°C.

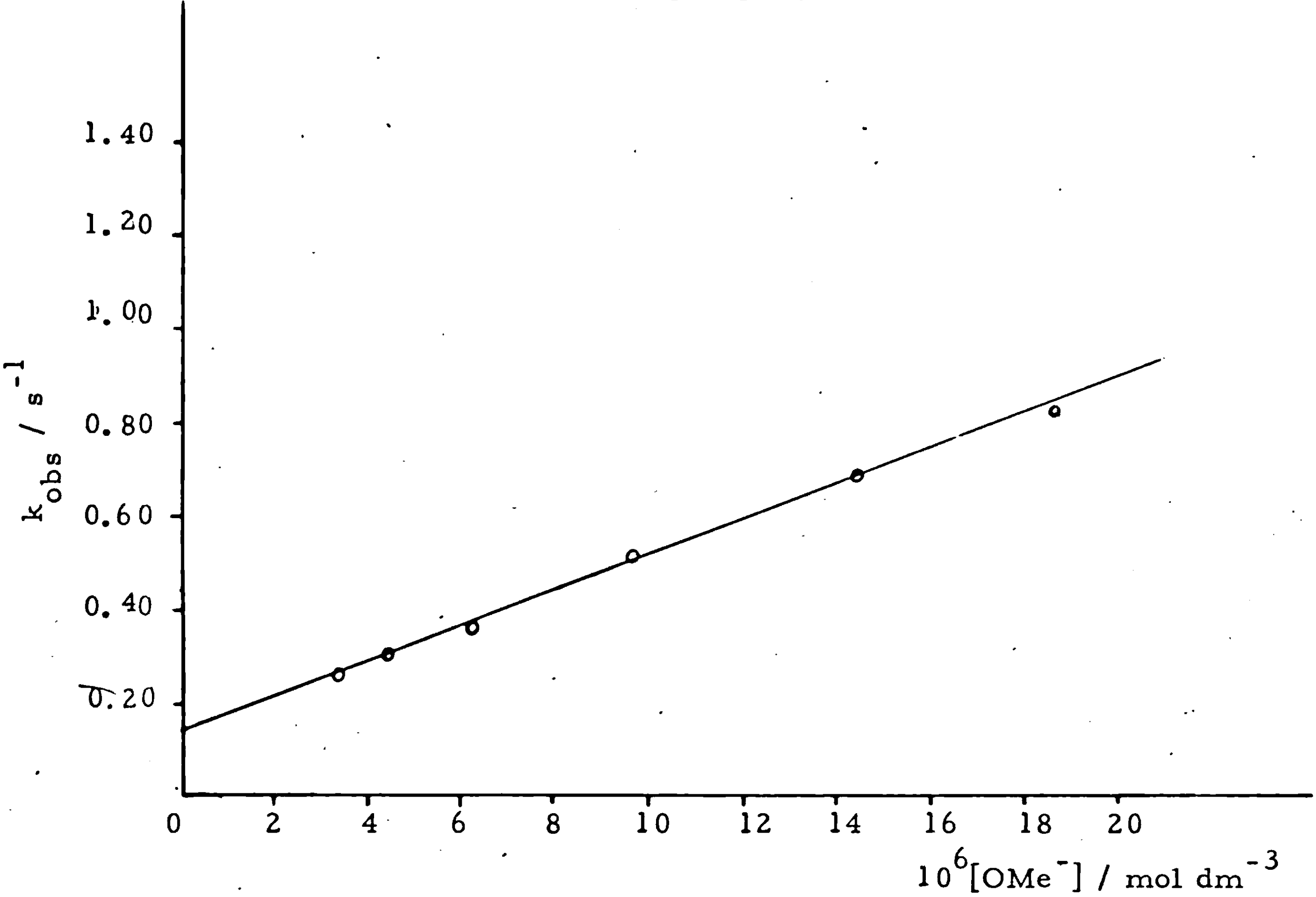


Fig. 4 - Plot of k_{obs} v. methoxide ion concentration for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and OMe^- at 37.0°C.

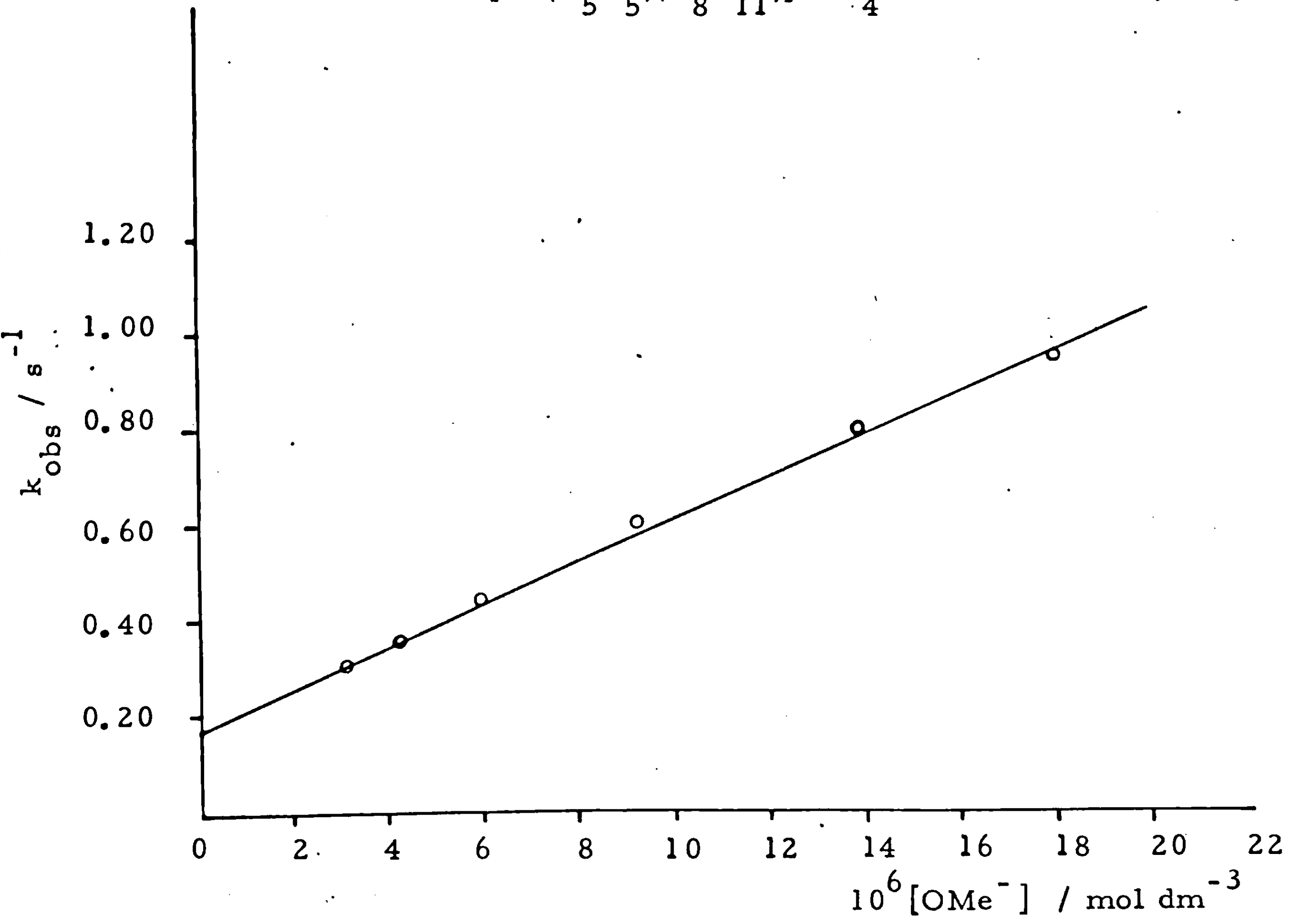


Fig. 5 - Plot of k_{obs} v. methoxide ion concentration for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and OMe^- at 41.0°C.

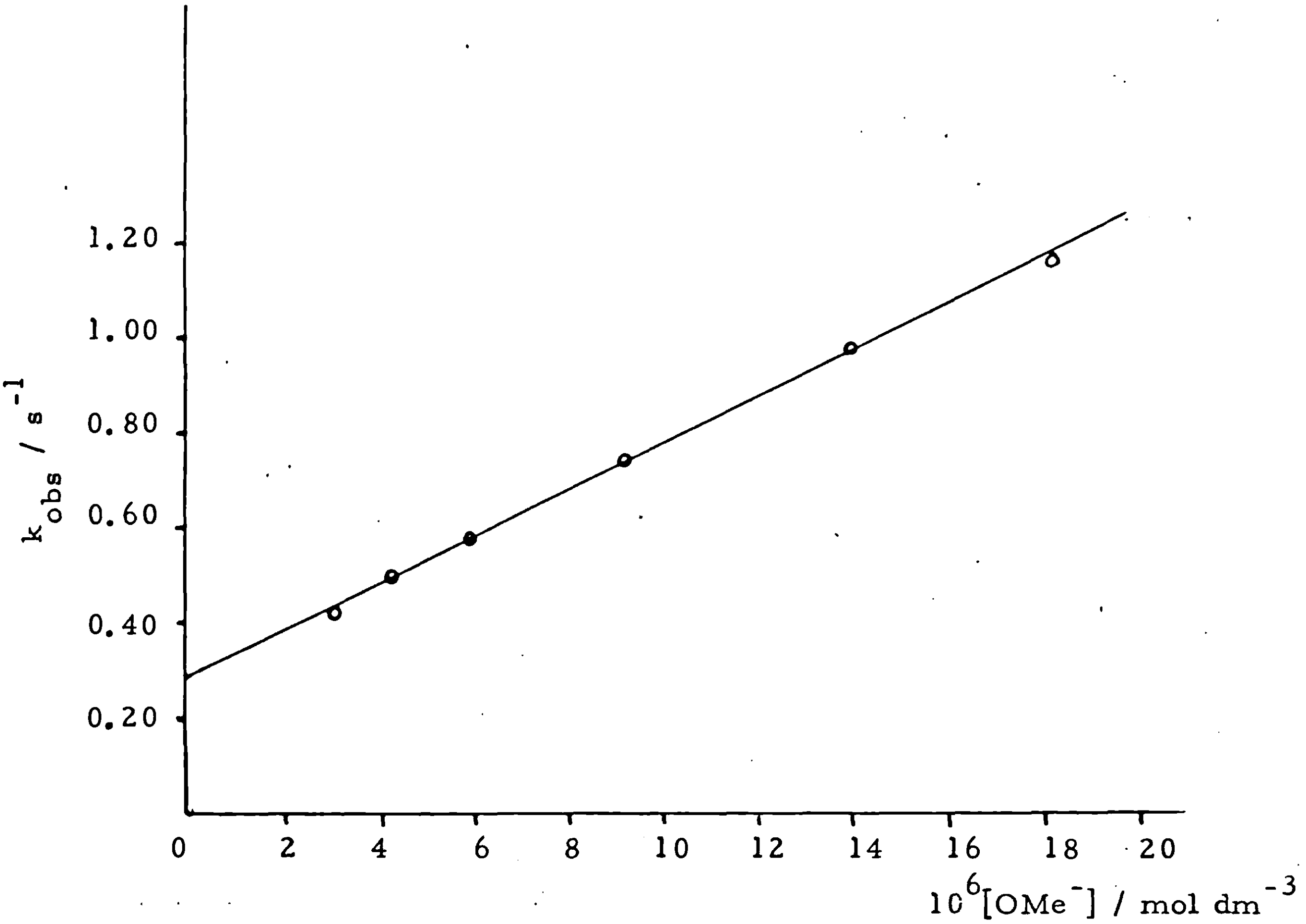


Fig. 6 - Plot of k_{obs} v. methoxide ion concentration for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and OMe^- at 45.0°C.

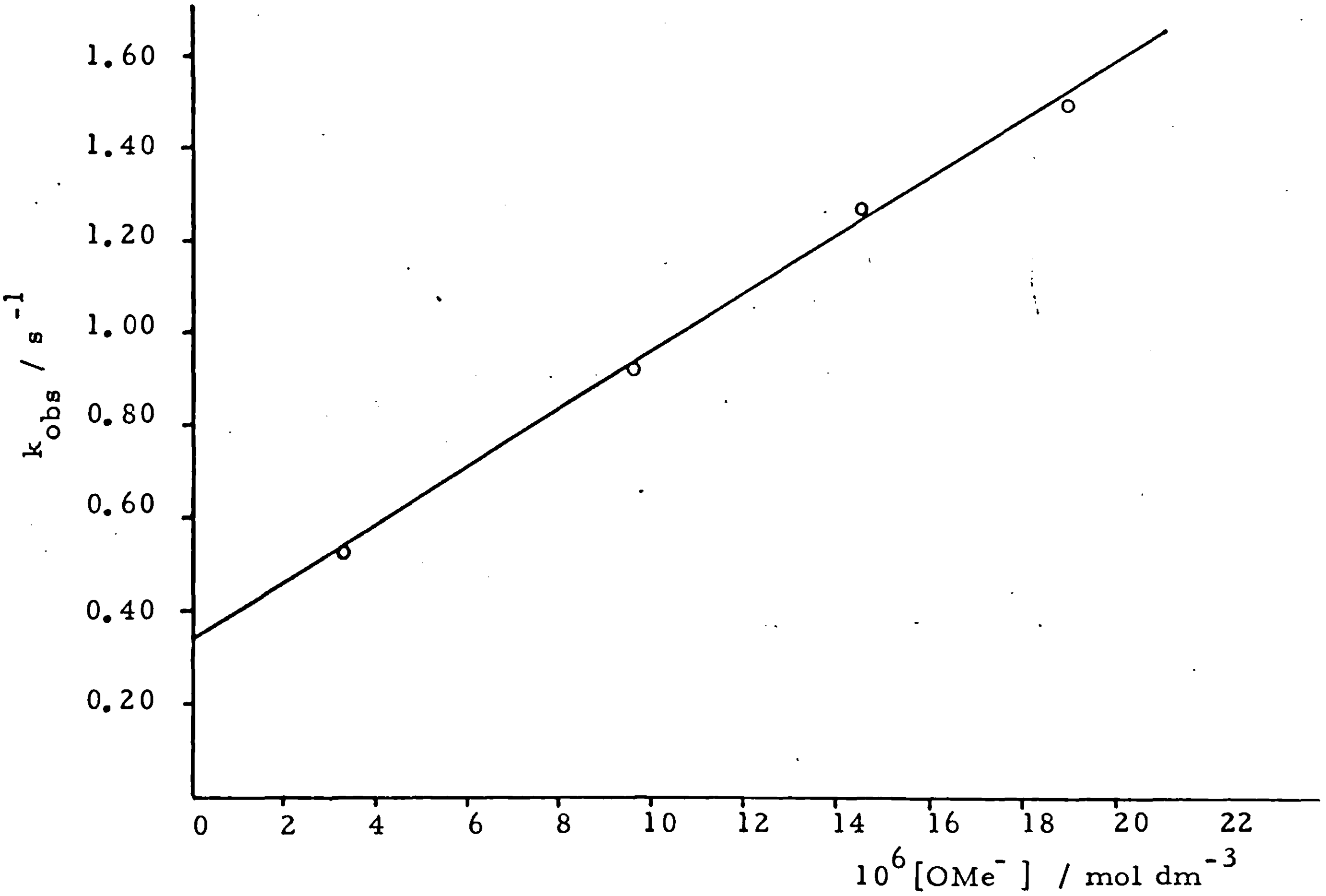


Fig. 7. - Arrhenius plot for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and methoxide.

