Reactions of Pentadienyl Iron Tricarbonyl Complexes and Related Systems

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A thesis
presented to the Faculty of Science
of the University of London
in candidature for the degree of
Doctor of Philosophy

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December 1975

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Abstract

Reactions of coordinated ligands in two organometallic systems are examined. Part I describes the work carried out on (diene)-, and (dienyl)- iron tricarbonyl complexes. Properties of π-enyl palladium II compounds are described in Part II.

In Part I, the preparation and properties of the open-chain (dienyl) iron tricarbonyl cations are examined using kinetic methods. The formation of (1-methyl, 5-phenyl) P.I.T. from the two diastereoisomers of (6-phenyl hexa-3,5-dien-2-ol) iron tricarbonyl is shown to be much slower with the ψ *endo* isomer than with the ψ *exo* isomer at room temperature. At low temperature, each isomer generates a different cationic species. The kinetic behaviour and products formed in this system are shown to be consistent with the involvement of *trans* ion intermediates.

The significance of the *trans* ion species is also demonstrated in the reactions of a series of substituted P.I.T. cations with arenes and with alcohols. The rate law observed for each reaction is shown to be dependent on both the nature and position of substituents on the dienyl system as well as the nucleophile. A mechanism consistent with the kinetic behaviour is discussed in terms of the role of the *trans* ion.

The (diene)- and (dienyl)- iron tricarbonyl systems are also examined by use of ^{1}H, and ^{13}C nmr together with i.r. and Mössbauer spectroscopic techniques. It is suggested that the charge on the dienyl complex is delocalised throughout the molecule from a comparison of the two systems.

In Part II, the stability of 4-substituted (but-2-enyl) palladium II complexes in acid solution is shown to be decreased if the chloro-bridge is replaced by a group V ligand. The decomposition is also controlled by the ease of departure of the leaving group at the 4-position. The nmr spectra of the π-enyl compounds are temperature dependent and indicate that π, σ -transitions can occur.

Acknowledgements

The author is deeply indebted to his supervisor, Dr P. Powell, for much help and encouragement both during and after his study at Royal Holloway College. The author would also like to thank Professor T. G. Bonner for many helpful discussions.

The author will always be grateful to the late Professor E. J. Bourne for help and guidance during his six years at Royal Holloway College.

The work described in this thesis was supported by a Science Research Council Studentship grant.

Finally, the author is also indebted to Mrs E. I. Kearsey for typing the thesis.

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Abbreviations

P.I.T.	Pentadienyl iron tricarbonyl
1,2-dmb	1,2-dimethoxybenzene
1,3-dmb	1,3-dimethoxybenzene
1,4-dmb	1,4-dimethoxybenzene
1,3,5-tmb	1,3,5-trimethoxybenzene
TFA	trifluoroacetic acid
TMS	tetramethylsilane
i.r.	infrared
nmr	nuclear magnetic resonance
tlc	thin layer chromatography

Nomenclature

Open chain (dienyl)iron tricarbonyl complexes have been named in this thesis as substituted derivatives of pentadienyl iron tricarbonyl (P.I.T.) These are shown below together with their systematic names.

Pentadienyl iron tricarbonyl

tricarbonyl (η -pentadienylium)iron

(1-Methyl) P.I.T.

tricarbonyl (1—5-η -hexadienylium)iron

(1,5-Dimethyl) P.I.T.

tricarbonyl (2—6-η -heptadienylium)iron

(1,3,5-Trimethyl) P.I.T.

tricarbonyl (2—6-η -4-methylheptadienylium)iron

(1-Methyl,5-phenyl) P.I.T.

tricarbonyl (1—5-η -1-phenylhexadienylium)iron

(1,4-Dimethyl,5-phenyl) P.I.T.

tricarbonyl (1—5-η -2-methyl-1-phenylhexadienylium)iron

(1-^{t}Butyl,5-phenyl) P.I.T.

tricarbonyl (2— 6-η -1,1-dimethyl-6-phenylhexadienylium)iron

(1,5-diphenyl) P.I.T.