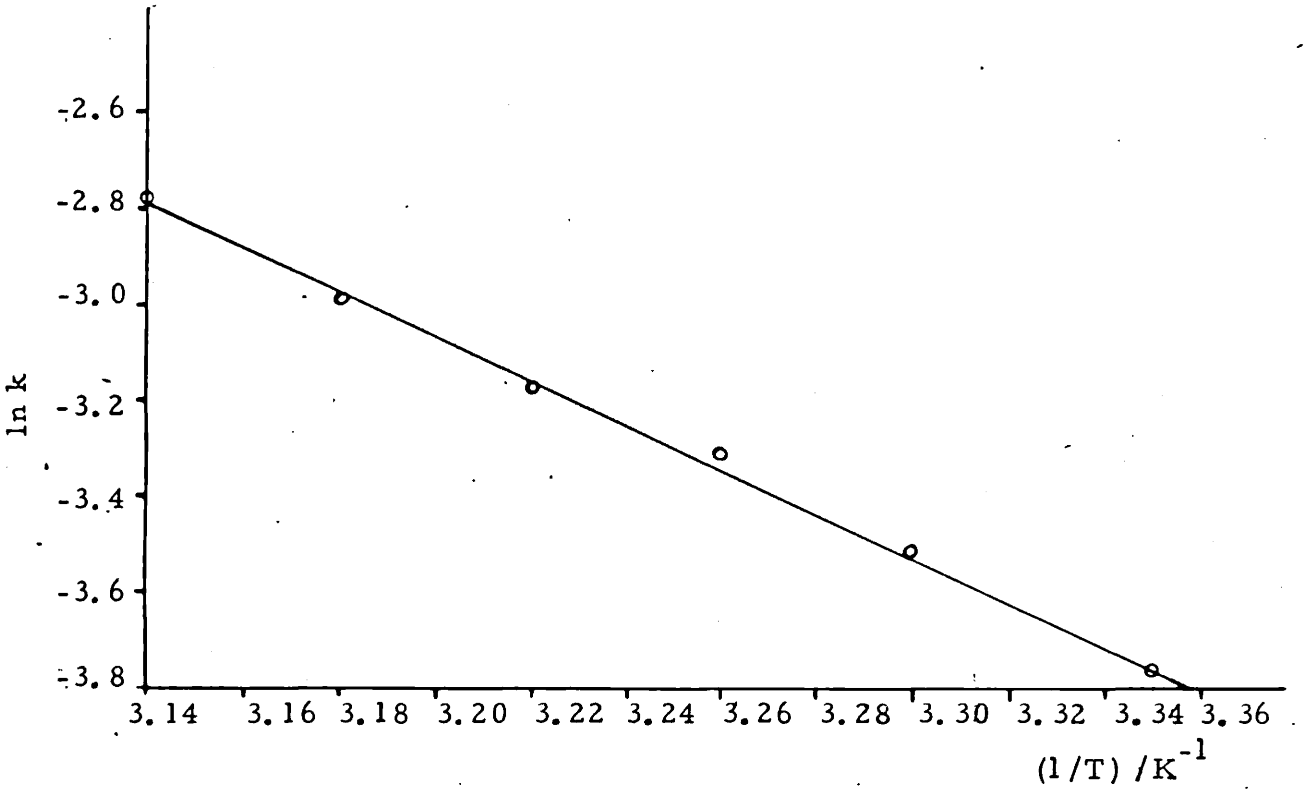
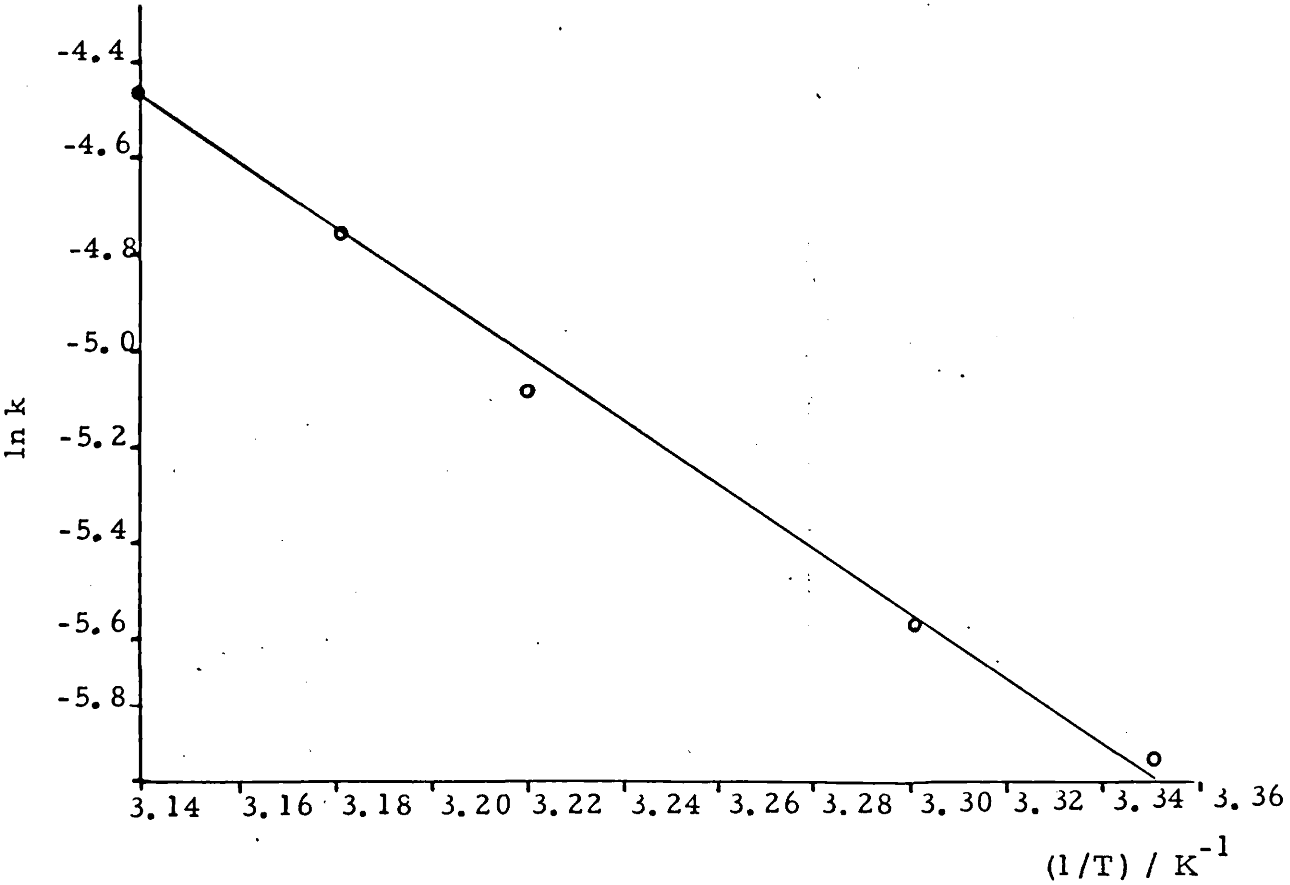


Fig. 8 - Arrhenius plot for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and methanol.



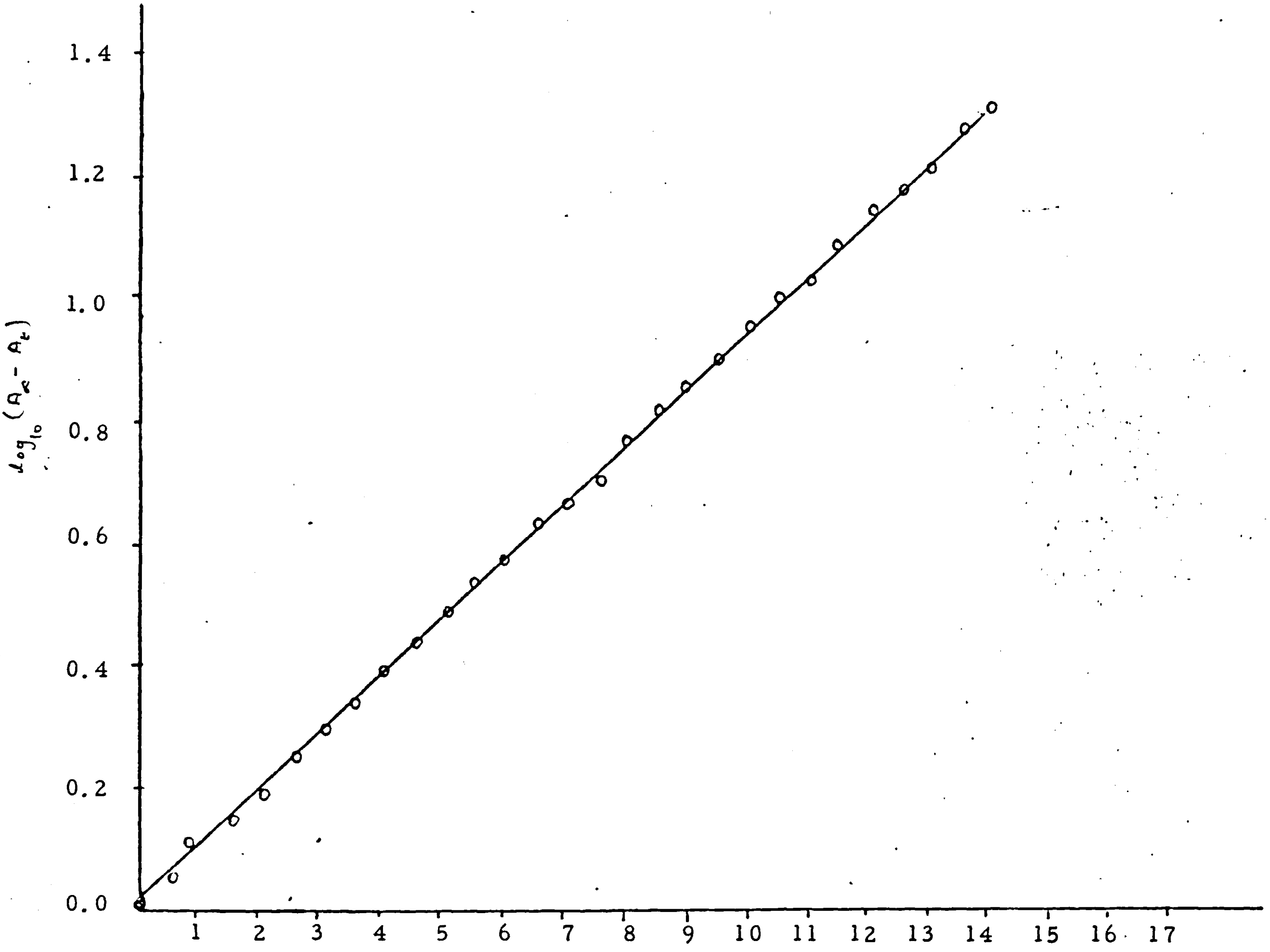
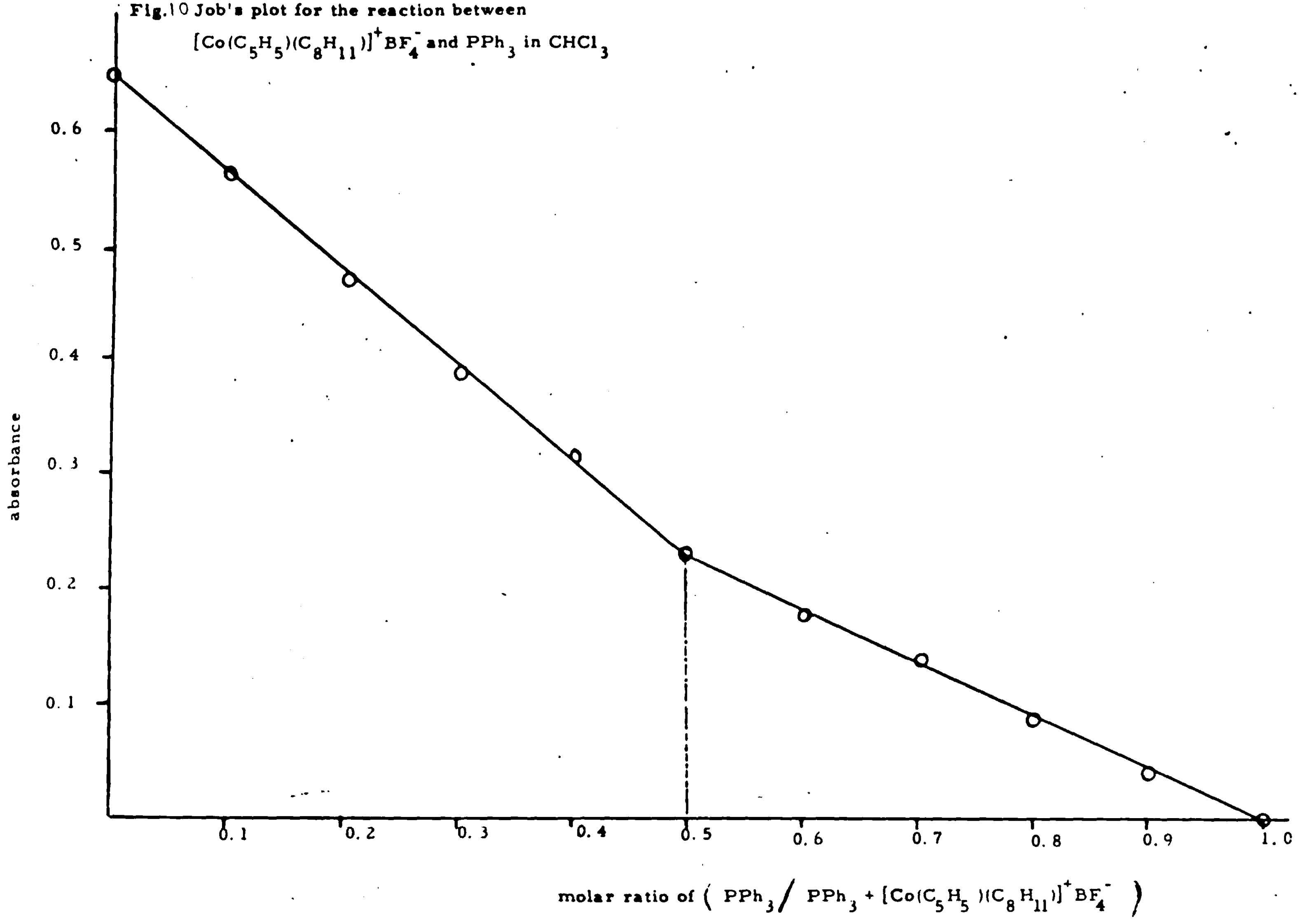


Fig. 9. Pseudo first order kinetic plot for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and OMe^- in methanol at 25°C

Fig.10 Job's plot for the reaction between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and PPh_3 in $CHCl_3$



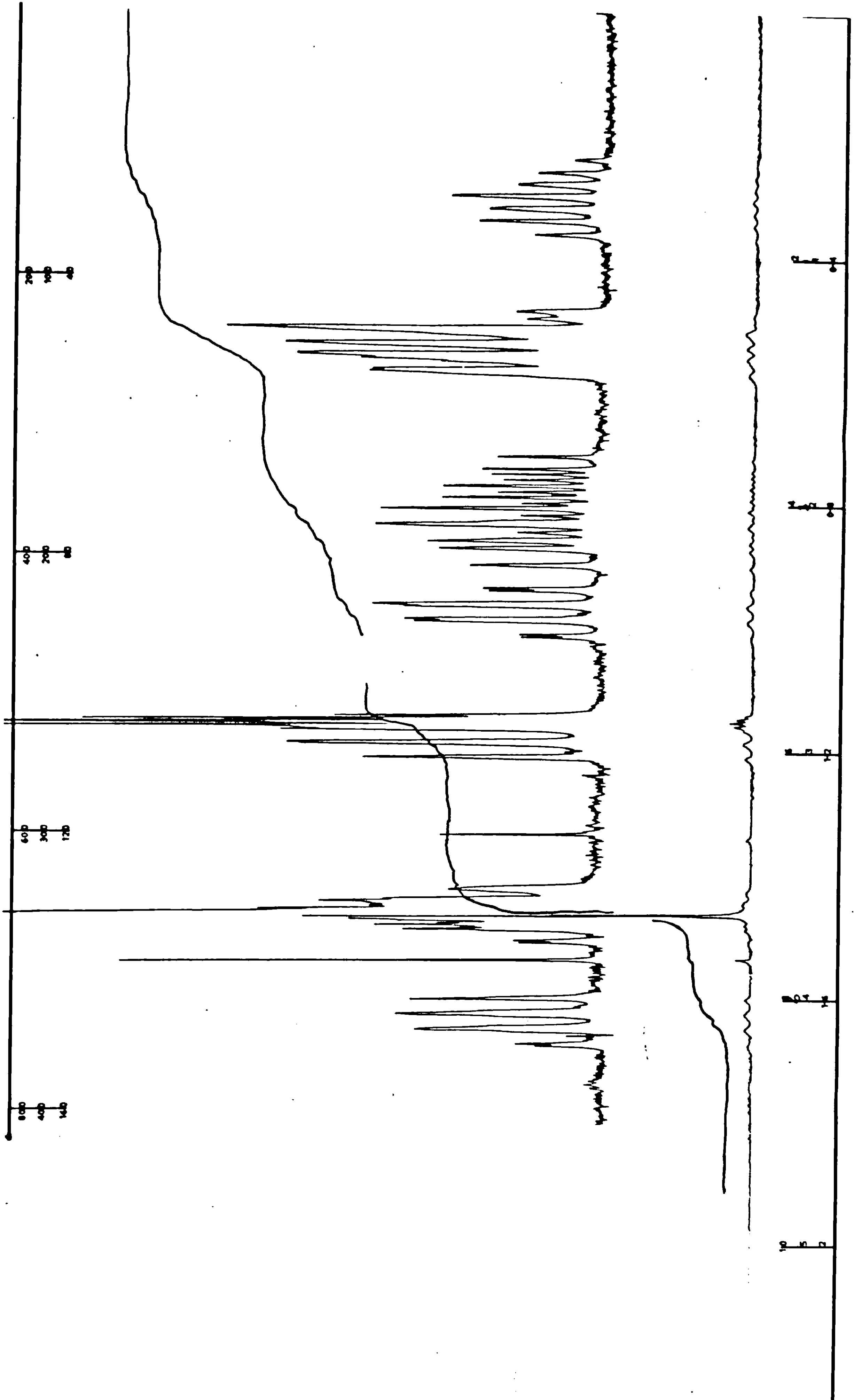
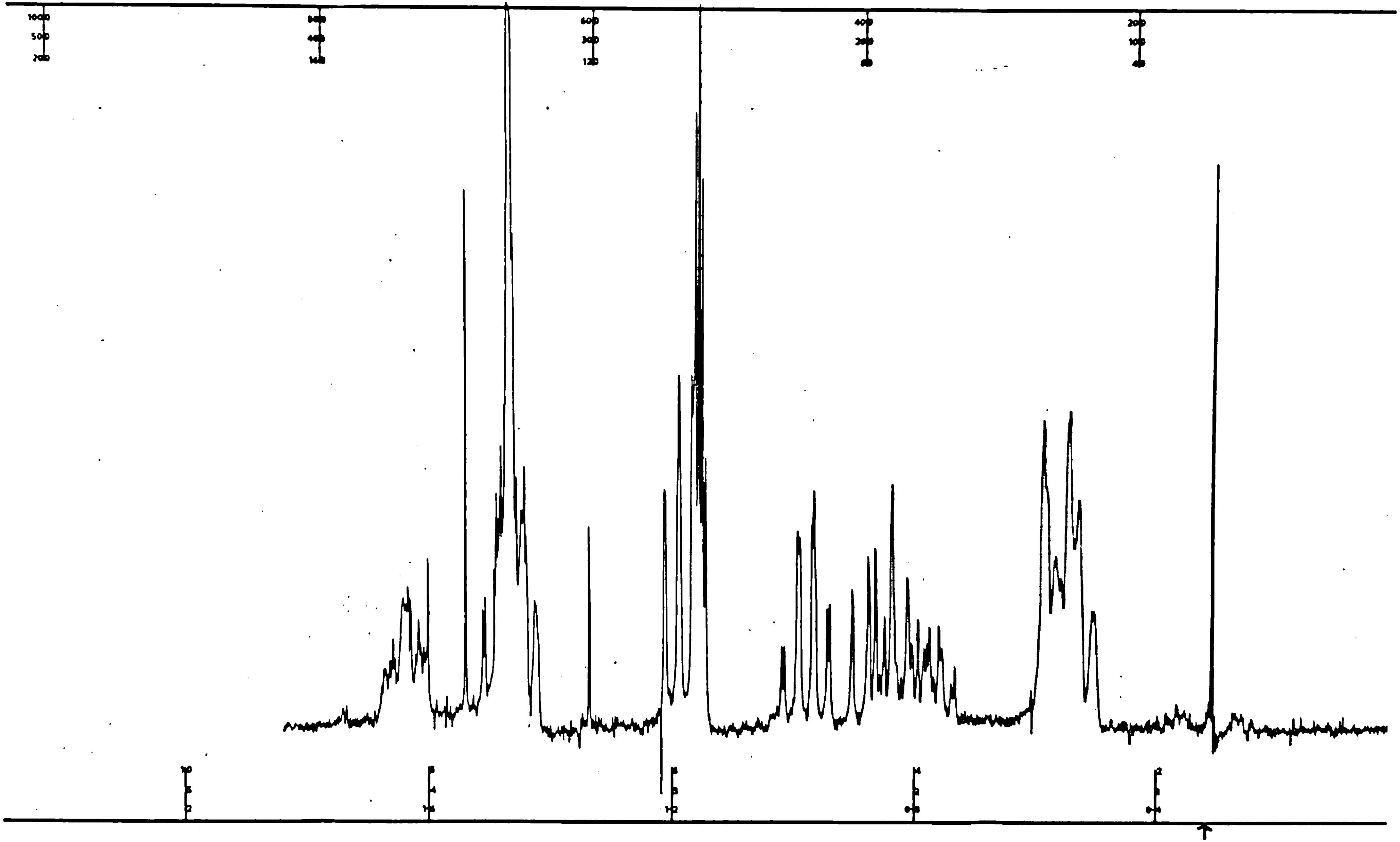


Fig.11. ^{1}H n.m.r. spectrum of $[Co(C_5H_5)(C_8H_{11})]^+BF_4$ in CD_3NO_2 at 90 MHz.

Fig 12.Irradiation at 1.22δ



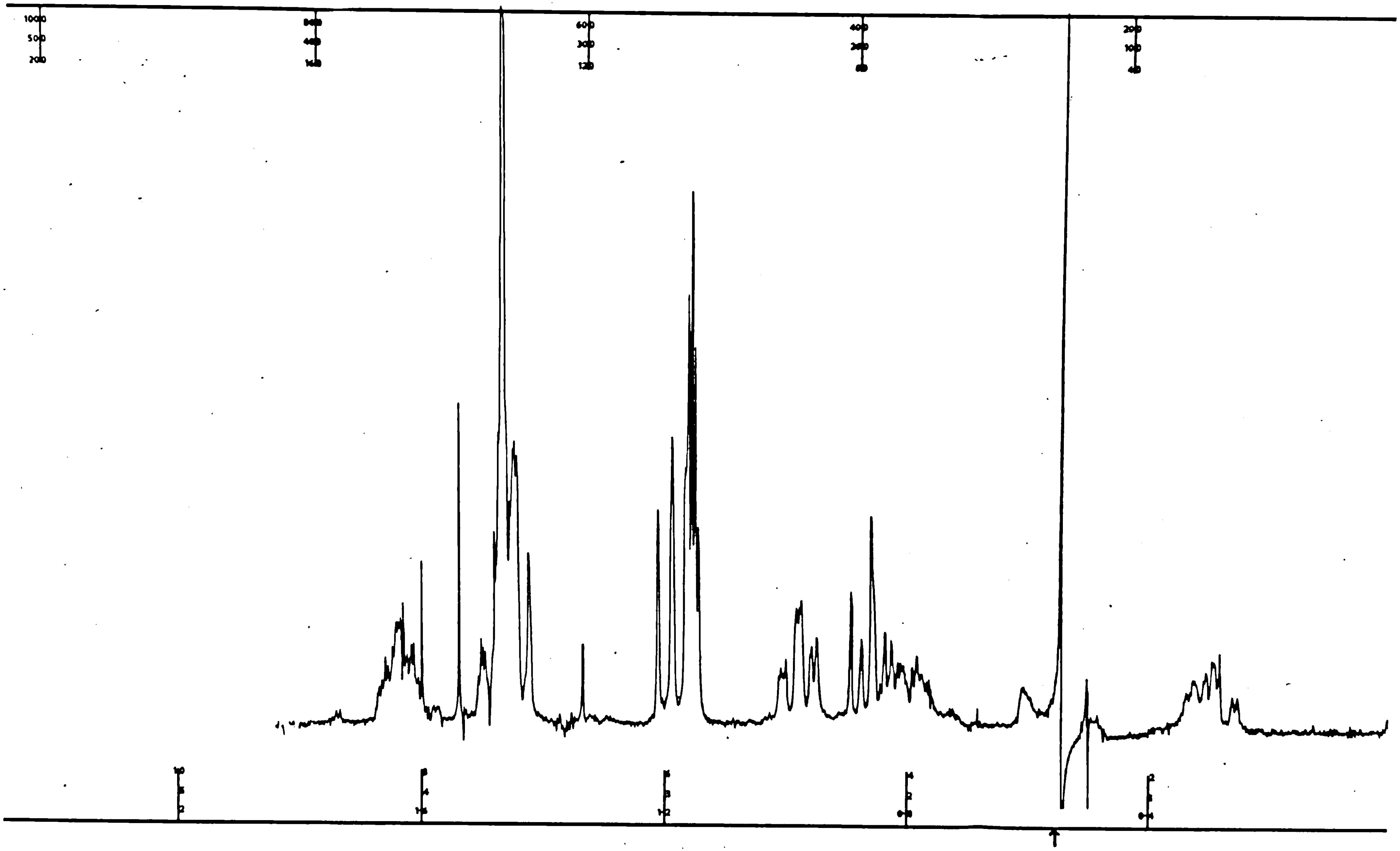
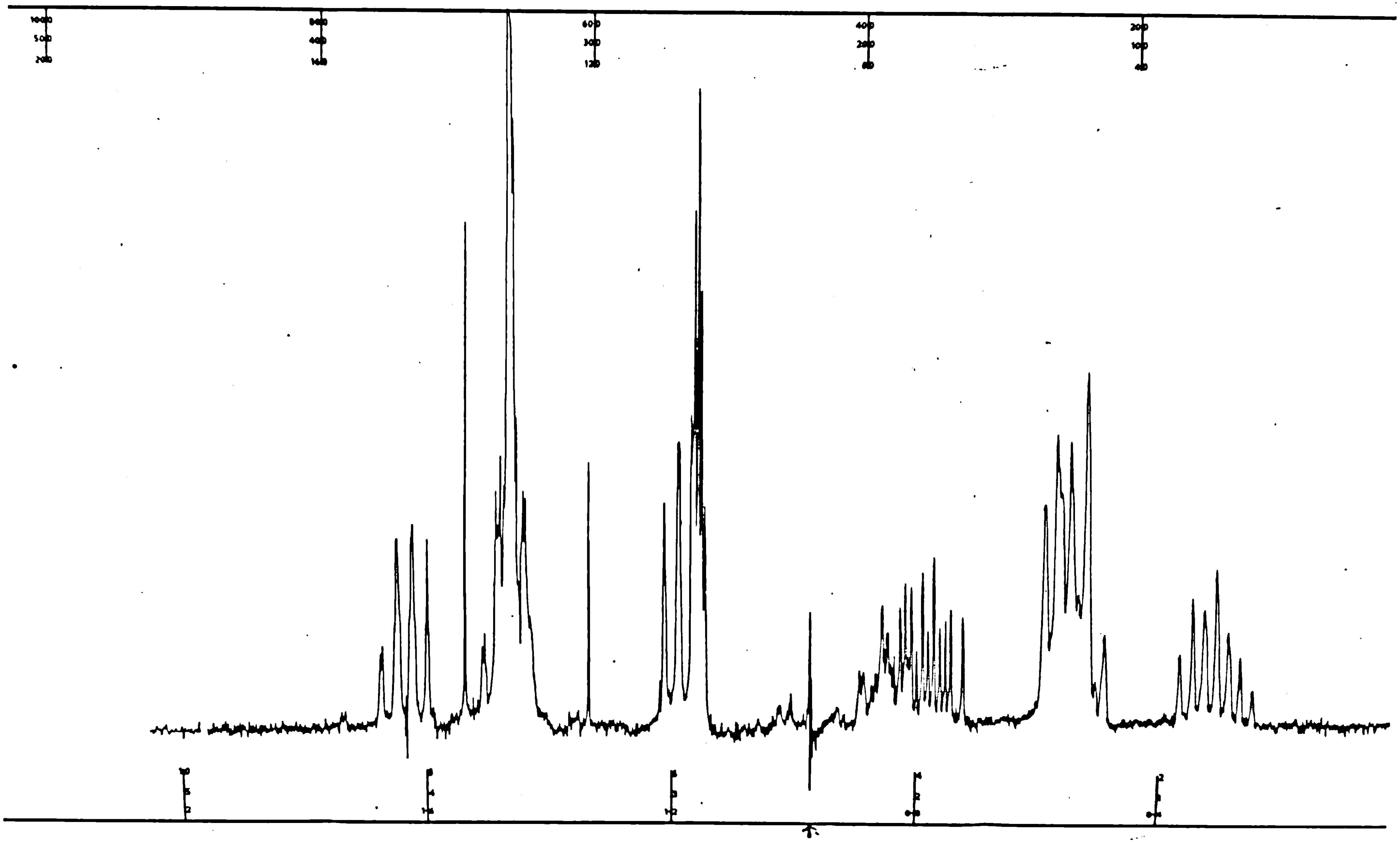


Fig.13. Irradiation at 2.1δ

Fig.14. Irradiation at 3.66δ



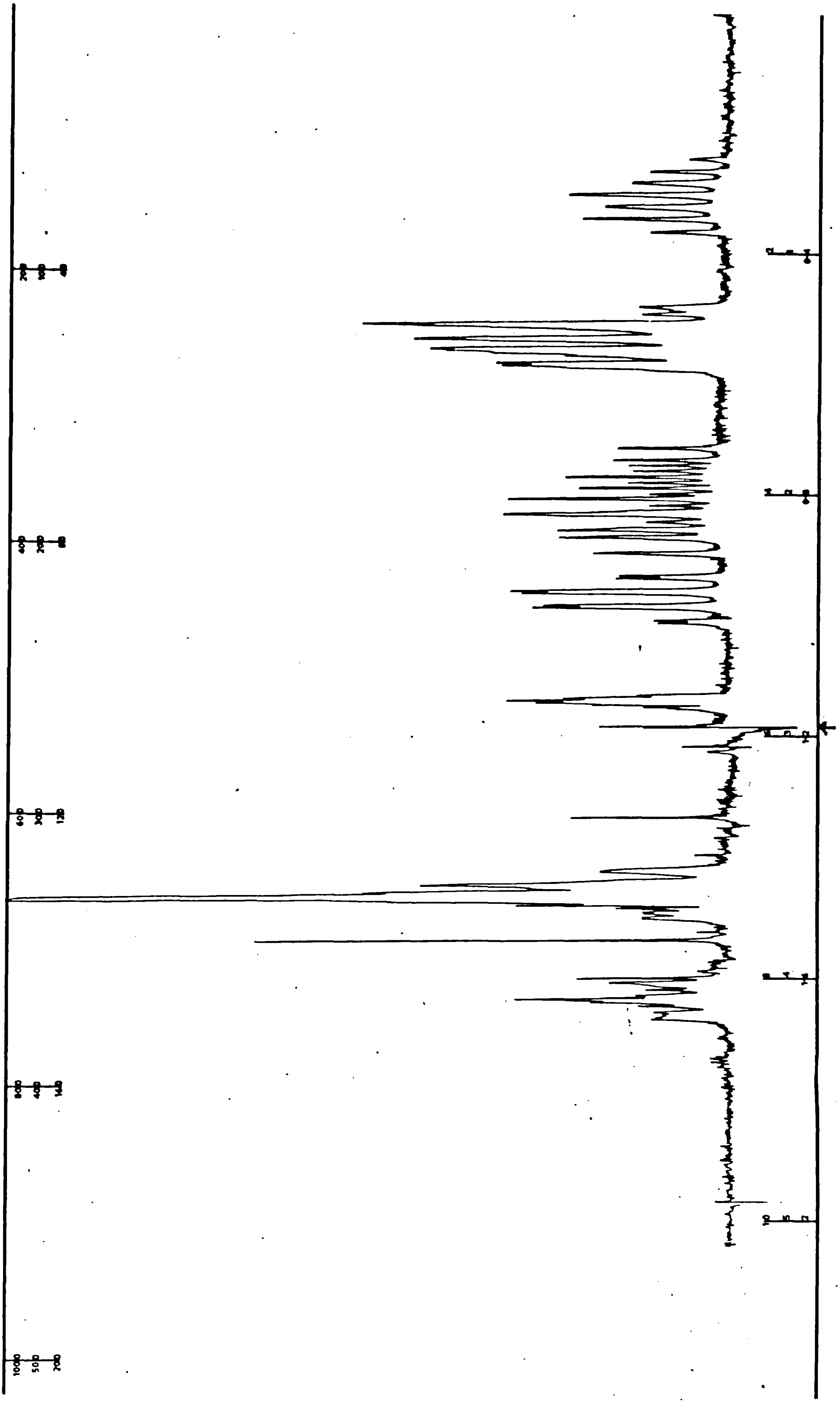


Fig.15. Irradiation at 4.46δ

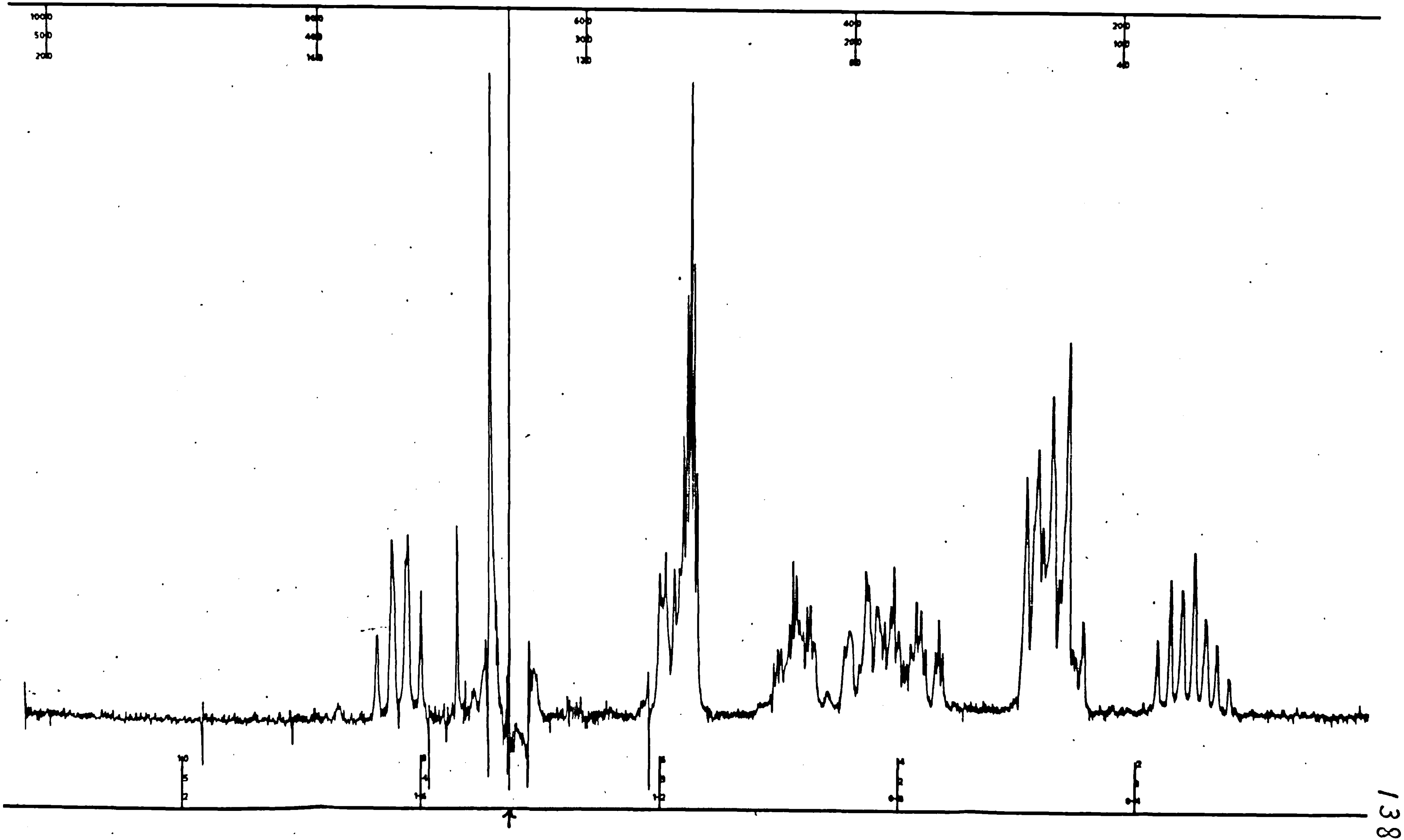
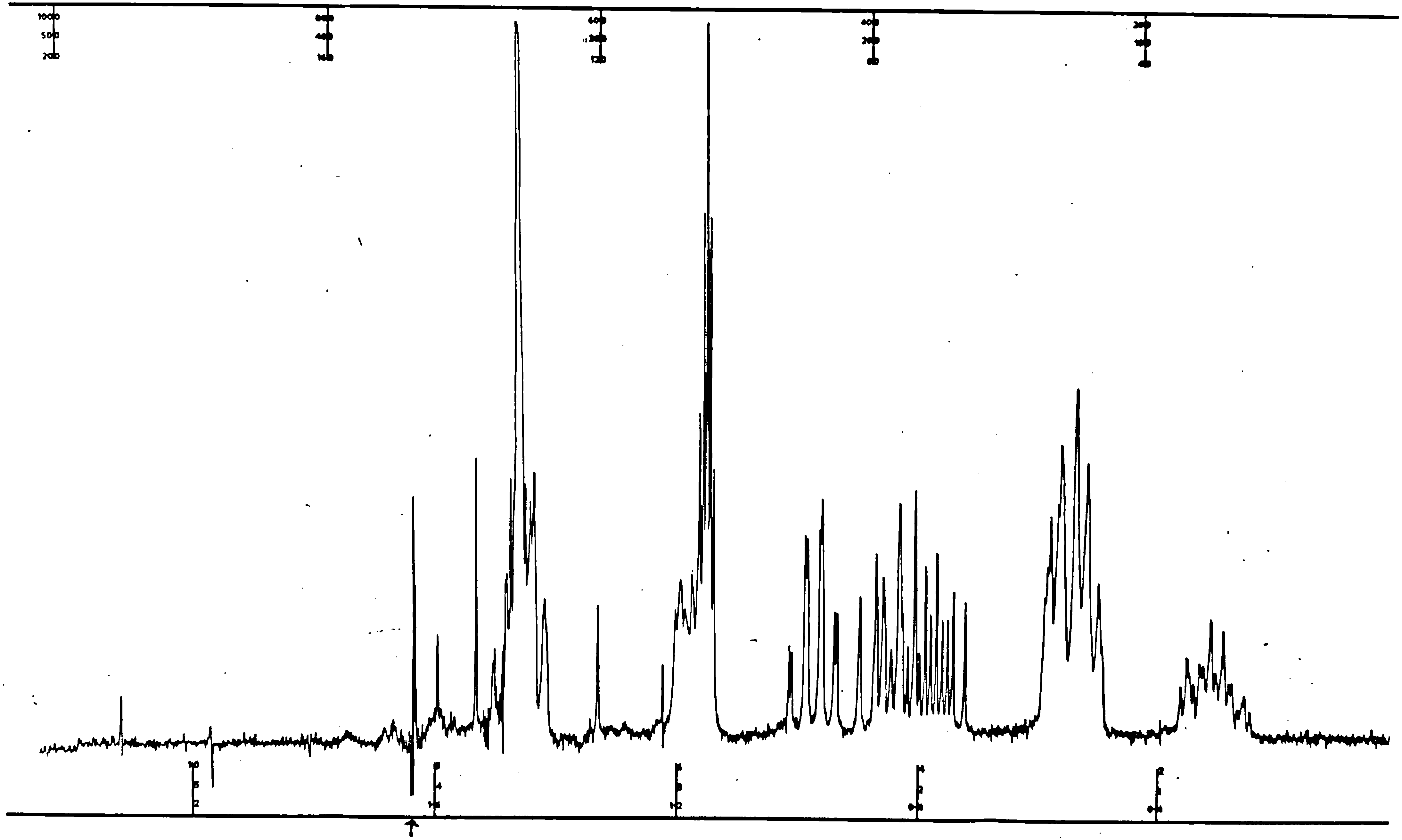


Fig. 16. Irradiation at 5.65δ

Fig. 17. Irradiation at 6.14δ



4.7 Experimental

a. Materials

Cyclopentadienyl (cyclo- octa-1,5 diene)cobalt (I): the compound was prepared by Dr L J Russell according to the method of King.

Triphenylphosphine: The commercial product was used.

Chloroform: Analar BDH was used without further purification.

Methanol: Analar BDH product was used.

b. Determination of the stoicheiometry of adduct formation between $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and PPh_3.

First a study of Beer's Law for the cobalt compound was carried out, by preparing seven different concentrations of the complex in Analar chloroform over the range 10^{-3} - 10^{-2} $mol.dm^{-3}$. The absorbance was measured for each solution separately against a reference cell containing the solvent. A Pye-Unicam SP-500 Spectrometer was used for this purpose. When the absorbance value was plotted out against concentration, a good straight line was obtained indicating that the compound obeys Beer's Law.

The solvent was chosen after trying several other solvents qualitatively in a test tube. For instance both $[Co(C_5H_5)(C_8H_{11})]^+BF_4^-$ and triphenylphosphine are soluble in acetone, but the reaction seems to be very slow. In dioxane, only triphenylphosphine dissolves. However in dichloromethane, both the cobalt compound and the phosphine ligand were soluble, but this is excluded because of its high volatility. In acetonitrile triphenylphosphine was less soluble than the organometallic compound, which makes a turbidity if it is used in excess. So, the Analar chloroform was the most convenient for this reaction.

b. Apparatus:

A Nortech Laboratories, Canterbury SF3A Mk. III stopped-flow spectrophotometer was used in conjunction with a Datalab DL901 transient recorder linked to a cathode-ray oscilloscope, chart recorder and tape punch. Fig. v shows a block diagram for the stopped-flow apparatus.

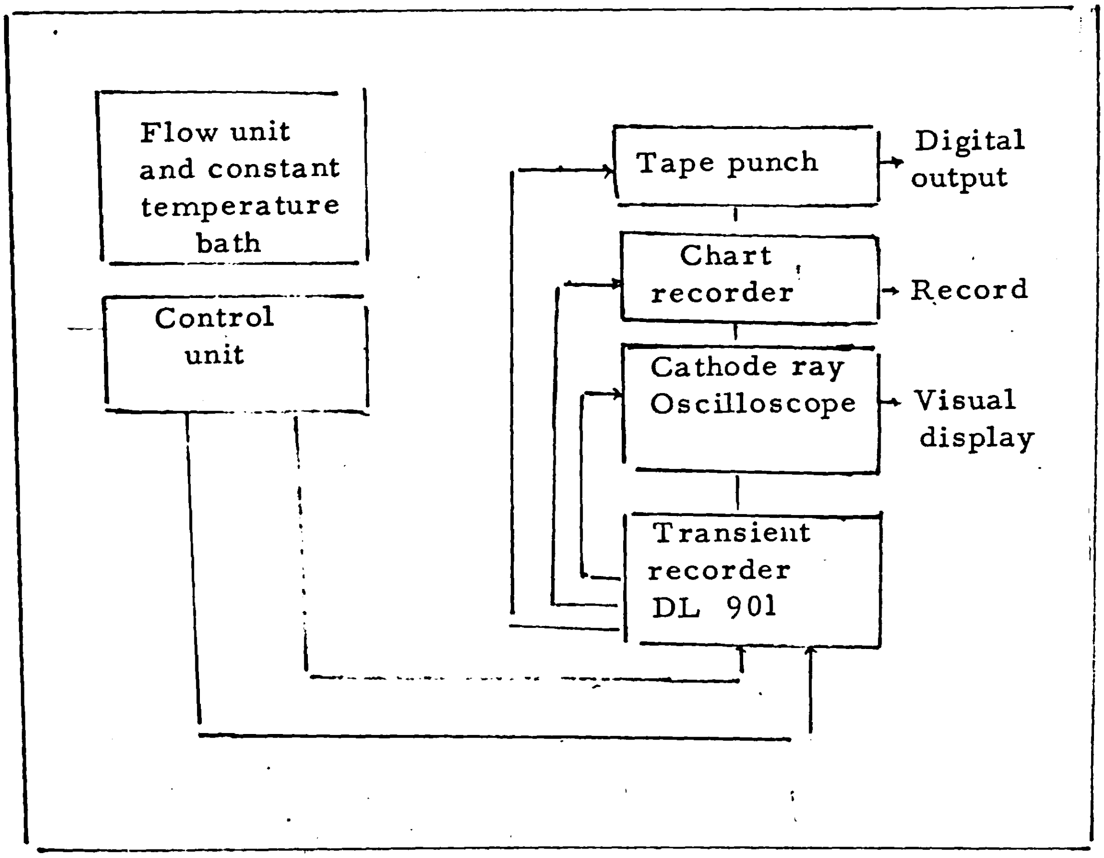


Fig. v

There are three main units from which the apparatus is constructed, i) A flow unit (Fig.vi), ii) an optical system, iii) an electronic unit. The reactants are withdrawn from reservoirs and held inside two syringes (2 cm^3), the plungers of which can be pushed simultaneously. Each syringe is connected to a coil of glass tubing filled with reactant and leading to the mixing-chamber, where the reaction starts. The mixture then flows past the observation point 3 and into a third syringe, the plunger of which is pushed back by the liquid pressure until it comes against a stop. When the flow is thus stopped suddenly the solution at the observation point is of freshly mixed reactants. The reaction now proceeds and its progress can be followed by measuring the absorption of the beam of light by reactants or products. The intensity of light transmitted by the sample at the observation point is displayed on an oscilloscope as a function of time following the stopping of the flow. The light source emits the monitoring beam which passes through a filter monochromator. The intensity of transmitted light is measured by a photomultiplier. In this apparatus the signal from the stopped flow instrument is passed to a transient recorder (memory) which stores the transmittance values in digital form (1024 values during the scan time specified). This information can be fed out on to a chart recorder or on to punched tape for computing process when it appears in binary form. The kinetic trace also appears on an oscilloscope screen. The stored information about a specific kinetic run is cleared automatically as more samples are fed into the transient recorder. When the trigger pulse is applied, the input into the memory is stopped at the end of the sweep so that the information of the one sweep following the trigger is retained.

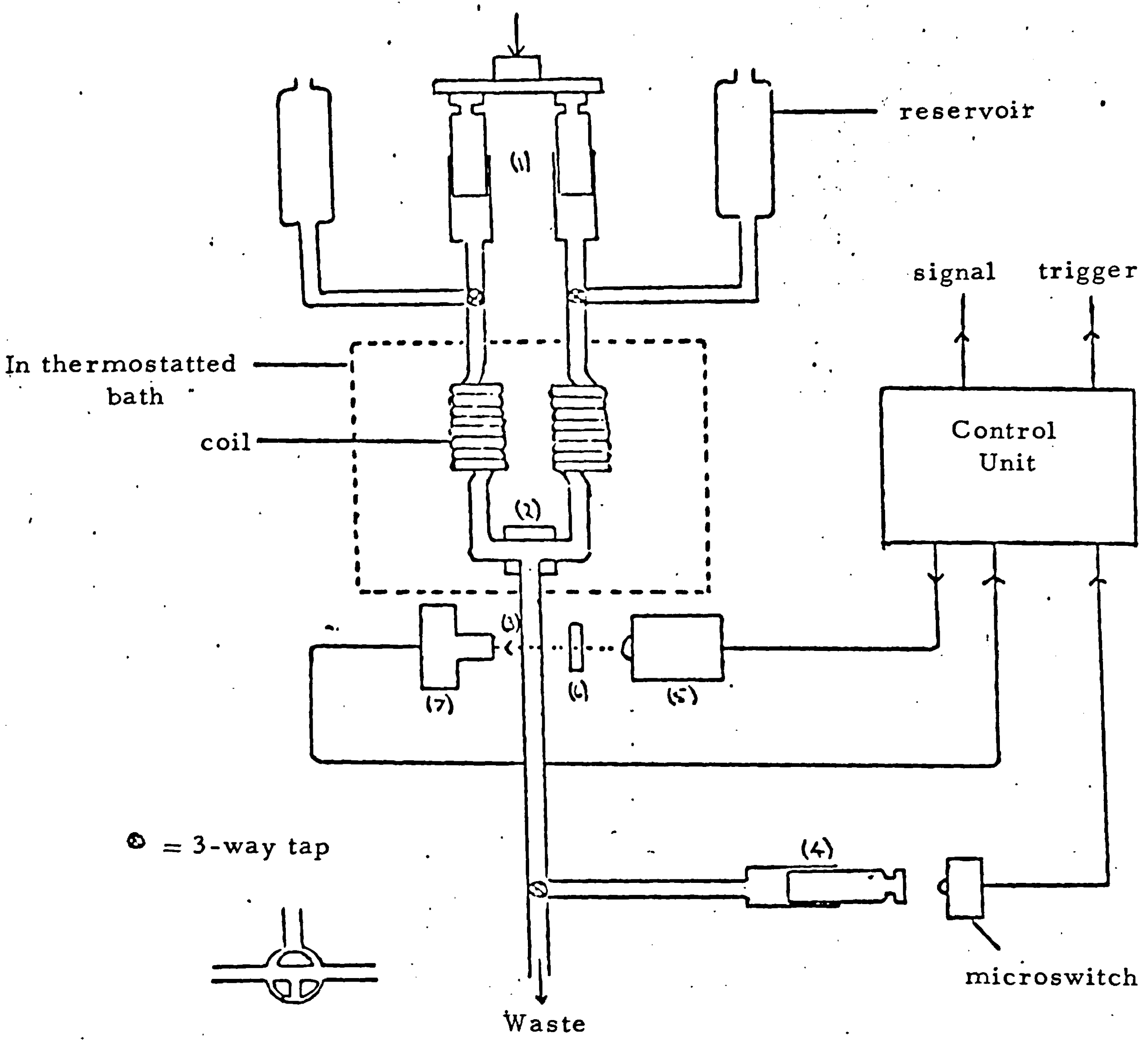

reservoir
(1)
signal
trigger
In thermostatted bath
coil
Control Unit
(2)
(3)
(7)
(6)
(5)
(4)
⊗ = 3-way tap
microswitch
Waste

Fig. VI

The stopped-flow apparatus has been designed to fulfil the requirements of accurate kinetic investigation. It has many advantages in particular:
a.) Ease and speed of operation, the result can be inspected at once on an oscilloscope screen. b.) Sensitive detection by means of a photomultiplier, high sensitivity is secured by the use of high light intensity. A change in concentration of 1% can be followed with an error of ± 1% and rate constants determined with ± 1 or 2% errors. c.) The mixing chamber, observation tube and the glass coils are all immersed in a thermostat bath in order to achieve good temperature control. Moreover the whole system is resistant to all normal reagents and solvents.

The stopped-flow technique has found a wide range of applications, in following enzyme reactions, reactions of haemoglobin and myoglobin, electron-transfer and ligand-substitution in inorganic chemistry, proton-transfer and sigma-complex formation in organic systems and reactions of organometallic compounds.

c. Job's Method.

Solutions of the cobalt compound and triphenylphosphine in Analar chloroform were prepared each having the concentration 5×10^{-3} mol. dm^{-3}. A series of solutions with different molar fractions was prepared by mixing appropriate volumes of the reactants. In each case the absorbance was recorded. These values were plotted out against the mole fractions from which the stoicheiometry of the complex formed could be determined. Precautions had to be taken to exclude air; this could be achieved by the use of a glove bag. This was first evacuated, then flushed with nitrogen. The process being repeated at least three times. The solvent was degassed first, flushed with nitrogen and kept in the glove bag.

d. Generation of methoxide ion.

Methoxide ion was generated from a buffer mixture of perchloric acid and triethylamine in methanol. The acid concentration (0.05 mol.dm^{-3}) was measured exactly by standardisation with borax. The triethylamine concentration used was 0.5 mol.dm^{-3}. Different ratios of acid-amine mixture were chosen to obtain several concentrations of the methoxide.

From literature value used by Ritchie

$$-\log \frac{[Et_3N]\,[MeOH_2^+]}{[Et_3NH^+]} = 10.88$$

$$-\log\,[MeOH_2] = 10.88 - \log \frac{[Et_3NH^+]}{[Et_3N]}$$

$$-\log\,[OMeH_2^+]\,[OMe^-] = 16.73 \qquad \text{literature value}$$

$$-\log\,[OMe^-] = 16.73 - 10.88 + \log \frac{[Et_3NH^+]}{[Et_3N]}$$

$$= 5.82 + \log \frac{[Et_3NH^+]}{[Et_3N]}$$

e. Kinetic procedure:

The stopped-flow apparatus described on page 141 was used for the kinetic study of the reaction between the cobalt compound and methoxide.

For each series of kinetic runs, fresh solutions of the reactants in methanol were prepared. Both solutions of the organometallic compound and the required methoxide buffer were transferred to the reservoirs of the flow unit of the stopped-flow apparatus; flushed through the thermostatted coils and allowed to equilibrate at constant temperature for 10 - 15 minutes. Air bubbles should be avoided because this causes unsatisfactory traces. The light source was a tungsten projector bulb. Monochromatic light of the required wavelength was selected using a filter monochromator. A UV/visible spectrophotometer of the type Pye-Unicam SP1800 was used to determine the suitable wavelength for observation. The plungers of the reservoir syringes were operated manually. As the reactants entered the mixing cell, the stopping syringe was forced against a micro-switch which triggered the recording device. The change in transmitted light intensity was monitored against time. The trace being observed on the oscilloscope could be stored in the transient recorder, then plotted by means of a chart recorder and stored on punched tape; this procedure was repeated at least five times for each concentration of methoxide.

Before any kinetic run it is necessary to convert the transmitted light intensity into optical density, this was possible by determining two values "I"$_{\text{black}}$ and "I"$_{\text{blank}}$. "I"$_{\text{black}}$ is the value of the infinite absorbance, was taken without any light being transmitted.

"I"$_{\text{blank}}$ is measured by running a colourless solution into the cell. (Fig. vii)

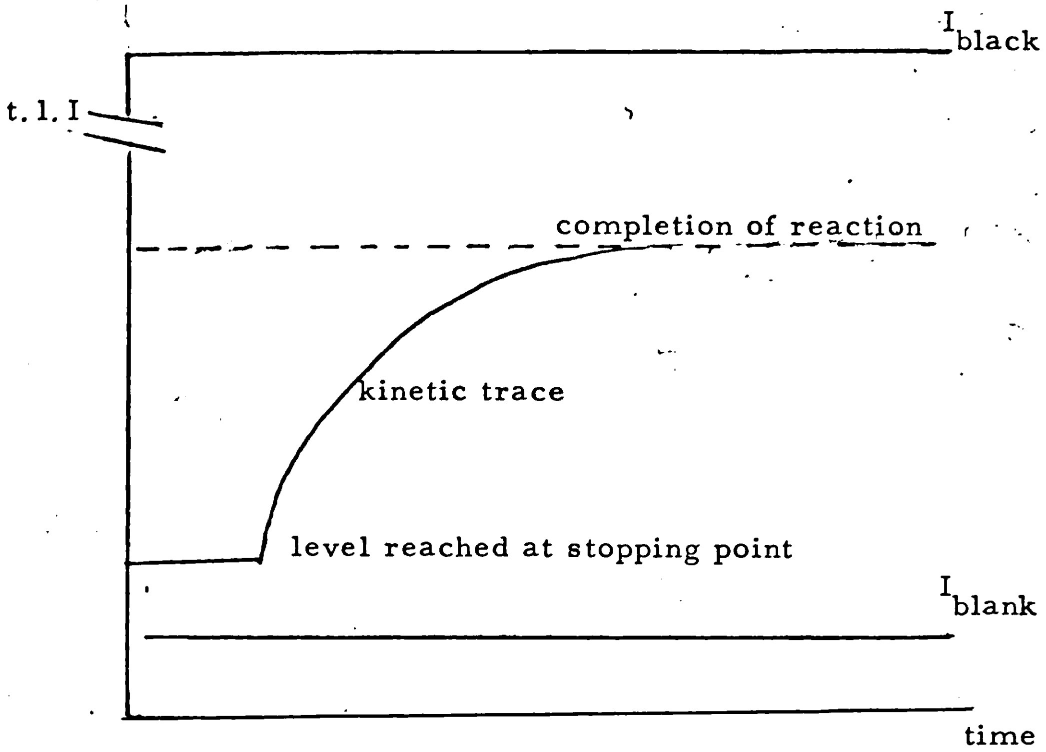


Fig. vii

The methoxide solution was used as the blank.

These values were then fed into a suitable computer program (Appendix p. 182) and processed using the ~~relating~~ equation

$$\text{Optical density} = \log \frac{I_o}{I} \quad \text{i.e.} \quad \frac{I_{black} - I_{blank}}{I_{black} - I_t}$$

The program was written to give the log optical density and rate constant values were calculated by the use of least mean squares analysis. Pseudo first order rate constants were obtained as the methoxide concentration was buffered. The order of the reaction with respect to methoxide was established by finding the rate constants at several concentrations of the methoxide ion.

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CHAPTER FIVE

KINETIC STUDY OF THE REACTION OF CYCLOHEPTATRIENYLTRICARBONYL CATIONS OF METALS IN GROUP (VI) WITH METHOXIDE ION

CHAPTER 5

Kinetic Study of the reaction of Cycloheptatrienyltricarbonyl Cations of metals in group (VI) with methoxide ion

Introduction

The study of nucleophilic attack on coordinated tropylium cations has interested many workers in the field of organometallic chemistry both in its synthetic and kinetic aspects. Specifically we will discuss work done on nucleophilic attack on the tricarbonyl tropylium cations of metals in group VI.

In 1961, Munro and Pauson[1] studied the reaction of tricarbonyl tropylium chromium salts with anions. They considered two possible reaction pathways:

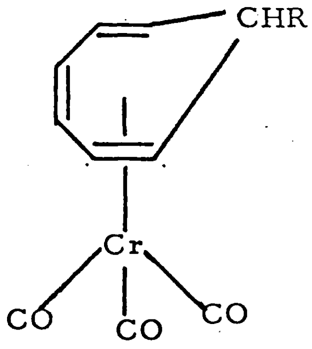
(i) $[Cr(C_7H_7)(CO)_3]^+ + X^- \longrightarrow [Cr(XC_7H_7)(CO)_3]$ or

(ii) $[Cr(C_7H_7)(CO)_3]^+ + X^- \longrightarrow [Cr(C_7H_7)(CO)_2X] + CO$

The first reaction is more likely to happen because it is thought that the positive charge is more concentrated on the seven-membered ring, and hence the anions can add to this ring as they do to free tropylium ions. The second possibility assumes that sufficient of the charge is located on the metal atom for anionic attack at this point and is also based on the analogy with the behaviour of the tricarbonylbenzene-manganese cation with cyanide.[2]

$$[Mn(C_6H_6)(CO)_3]^+ + CN^- \longrightarrow [Mn(C_6H_6)(CO)_2CN] + CO$$

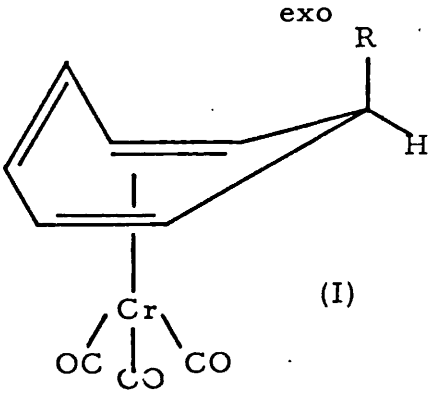
Pauson's work considered the first possibility as the normal reaction which led to products such as



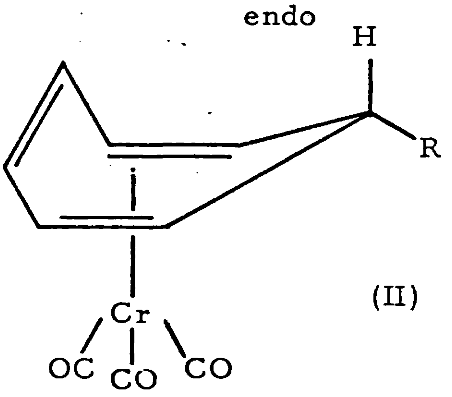
[where R = H, OMe, SH, $C_5H_5CMe_3$, $CMe(CO_2Et)_2$]

R can be on the same side of the ring as the metal tricarbonyl group (the endo-isomer) or on the opposite side, (the exo-isomer). It was noticed that the tricarbonyltropyliummolybdenum ion is much less stable than the chromium salts under the reaction conditions employed.

In a later piece of work, Pauson et al[3] reported the reaction of tricarbonyltropyliumchromium salts with various nucleophiles to be of the normal type and that there are two stereoisomeric substituted tricarbonylcycloheptatrienechromium species, the exo-isomer and the endo-isomer. Related additions to cationic complexes have been studied in the tricarbonylbenzenemanganese[4], the benzenecyclopentadienyliron,[5] and the cobalticenium series.[6] The addition of anions occurs from the less sterically hindered exo-side as was shown by X-ray crystallographic study.[7]



(I)

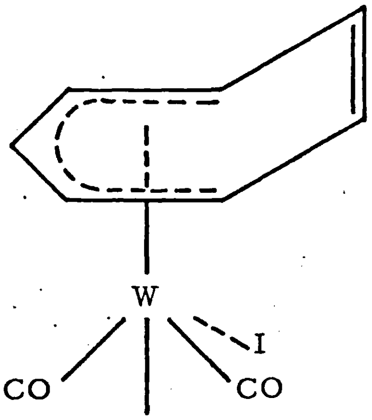


(II)

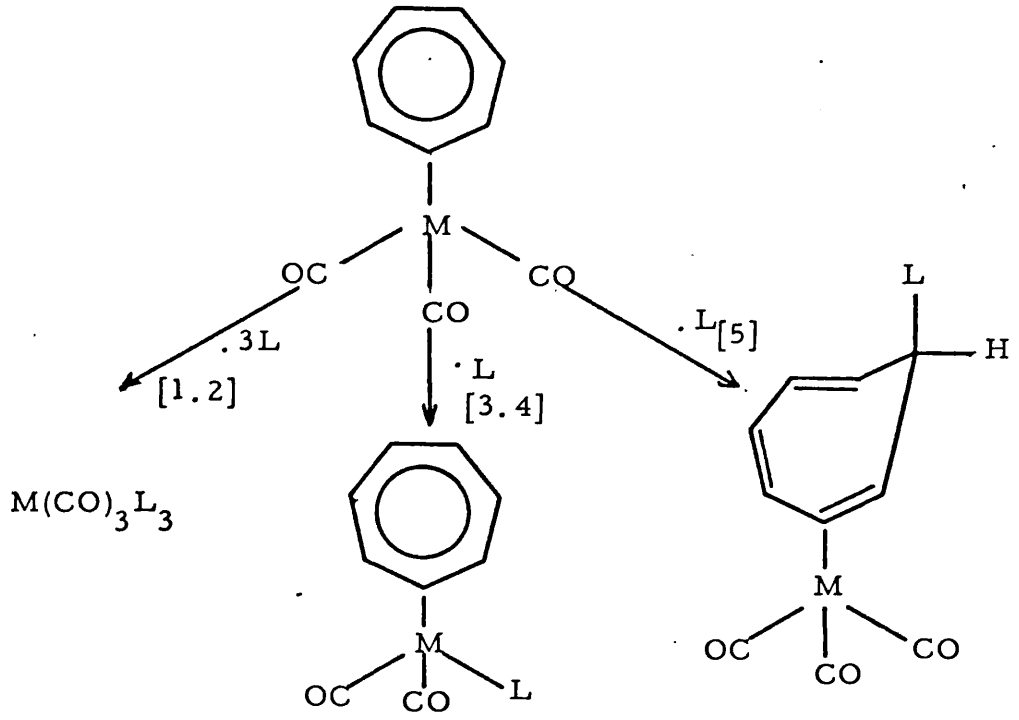
All other related additions mentioned follow the same stereochemical course and bonding of anions to the metal to form an intermediate is apparently excluded here in such reactions.

In a few other cases[8], for instance, when alkoxycycloheptatrienes react with trisacetonitriletricarbonylchromium the corresponding 7-endo isomer was obtained. The n.m.r. spectra play an important role in distinguishing the exo from the endo-isomer. The difference is associated with the H-7 in the endo isomers and also in the metal-free compounds. This hydrogen is "axial" and is shielded by the triene system, its resonance occurs at δ values δ 1 - 1.5 to higher field than that of the equatorial H-7 of the exo-isomer. The appearance of peaks due to H-1, 6 at δ 6 is the most characteristic feature of the exo-series.

An example of a reaction which eventually leads to nucleophilic substitution of a carbonyl ligand is attack by iodide ion. The compound $[Mo(C_7H_7)(CO)_2I]$, was described in a thesis by Bertelli[9], and $[W(C_7H_7)(CO)_2I]$ was first prepared by King.[10] The procedure followed was by reacting the salt $[W(C_7H_7)(CO)_3][BF_4]$ with sodium iodide in acetone. A brown solution is formed which becomes green-black after a few hours at room temperature. From this solution the $[W(C_7H_7)(CO)_2I]$ was isolated completely analogous to the known molybdenum compound $[Mo(C_7H_7)(CO)_2I]$. The initial observation of a transient dark brown solution in the reaction between iodide and $[W(C_7H_7)(CO)_3]BF_4$ suggests appreciable stability of an intermediate tricarbonyl derivative, possibly which eventually loses CO to give $[W(C_7H_7)(CO)_2I]$. Some kinetic studies of these reactions are mentioned below.



The reaction of tertiary phosphines with tropylium tricarbonyl cations has been investigated by many research workers since 1959[11-15] Three routes by which the reaction can proceed have been established as follows:



The course of the reaction is dependent on the amount of ligand L and also on its base strength. It was found that if the ligand was used in excess (L = PPh$_3$) the product is [M(CO)$_3$(PPh$_3$)$_3$] but if equal amounts of complex and ligand were used a different product [M(C$_7$H$_7$)(CO)$_2$PPh$_3$] was isolated.[14]

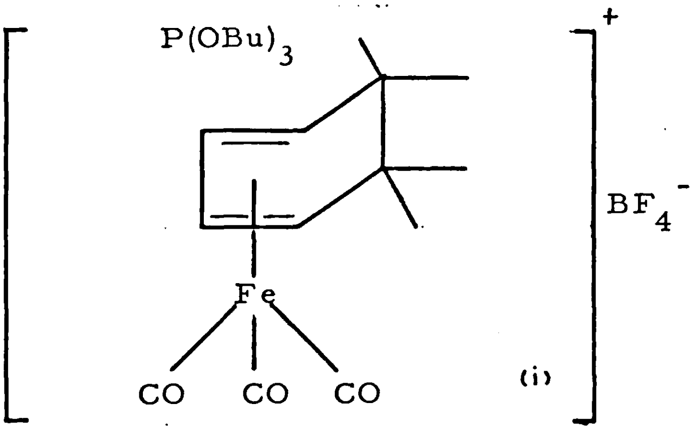
The mechanism proposed for both reaction paths 1 and 2 is through an intermediate [M(η^5-C$_7$H$_7$)(CO)$_3$L]$^+$ [12, 13] which then reacts either by displacement of a CO group to give [M(C$_7$H$_7$)(CO)$_2$L]$^+$ or by ring displacement giving ultimately fac-[M(CO)$_3$L$_3$]. Hackett and Jaouen observed path 3 in the case of the reaction of [Cr(C$_7$H$_7$)(CO)$_3$]$^+$ with alkylphosphines.[15] Under similar conditions the molybdenum compound, however, afforded [Mo(C$_7$H$_7$)(CO)$_2$L], apparently by path 2. The authors suggested that the tropylium ring in the chromium cation is more electrophilic than in its molybdenum analogue. They suggested that the higher carbonyl stretching frequencies of the molybdenum compared with the chromium compound may indicate less metal to ring back bonding in the latter. Thus more charge is drained out of the tropylium ring in the chromium compound than in its molybdenum analogue with the result that the incoming nucleophile is directed towards the ring rather than to the metal.

Salzer, however, found that tri-iso-propylphosphine adds initially to the ring in $[Mo(C_7H_7)(CO)_3]^+$, and was able to isolate the phosphonium salt (path 3) by working at -40°C. At room temperature this adduct decomposed to the substituted complex $[Mo(C_7H_7)(CO)_2PPr^i_3]$ [16].

John, Kane-Maguire and Sweigart[17] studied in 1976 the kinetics of the reaction of tri-n-butylphosphine with $[M(C_7H_7)(CO)_3]BF_4$ (M = Cr, Mo, W). The reaction was investigated in acetone by stopped-flow techniques. The reaction followed the rate law Rate = k [complex][PBu_3], significantly, the rates for this reaction depend very little on the nature of the metal. A factor of only two separates the fastest Cr complex from the Mo and W compounds which have nearly the same k values. These results agree with the authors' contention that the tropylium rings in $[M(C_7H_7)(CO)_3]^+$, (M = Cr, Mo, W) have similar electrophilicities. Furthermore, the close similarity in rates supports direct addition by tri-n-butylphosphine to the tropylium ligand in each case. An alternative mechanism involving initial rate-determining attack by the phosphine ligand at the metal followed by rearrangement to the ring would be expected to lead to large rate differences. For example, the relative rates of ring displacement by trimethylphosphite from $[M(C_7H_8)(CO)_3]$ are $Mo > W > Cr = 2200: 350: 1$.[18, 19]

The rates of attack of tributylphosphine on the isoelectronic cations $[Fe(C_6H_7)(CO)_3]^+$ and $[Mn(C_6H_6)(CO)_3]^+$ were compared giving the reactivity sequence $[Fe(C_6H_7)(CO)_3]^+ > [Cr(C_7H_7)(CO)_3]^+ > [Mn(C_6H_6)(CO)_3]^+$, and the quantitative electrophilicity order[20] as 160:60:1

The reactions of tri-n-butyl phosphite with $[Fe(C_6H_7)(CO)_3]^+BF_4^-$, $[Fe(C_6H_7)OMe(CO)_3]^+BF_4^-$ and $[Cr(C_7H_7)(CO)_3]^+BF_4^-$ were reported by John and Kane-Maguire in 1976.[20] From the first reaction an adduct was isolated having the structure (i) which was confirmed by chemical analysis and by the I R spectrum in acetone, which closely resembled that of the analogous tri-n-butylphosphine



(i)

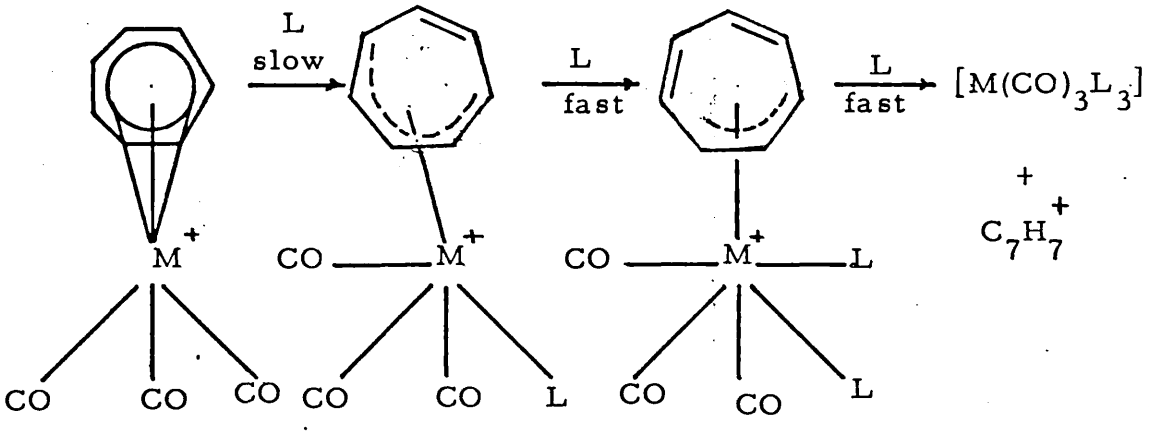
adducts. Formulation as the BF_4^- salt was shown by the presence of a strong band at 1060 cm^{-1}. Also the ^1H nmr spectrum in acetone for the adduct was studied. The presence of multiplets centred at (δca 4.21, 5.30 and 6.17 ppm) is also consistent with the adduct structure. Similar compounds were obtained not only with the iron triad, but also with the chromium compound. Preliminary kinetic measurements indicate that $P(OBu)_3$ adds to the compounds 8000 times slower than $P(Bu)_3$.

A kinetic study has been reported by Al-Kathumi and Kane-Maguire of the reaction of acetonitrile as a nucleophile and tropylium cations of Cr, Mo and W.[21] The reactions show second order kinetics interpreted in terms of SN2 displacement of $C_7H_7^+$ from the complex by MeCN ligands. The reactions were followed by infrared spectrometry by following the appearance of strong carbonyl group bands at 1920 and 1800 cm^{-1}. The solvent was deoxygenated first. Spectral changes during the reaction were consistent with the following overall reaction

$[M(C_7H_7)(CO)_3]BF_4 + 3MeCN \longrightarrow fac.[M(MeCN)_3(CO)_3] + C_7H_7BF_4$

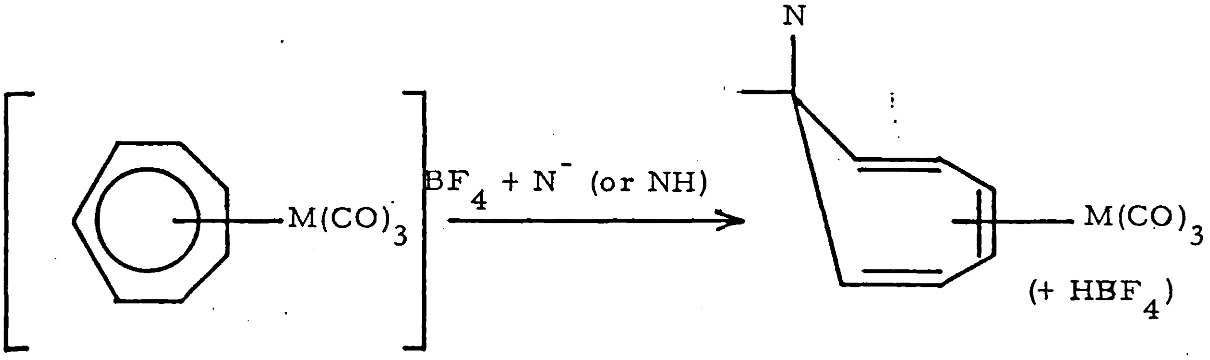
$\Delta H^{\ddagger}$ values for this reaction were obtained by measurement over a range of temperatures from 50 to 70°C for M = Cr, 25 - 45°C for M = Mo compound and from 27 to 50°C for M = W. The data showed that the ease of displacement of tropylium ring decreases in the order $Mo^+ > W^+ > Cr^+$ (850 : 280 : 1).

The second order rate law observed is consistent with a rate-determining displacement of $C_7H_7^+$ by MeCN, followed by rapid addition of another two MeCN ligands. However as has been pointed out for similar reactions of $[Mo(arene)(CO)_3]$ complexes with phosphines[22] it seems doubtful whether a two-electron donor (e.g. MeCN) could replace unaided a seven-electron donor such as $C_7H_7^+$. So, a mechanism was favoured in which the bonding of the C_7H_7 group to the metal alters from involving all seven carbon atoms in the complex $[M(C_7H_7)(CO)_3]BF_4$ to essentially five and finally only three carbon atoms as MeCN ligands (L) are progressively added to the metal. An alternative mechanism, involving a pre-equilibrium (K) association between the complex $[M(C_7H_7)(CO)_3]BF_4$ and MeCN to form a reactive species which then loses $C_7H_7^+$ by unimolecular dissociation (k), can be discounted since the rate law for such a mechanism $k_{obs} = kK[MeCN] / (1 + K[MeCN])$ requires that the reaction will become first order at high [MeCN].



The reaction between iodide and $[M(C_7H_7)(CO)_3]^+$, M = Mo, W) has been investigated by Powell[23] and his coworkers. The results showed that the reaction proceeded first through an intermediate possibly involving a metal-iodide bond but which may be an ion pair, followed by transfer of the nucleophile to the aromatic ring. This intermediate then decomposed in a slow step to give the final product $[M(C_7H_7)(CO)_2I]$. According to King's postulate, the intermediate in this reaction was formed by attack on the metal through an η^5-cycloheptatrienyltricarbonyl derivative giving the final product by loss of one carbonyl group. The mechanism suggested by Powell et al about the production of the intermediate was similar to that declared by Brown[24] and others for the reaction between $[Fe(C_7H_9)(CO)_3]^+$ and nucleophiles such as (N_3^-, OEt^-, Bu_3P).

Kinetic results on the additions of acetylacetone and methoxide ion to $[M(C_7H_7)(CO)_3]^+$, (M = Cr, Mo, W) have been reported. In contrast to Hackett's suggestion,[15] the authors[25] here showed that the chromium and molybdenum species have very similar electrophilicities . The study also supports a mechanism involving direct nucleophilic attack at the tropylium rings as in



5.2 Results and Discussion

The reaction of the cations $[M(C_7H_7)(CO)_3]^+$, (M = Cr, Mo, W) with methoxide ion in methanol at 26 ± 0.1 °C was studied kinetically by the use of a stopped flow spectrophotometer. Preliminary investigations showed that the reaction would be over in a fraction of a second if the methoxide concentration was about 1 mol dm^{-3}. Very low concentrations of methoxide have to be generated from a buffer mixture. By using triethylamine (0.5M)/perchloric acid (0.05M) mixture a range of methoxide ion concentration between 3.8×10^{-6} M and 21.9×10^{-6} M was obtained. Because the methoxide ion concentration remains constant (buffered), the kinetic equation was pseudo first order, Rate = k_{obs}[Complex].

Using a scan time from 0.5 - 50 sec. depending on the buffer ratio used, satisfactory traces could be shown on the oscilloscope screen. The kinetic runs were repeated six times for each concentration of methoxide. The runs were recorded on paper tapes and these were fed into a computer for calculation of the rates.

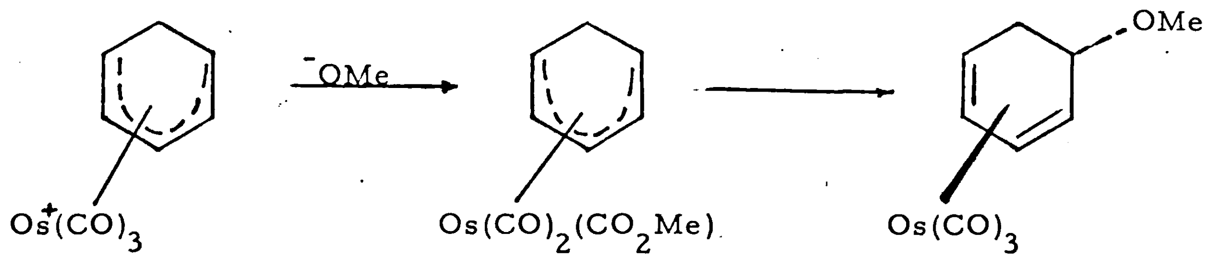
Reaction of $[M(C_7H_7)(CO)_3]^+BF_4^-$ with methoxide at 26 ± 0.1 °C :

The reaction was carried out at the selected wavelength. This was checked first by using the ultraviolet/visible spectrometer SP1800. The results showed that the reaction proceeded in two steps. The first one which is the fast step happens in a range of scan 0.2-0.5 sec. This may suggest very quick attack by the nucleophile OMe^- either at the metal or at a carbonyl ligand and subsequent transfer to the ring. The slow reaction occurred in the range of scan 20.0 - 50.0 sec., and this represents the second step of the reaction. One possible explanation for our observations is the initial formation of a carbomethoxy intermediate by attack of methoxide at a carbonyl group, (fast reaction), followed by transfer of the methoxy group to the ring (slow reaction). At present we cannot distinguish between this mechanism and initial attack of methoxide ion at the metal. Although Powell et al[23] have suggested that iodide may first add rapidly to the metal centre in $[M(\eta^7\text{-}(C_7H_7)(CO)_3]^+$ to give $[M(\eta^5\text{-}C_7H_7)(CO)_3I]$,[23] the formation of an aryl iodide $[M(\eta^5\text{-}C_7H_7)(CO)_2(COI)]$ is another possibility, which is supported by infrared evidence in the case of iodide attack on $[Fe(C_6H_7)(CO_3]^+$.[32]

Attack of alkoxide ion on coordinated carbonyl groups to give stable carbomethoxy complexes is well established for the manganese complexes.[26-28]

$$[Mn(C_5H_5)(CO)(NO)(PPh_3)]^+ + OR^- \longrightarrow [Mn(C_5H_5)(COOR)(NO)(PPh_3].$$

In 1977 Lewis et al [29] showed that the reaction of the cyclohexadienyltricarbonylosmium cation with methoxide ion first gives the carbomethoxy complex $[Os(C_6H_7)(CO)_2(CO_2Me)]$ which on heating undergoes rearrangement to give a ring substituted product as follows:



The intermediate product was identified by spectroscopic properties and elemental analysis. The presence of a band at 1635 cm^{-1} in the infrared spectrum of this complex suggested initial attack at a coordinated carbonyl group. This result was consistent with what was found for the ruthenium analogue in previous work by Lewis and coworkers. They mentioned in their study of the reaction of the salts $[Ru(C_6H_7)(CO)_3]BF_4$ and $[Ru(C_8H_{11})(CO)_3]BF_4$[30] with methoxide ion that the initial product is an ester $[Ru(C_6H_7)(CO)_2(CO_2Me)]$ or $[Ru(C_8H_{11})(CO)_2(CO_2Me)]$. This indicated that the nucleophilic addition occurs in the first instance at a coordinated carbonyl group followed by rearrangement to give the substituted complex.

The pseudo first order rate constants for the fast reactions of the molybdenum and tungsten complexes are listed in tables 2 and 4 and are also plotted against methoxide concentration in figures 1 and 2.

The intercept in the fast reaction plots could be due to the possibility of the presence of a back reaction. The following equation might be applicable in this case:

$$M^+ + OMe^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Intermediate}$$

$$\text{Since } k_{obs} = k_1[OMe^-] + k_{-1} \quad {}^{31}$$

So, by plotting k_{obs} vs the methoxide concentrations, the slope represents k_1, and k_{-1} is represented by the intercept. This sort of interpretation was given by Kane-Maguire[32] for similar reactions of R_3P compounds.

From the fast reaction plots, the forward reaction rate constants k_1 for both the molybdenum and tungsten compounds were calculated and found to be 3.36×10^6 and $3.50 \times 10^6/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ respectively. The intercepts which give the k_{-1} values were $16.5\ \text{s}^{-1}$(Mo) and $10.0\ \text{s}^{-1}$(W).

In the case of the chromium compound, however, the first step was not clearly observed under the same conditions. The slow step of the reactions was followed in all three complexes, of chromium, molybdenum and tungsten. A proposed mechanism for the reaction is as follows:.

$$M^+ + OMe^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{intermediate (I)} \qquad \text{fast step}$$

$$I \xrightarrow{k_2} \text{products} \quad (C) \qquad \text{slow step}$$

In this mechanism there is a fast formed intermediate. Since this intermediate does not reach a stable state, the fast equilibrium approximation is applied here. The ratio k_1/k_{-1} can be considered as an equilibrium constant K.

$$K = \frac{[I]}{[M^+][OMe^-]}$$

$$[M]^+_{init} = [M^+] + [I]$$

$$[M^+]_{init} = [M^+] + K\,[M^+]\,[OMe^+]$$

therefore

$$[M^+] = \frac{[M^+]_{init}}{1 + K[OMe^-]}$$

$$\frac{d[c]}{dt} = \frac{-d[I]}{dt}$$

$$\frac{d[c]}{dt} = k_2[I]$$

$$= k_2K[M^+][OMe^-]$$

$$= \frac{k_2K[M^+]_{init}[OMe^-]}{1 + K[Ome^-]}$$

$$\text{Rate} = k_{obs}[M^+]_{init}$$

therefore

$$k_{obs} = \frac{K\,k_2[OMe^-]}{1 + K\,[OMe^-]} \qquad (1)$$

From (1) it can be seen that the relationship between k_{obs} and [OMe$^-$] will give a curve as observed in our reaction, (Fig. 3,5). At low concentrations of OMe$^-$ the term K[OMe] can be neglected and equation (1) can be expressed as: $k_{obs} = K k_2[OMe^-]$, but at high concentrations of methoxide the term K[OMe$^-$] will be significant and the expression in this case becomes

$$k_{obs} = k_2$$

i.e., the plot tends to a limiting value of k_2 which was confirmed by using a high concentration of sodium methoxide solution (10^{-2} mol dm^{-3}).

Taking reciprocals in equation (1) gives

$$\frac{1}{k_{obs}} = \frac{1 + K[OMe^-]}{K k_2 [OMe^-]}$$

$$\frac{1}{k_{obs}} = \frac{1}{K k_2 [OMe^-]} + \frac{1}{k_2} \qquad (2)$$

i.e., if the relationship between $\frac{1}{k_{obs}}$ and $\frac{1}{[OMe^-]}$ is plotted out a straight line should be obtained of slope $1/Kk_2$ and intercept $1/k_2$.

According to the preceding mechanism, from the slow reaction plots, we were able to calculate the values of k_2 for the three complexes (Table 6). It is noticed that the rate of the decay of the intermediate decreases in the order Cr$>$Mo$>$W. Values of the equilibrium constant K, also were calculated and found to be very large for all the complexes.

Angelici and Blacik[33] investigated the reaction between the $[Mn(arene)(CO)_3]^+$ complexes with primary alkylamines. They found that the reactions proceed as follows:

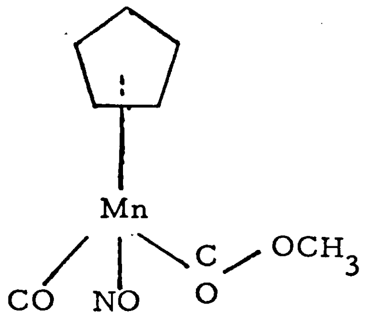
$$[Mn(arene)(CO)_3]^+ + 2RNH_2 \rightleftharpoons [Mn(arene)(CO)_2(CONH\,R)] + RNH_3^+$$

where arene = toluene, p-xylene, mesitylene and durene. Other carboxamido complexes of Fe, Ru, Mn, Re, Pd, Pt, Mo and W have been prepared. Only in a few cases can the carboxamido complex be isolated. These workers tried to correlate the tendency of the carbonyl groups to react with amines to form carboxamido complexes with the carbonyl stretching force constants. The electron density on the carbonyl carbon is reflected by its CO stretching force constant. It appears possible to predict on the basis of force constants which carbonyl group will be more reactive towards nucleophilic additions.

Angelici[34] in his review of carbamoyl and alkoxycarbonyl complexes of transition-metals, gave a classification of the complexes in their reactions with amines. The carbonyl complexes are divided into three groups which reflect their tendency to form carboxamido complexes. Those from which a carbamoyl complex was isolated and there was no evidence for a reverse reaction, those which were not completely converted to the carbamoyl derivative, and those for which there was no evidence of reaction even when the carbonyl complex was dissolved in pure alkylamine. It appears that CO ligands with force constants greater than 1.7×10^{-4} Nm^{-1} readily form carbamoyl complexes, those with force constants between 1.6×10^{-4} and 1.7×10^{-4} Nm^{-1} give reversible equilibrium mixtures, and those having force constants below $1.6 \times 10^{-4} Nm^{-1}$ do not form carbamoyl complexes. In terms of CO stretching frequencies it appears that carbonyl complexes with CO stretching absorptions below 2000 cm^{-1} do not yield carbamoyl complexes.

A similar study for reaction of transition-metal carbonyls and organolithium compounds was carried out by Darensbourg and Darensbourg.[35] They reported that some metal carbonyls such as $[Re(CO)_6]^+$ undergo nucleophilic attack on a carbonyl carbon atom by H_2O or OH^- to give intermediates of the type $[Re(CO)_5(COH_2)]^+$ or $Re(CO)_5COOH$ respectively. Also reactions of $[M(CO)_4L_2]^+$ complexes, M = Mn, Re, L = PPh_3 with alkoxides (OR^-, R=CH_3, C_2H_5, C_5H_{11}, $CH_2C_6H_5$) give products of the type $[M(CO)_3(L_2)COOR]$.[36-38] The Darensbourgs concluded in their study that prediction of reactivity toward attacking nucleophiles at carbon is dependent on the CO force constants. The most reactive carbonyls have the largest CO force constants. Organolithium reagents LiR (R = CH_3 or C_6H_5) were the chosen attacking nucleophiles for a group of metal carbonyls. From their calculation of CO force constants for these carbonyl complexes, they indicated that reaction to occur between LiR and $MC \equiv O$ whenever $k > 1.53 \times 10^{-4} Nm^{-1}$.

King et al. investigated the reaction between $[Mn(C_5H_5)(CO)_2NO]^+PF_6^-$ and methanolic sodium methoxide. They found that the product is $[Mn(C_5H_5)(CO)(NO)(COOCH_3)]$, with spectroscopic properties favouring the following structure:



The manganese compound is significant in representing the first known compound of the type $[Mn(C_5H_5)(CO)(NO)(COOR)]$, $R=CH_3$.

The infrared spectrum of cyclopentadienyldicarbonylnitrosylmanganese hexafluorophosphate exhibits strong metal carbonyl bands[40] at 2125 and 2075 cm^{-1}.

We measured the infrared spectra of our three complexes $[M(C_7H_7)(CO)_3]^+BF_4^-$, M = Cr, Mo or W in the carbonyl stretching region as shown in Table 1 from which the force constants by the method of Cotton and Kraihanzel[41] were calculated.

TABLE 1

Infrared spectra and force constants of $[M(C_7H_7)(CO)_3]^+BF_4^-$ M = Cr, Mo or W in CH_3NO_2(CaF_2 cell)

Compound	CO(cm^{-1})	force constants (k) Nm^{-1}
$[Cr(C_7H_7)(CO)_3]^+BF_4^-$	2071, 2029	1.68×10^{-4}
$[Mo(C_7H_7)(CO)_3]^+BF_4^-$	2080, 2029	1.69×10^{-4}
$[W(C_7H_7)(CO)_3]^+BF_4^-$	2075, 2017	1.67×10^{-4}

The frequencies of the carbonyl stretching bands for our compounds are quite close to those of the manganese compound $[Mn(C_5H_5)(CO)_2(NO)]^+PF_6^-$. It is therefore reasonable to postulate that methoxide may initially attack a carbonyl group in our reaction to form a carbomethoxy intermediate.

The reaction between $[M(C_7H_7)(CO)_3]^+BF_4^-$ and methoxide can be represented as follows:

$$[M(C_7H_7)(CO)_3]^+ + OMe^- \overset{fast}{\rightleftharpoons} [M(C_7H_7)(CO)_2(COOCH_3)]$$

$$\xrightarrow[slow]{rearrange} [M(C_7H_7OMe)(CO_3)]$$

Since the structure of the compound $[Mn(C_5H_5)(CO)(NO)(COOCH_3)]$ was determined from its spectroscopic properties: thus the infrared spectrum exhibits a terminal metal band at 2023 cm^{-1}, a terminal metal nitrosyl band at 1786 cm^{-1}; and an ester carbonyl band at 1653 cm^{-1}. The proton n.m.r. spectrum for the same compound exhibits sharp singlet resonances at 5.1δ and 3.46δ of approximate relative intensities 5:3 which may be assigned to the -cyclopentadienyl and methyl protons, respectively. Similar spectroscopic studies carried out at low temperature might allow one to recognise the intermediate in this reaction.

TABLE 2

Values for k_{obs} and k_1 for the fast reaction between $[Mo(C_7H_7)(CO)_3]^+BF_4^-$ and OMe^- in methanol at 26.0°C

$[OMe^-]$ / mol dm^{-3}	k_{obs} / s^{-1}	k_1 / dm^3 mol^{-1} s^{-1}
3.8×10^{-6}	29.2	3.34×10^6
5.1×10^{-6}	36.0	3.82×10^6
7.3×10^{-6}	39.0	3.08×10^6
11.1×10^{-6}	56.4	3.59×10^6
16.7×10^{-6}	69.3	3.16×10^6
21.9×10^{-6}	86.6	3.20×10^6

TABLE 3

Values for $1/k_{obs}$ and $1/[OMe^-]$ for the slow reaction between $[Mo(C_7H_7)(CO)_3]^+BF_4^-$ and OMe^- in methanol at 26.0°C

OMe^-	k_{obs} / s^{-1}	$1/[OMe^-]$ / $dm^3 mol^{-1}$	$1/k_{obs}$ / s
3.8×10^{-6}	0.37	26.31×10^4	2.70
5.1	0.43	19.60	2.32
7.3	0.54	13.69	1.85
11.1	0.62	9.00	1.60
16.7	0.73	6.02	1.37
21.9	0.75	4.56	1.33

TABLE 4

Values of k_{obs} and k_1 for the fast reaction between $[W(C_7H_7)(CO)_3]^+BF_4^-$ and OMe^- in methanol at 26.0°C.

$[OMe^-]$ / mol dm^{-3}	k_{obs} / s^{-1}	k_1 / dm^3 mol^{-1} s^{-1}
3.8×10^{-6}	23.1	3.45×10^{6}
5.1×10^{-6}	27.7	3.47×10^{6}
7.3×10^{-6}	34.6	3.40×10^{6}
11.1×10^{-6}	50.5	3.64×10^{6}
16.6×10^{-6}	69.3	3.57×10^{6}

TABLE 5

Values of k_{obs} for the slow reaction between $[W(C_7H_7)(CO_3)]^+BF_4^-$ and OMe^- in methanol at 26.0°C

$[OMe^-]$ / mol dm^{-3}	k_{obs} / s^{-1}
3.8×10^{-6}	0.122
5.1×10^{-6}	0.123
7.3×10^{-6}	0.121
11.1×10^{-6}	0.123
16.6×10^{-6}	0.121
21.9×10^{-6}	0.122

TABLE 6

Values of k_1, k_{-1} and k_2 for the reaction between $[M(C_7H_7)(CO)_3]^+BF_4^-$, $M = Cr^2$, Mo, W and OMe^- in methnal at 26.0°C.

Metal	k_1 /dm^3 mol^{-1} s^{-1}	k_{-1} / mol dm^{-3} s	k_1/k_{-1}	k_2 / s^{-1}
Cr	*	*	1.76×10^5	4.73
Mo	3.3×10^6	16.5	2.04×10^5	0.76
W	3.5×10^6	10.0	3.50×10^5	0.12

* Fast reaction not observed under the chosen conditions.

Fig 1 Plot of k_{obs} v. methoxide ion concentration for the fast reaction between $[Mo(C_7H_7)(CO)_3]^+BF_4^-$ and OMe^- in methanol at 26.0°C.

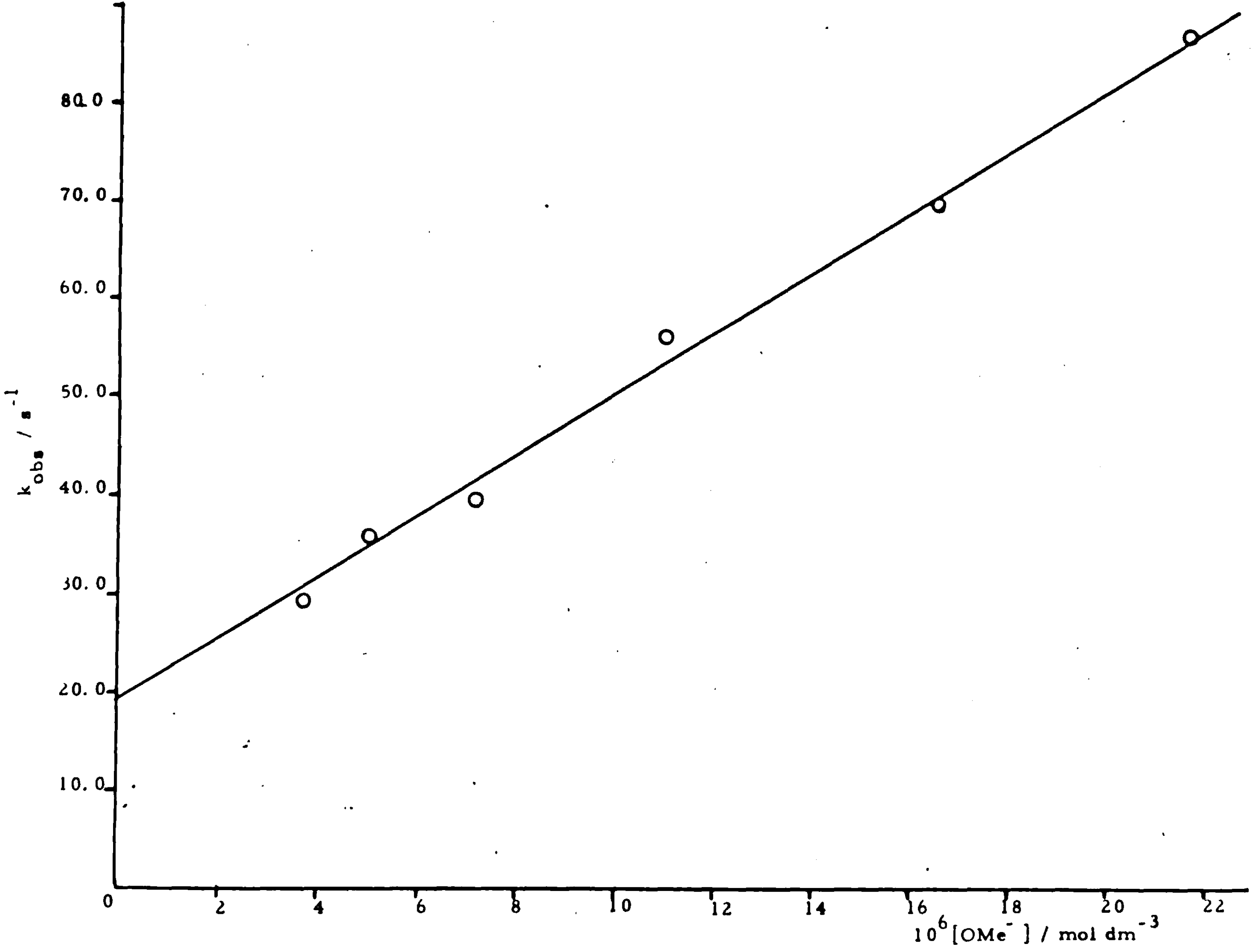


Fig 2 Plot of k_{obs} v. methoxide ion concentration for the fast reaction between $[W(C_7H_7)(CO)_3]^+BF_4^-$ and OMe^- in methanol at 26.0°C.

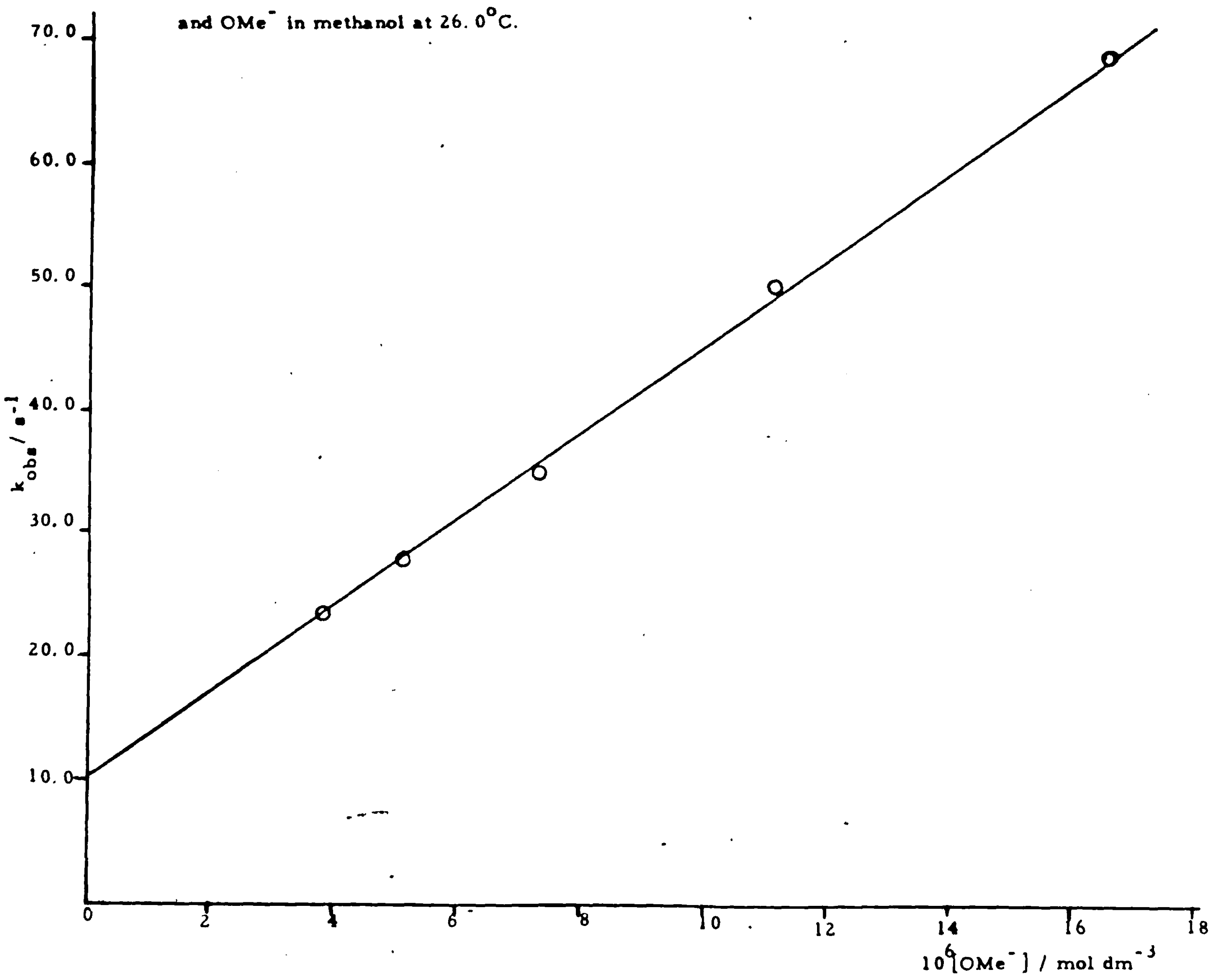


Fig 3 Plot of k_{obs} v. methoxide ion concentration for the slow reaction between $[Mo(C_7H_7)(CO)_3]^+BF_4^-$ and OMe^- in methanol at 26.0°C.

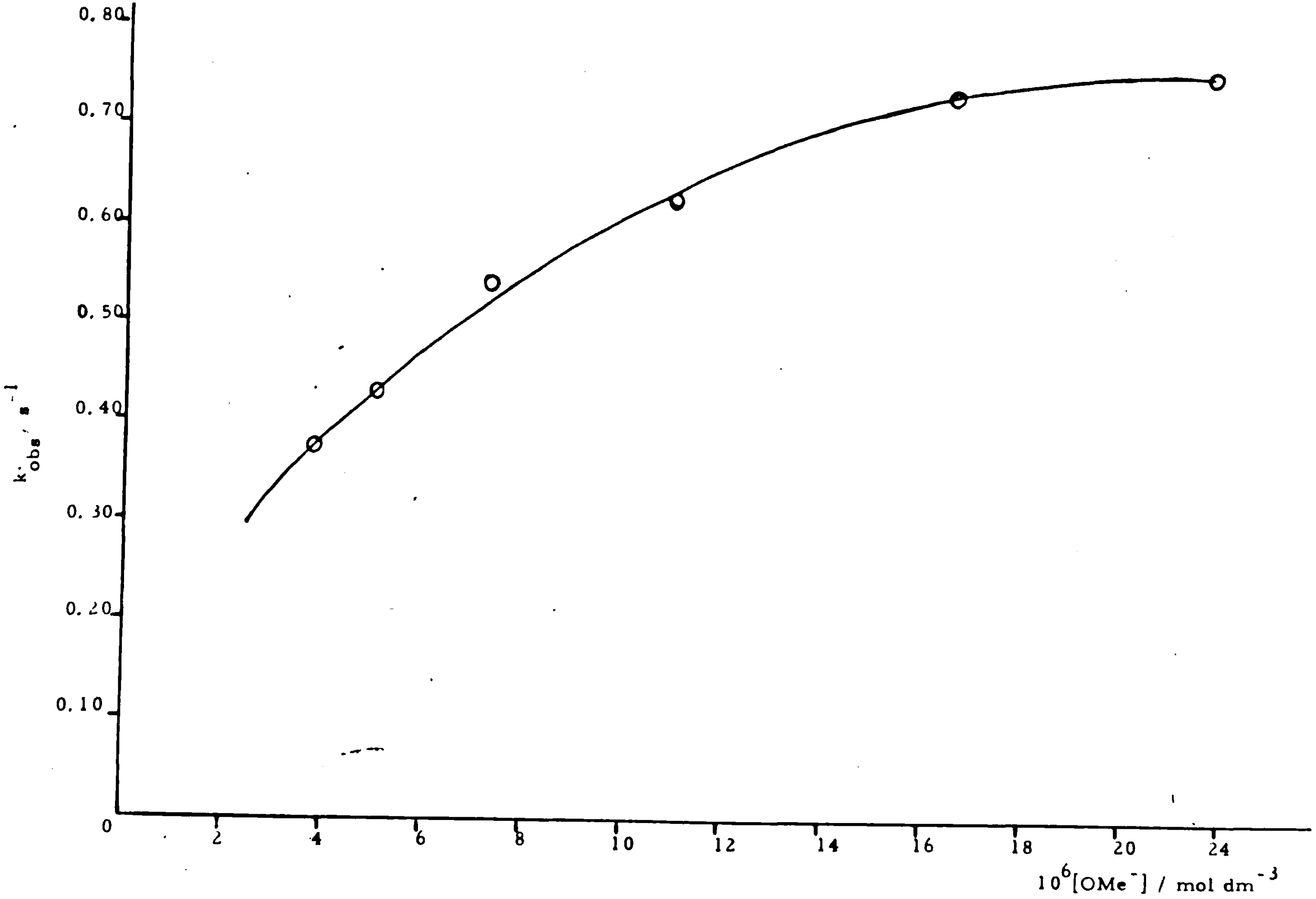


Fig. 4 Plot of $1/k_{obs}$ v. $1/[OMe^-]$ for the slow reaction between $[Mo(C_7H_7)(CO)_3]^+BF_4^-$ and OMe^- in methanol at 26.0°C

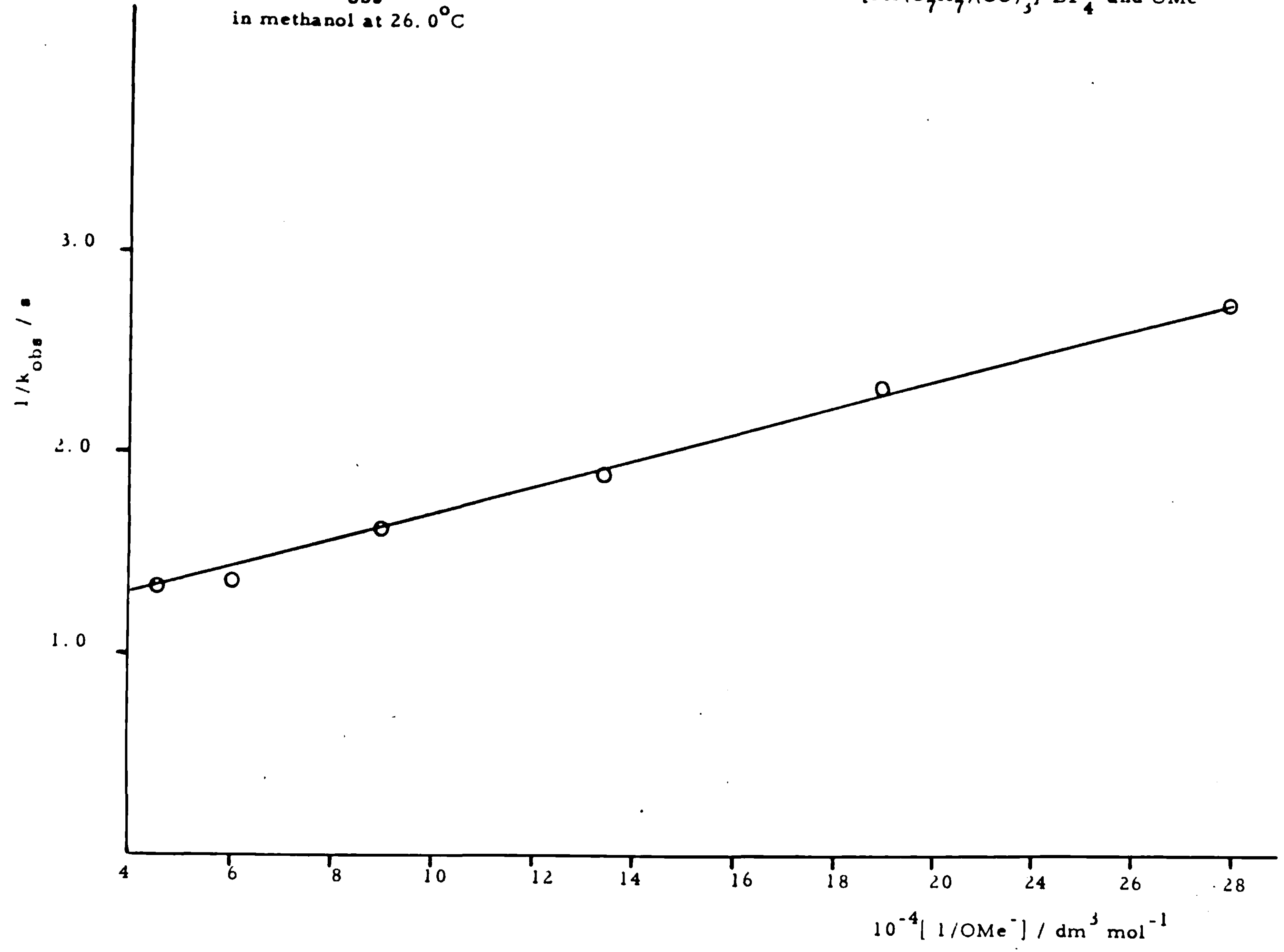


Fig. 5 Plot of k_{obs} v. methoxide ion concentration for the slow reaction between $[Cr(C_7H_7)(CO)_3]^+BF_4^-$ and OMe^- in methanol at 26.0°C.

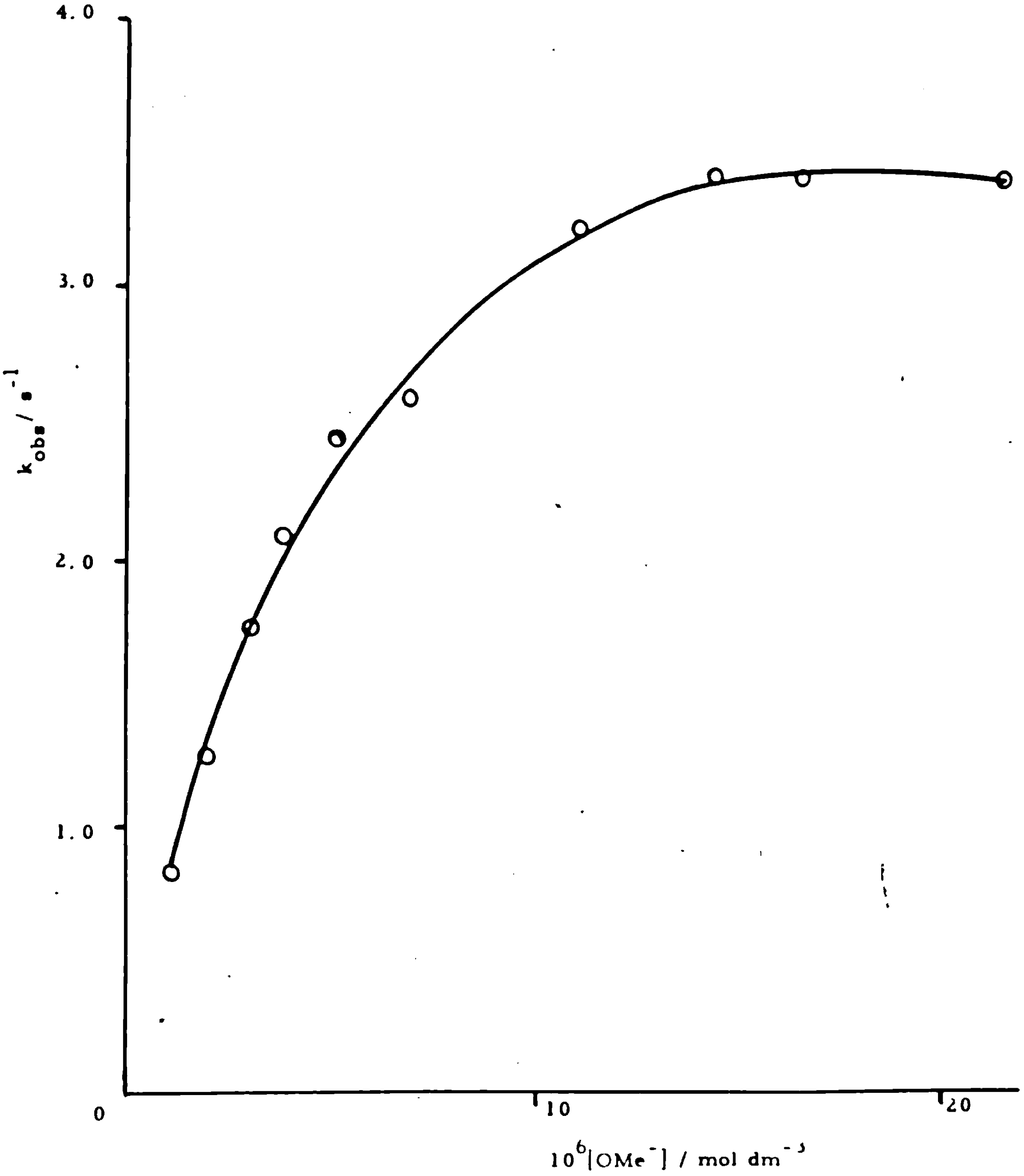
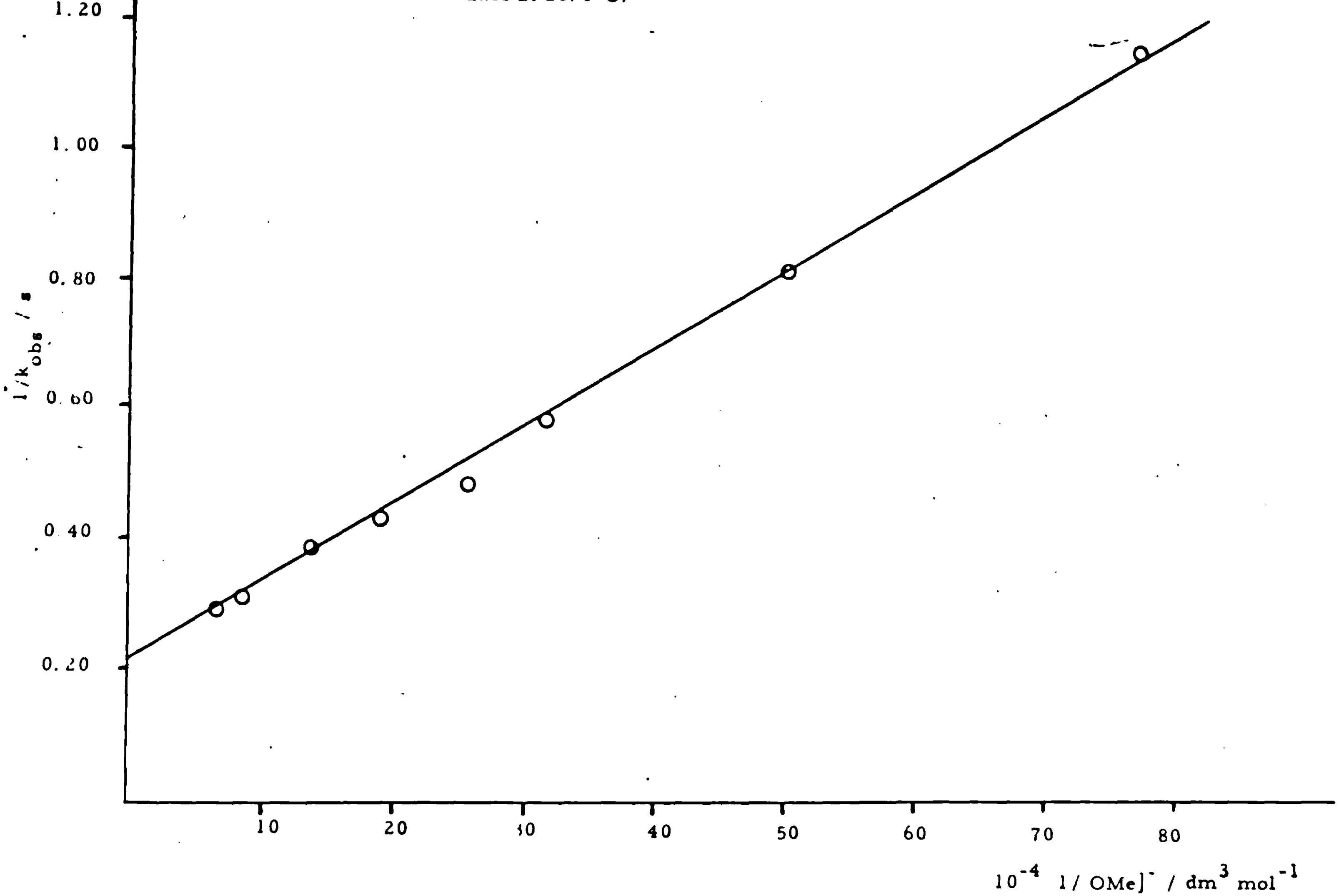


Fig. 6 Plot of $1/k_{obs}$ v. $1/[OMe^-]$ for the slow reaction between $[Cr(C_7H_7)(CO)_3]^+BF_4^-$ and OMe^- in methanol at 26.0°C.



4.3 Experimental

Materials: Molybdenumhexacarbonyl: commercial product (white crystals) used without any purification.

Triphenylcarbinol: beige crystals used as the commercial product.

Cycloheptatriene: yellow liquid (Koch-Light) was freshly distilled under nitrogen before use b.p. 114-115 °C.

n-Octane: was used without further purification.

Dichloromethane: the Analar product was used.

Tetrafluoroboric acid: 48% aqueous acid was used for the preparation of triphenylmethyltetrafluoroborate.

Propionic anhydride: liquid used without purification.

Methanol: (Analar BDH).

Perchloric acid: (Analar BDH).

Triethylamine: (anhydrous puriss)(Koch-Light) b.p. 89-91°C.

Preparation of cycloheptatrieneyltricarbonylmolybdenum[41]:

It was prepared by the method of R.B. King, but modified as follows:

A mixture of hexacarbonylmolybdenum (100mmol), cycloheptatriene (50 cm^3) and n-octane (200 cm^3) was heated under reflux to the boiling point with stirring for 16 hr. The red solution was allowed to cool at room temperature, then filtered under nitrogen. The filtrate was cooled to (-78°C) for several hours but failed to crystallize. The sticky black residue from the filtration was dissolved in dichloromethane, then passed through a silica gel column made up in cyclohexane. The process was done under nitrogen with the aid of very long needles and Schlenk tube for the solvent. A red band developed which was collected and evaporated under vacuum to yield the product as red crystals.

Preparation of cycloheptatrienyltricarbonylmolybdenum tetrafluoroborate:

This complex was prepared by Dauben and Honnen[42] by hydride abstraction from cycloheptatrienyltricarbonylmolybdenum with triphenylmethyl tetrafluoroborate according to the following equation:

$$\mathrm{Mo(C_7H_8)(CO)_3 + [(C_6H_5)_3C]BF_4 \xrightarrow{CH_2Cl_2} [Mo(C_7H_7)(CO)_3]BF_4 + (C_6H_5)_3CH}$$

Triphenylmethyl tetrafluoroborate is most conveniently prepared by treatment of triphenylcarbinol with 48% aqueous tetrafluoroboric acid in propionic anhydride solution.[43] A fresh solution of cycloheptatrienyltricarbonylmolybdenum (100 mmol) in methylene chloride (150 cm^3) was treated with triphenylmethyl tetrafluoroborate (110 mmol) and stirred for 30 min at room temperature. The reaction was carried out under nitrogen. After about 45 min the tan precipitate was filtered, washed with five (50 cm^3) portions of dichloromethane and sucked dry to give about 80% yield.

Preparation of cycloheptatrienyltricarbonyltungsten:

It was prepared according to the method of Salzer[44]. Tungsten hexacarbonyl (30 mmol) was mixed with freshly distilled cycloheptatriene (7 cm^3) and n-nonane (80 cm^3). The solution was heated with continuous stirring under reflux, fitted with nitrogen tap. Every 24 hr fresh cycloheptatriene (2 cm^3) was added to replace losses arising from polymerisation. The tungsten hexacarbonyl which sublimed into the condenser could be washed back to the reaction vessel by raising the bath temperature several times for a few minutes. At the end of

the reaction the solution was cooled to room temperature then to -30°C, a dark red precipitate separated. This was filtered rapidly, washed with cold hexane and dried in high vacuum. The product was purified by slow sublimation. At 50°C any of the excess of tungsten hexacarbonyl was removed together with other volatile organic compounds. Afterwards the product was sublimed for 2 days at 90°C, then 1 day at 130°C.
Yield 50%

Preparation of cycloheptatrienyltricarbonyltungsten tetrafluoroborate:

The same procedure followed in the case of the molybdenum compound was applied here.

Preparation of cycloheptatrienyltricarbonylchromium:

This was prepared by the method of Strohmeier and purified by sublimation in vacuo.[45]

Preparation of cycloheptatrienyltricarbonylchromium tetrafluoroborate:

Also the method of Dauben, Honnen and Harmon was followed here similar to the molybdenum and tungsten compound.

Kinetic Procedure.

As explained in experimental section in Chapter 4.

References for Chapter 5

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```
      PROGRAM FLSQ(INPUT,OUTPUT,TAPE1=INPUT,TAPE3=OUTPUT)
1 Q(INP
      DIMENSION D(1024),T(1024),INTD(1024),FD(1024)
      DIMENSION COMP(5),ALK(5),HAL(5)
C     UNWEIGHTED LEAST SQUARES METHOD FOR RATE CONSTANT INFINITY
C     VALUE KNOWN
      N=1024
      READ(1,113)COMP,ALK,HAL
113   FORMAT(3(5A2))
      READ(1,20)NS,IDS
20    FORMAT(2I3)
      READ(1,25)J,K,L
25    FORMAT(3I4)
      READ(1,10)CONC,TOTALT,ZB,TEMP
10    FORMAT(4F10.0)
      DELTAT=TOTALT/FLOAT(N)
      NT=1
      DO13NUS=1,NS
      CALL RDTAPE(INTD,N)
      WRITE(3,40)INTD
40    FORMAT(1H,32I4)
      DO15I=1,N
15    D(I)=FLOAT(INTD(I))
C     DISCARD FIRST J AND LAST K DATA POINTS
      M=N-K
      N=N-J
      DO45I=1,N
      IJ=I+J
45    D(I)=D(IJ)
C     REZERO TIME AT NEW INITIAL DATA POINT
      T(1)=0.0
      DO35I=2,N
35    T(I)=T(I-1)+DELTAT
      READ(1,610)ZR,DINF
610   FORMAT(2F10.0)
      DINF=DINF-ZR
      DO620I=1,N
      D(I)=D(I)-ZR
      D(I)=ABS(ZB/(ZB-D(I)))
      D(I)=ALOG(D(I))/2.302585
620   CONTINUE
      AINF=ABS(ZB/(ZB-DINF))
      AINF=ALOG(AINF)/2.302585
      DI=D(1)
      DO70I=1,L,IDS
      FD(I)=ABS((AINF-DI)/(AINF-D(I)))
      FD(I)=ALOG(FD(I))
70    CONTINUE
      WRITE(3,71)(FD(I),I=1,L,IDS)
71    FORMAT(12F10.6)
C     LEAST SQUARES ANALYSIS
      SD=0.0
      ST=0.0
      SDT=0.0
```

```
      ST2=0.0
      DO55I=1,L,IDS
      SD=SD+FD(I)
      ST=ST+T(I)
      SDT=SDT+FD(I)*T(I)
      ST2=ST2+T(I)**2
55    CONTINUE
      XN=FLOAT(L-1)/FLOAT(IDS)+1.0
      C=(ST**2-XN*ST2)
      A=(ST*SDT-SD*ST2)/C
      G=(SD*ST-XN*SDT)/C
      E=0.0
      DO66I=1,L,IDS
      DCALC=A+G*T(I)
      E=E+(DCALC-FD(I))**2
66    CONTINUE
      ERR=SQRT(E/(XN-1.0))
      Z=ABS(XN/C)
      ERRG=ERR*SQRT(Z)
      WRITE(3,114)COMP,ALK,HAL
114   FORMAT(5X,*REACTION OF*,1X,5A2,1X,*COMPLEX WITH*,1X,5A2,5A2,//)
      WRITE(3,14)NT
14    FORMAT(15X,*TAPE NO.*,I3)
      WRITE(3,90)CONC
90    FORMAT(15X,*CONCENTRATION OF HALIDE=*,E14.6,*MOL.DM-3*)
      WRITE(3,91)TOTALT
91    FORMAT(15X,*TIME OF SCAN=*,F10.6,*SEC*)
      WRITE(3,800)AINF
800   FORMAT(15X,*INFINITY VALUE OF ABSORBANCE=*,F10.6)
      WRITE(3,249)TEMP
249   FORMAT(15X,*TEMPERATURE=*,F5.2,*DEGREES CENTRIGRADE*)
      WRITE(3,250)XN
250   FORMAT(15X,*NUMBER OF POINTS USED IN LEAST SQUARES=*,F10.2)
      WRITE(3,92)G
92    FORMAT(15X,*GRADIENT=*,E14.6)
      WRITE(3,93)A
93    FORMAT(15X,*INTERCEPT=*,E14.6)
      WRITE(3,73)ERRG
73    FORMAT(15X,*ERROR IN GRADIENT=*,E14.6)
      PERR=ABS(ERRG*200.0/G)
      WRITE(3,94)PERR
94    FORMAT(15X,*PERCENT ERROR IN GRADIENT=*,F10.6)
      NT=NT+1
13    CONTINUE
      STOP
      END
```