tricarbonyl (1—5-η 1,5-diphenylpentadienylium)iron

Other compounds

(Buta-1,3-diene)iron tricarbonyl

(η -buta-1,3-diene)tricarbonyl iron

(Hexa-2,4-dien-1-ol)iron tricarbonyl

tricarbonyl (2— 5-η -hexa-2,4-dien-1-ol)iron

(6-Phenyl hexa-3,5-dien-2-ol)iron tricarbonyl

tricarbonyl (3—6-η -hexadien-2-ol)iron

(Hepta-3,5-dien-2-ol)iron tricarbonyl

tricarbonyl (3— 6-η -hepta-3,5-dien-2-ol)iron

(2-Methyl hepta-3,5-dien-2-ol)iron tricarbonyl

tricarbonyl(3—6-η -2-methylheptadien-2-ol)iron

(5-Methyl hepta-3,5-dien-2-ol)iron tricarbonyl

tricarbonyl(3—6-η -5-methylhepta-3,5-dien-2-ol)iron

(Cyclohexa-1,3-diene)iron tricarbonyl

tricarbonyl(η -cyclohexa-1,3-diene)iron

(Cyclohexadienyl)iron tricarbonyl

tricarbonyl(η -hexadienylium)iron

PART I

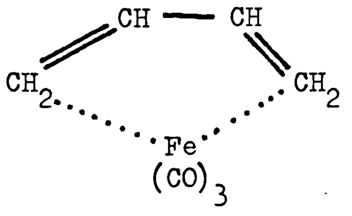
CHAPTER 1

INTRODUCTION

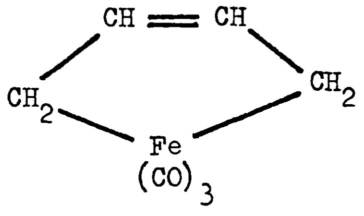
CHAPTER 1

INTRODUCTION

Although the discovery of ferrocene[1,2] is often regarded as the beginning of organo-iron chemistry, (butadiene)iron tricarbonyl was isolated over twenty years before by Reihlen and co-workers[3] in 1930. The original synthesis was from the reaction of butadiene with iron pentacarbonyl in a sealed tube at 150°C and was devised in order to throw more light on the nature of iron pentacarbonyl. The structure they proposed was (1.1), with the iron bonded to the terminal carbon atoms of the diene to form a five membered ring, though they did not rule out on alternative structure (1.2) with the iron σ-bonded to both terminal carbon atoms and a new π-bond between C_2 and C_3 which was not bonded to the metal.

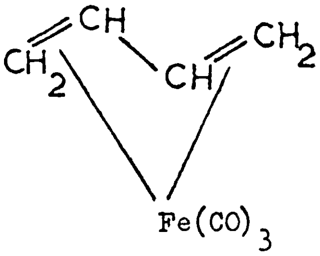


(1.1)



(1.2)

The complex was reinvestigated by Hallam and Pauson in 1958,[4] who suggested a third structure (1.3) with the diene moiety bonded in the trans conformation. However, (cyclohexa-1,3-diene)iron tricarbonyl had very similar chemical and physical properties, but could adopt only the cis conformation (1.4). This led to the conclusion that (butadiene) iron tricarbonyl must also have the cis structure.



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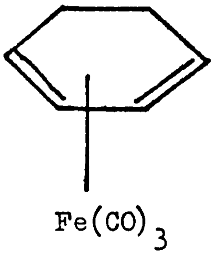
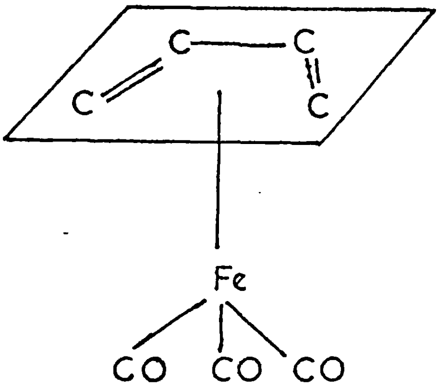


(1.4)

The chemical reactivity of (butadiene)iron tricarbonyl was also investigated, and was found not to be typical of a diene. It did not undergo Diels-Alder reactions and was not reduced by hydrogen in the presence of Adams' Palladium Oxide catalyst. The compound exhibited a stability which would not be expected from a chelating dialkyl structure (1.2). It resisted attack by coordinating solvents and strong acids, and could be recovered unchanged from solutions in pyridine, glacial acetic acid and concentrated sulphuric acid. Furthermore, ozonolysis gave some formaldehyde, and vigorous reduction with lithium aluminium hydride gave some butadiene, indicating that the diene remained intact in the complex. Infrared and ultraviolet spectra were consistent with the presence of a conjugated double bond, and an olefin π-bonded to the metal. X-ray crystallographic data[3] showed the carbon atoms of the diene to be coplanar and in the <u>cis</u> conformation supporting a structure similar to (1.1) but with the iron below the plane containing the diene. This is shown in (1.5).



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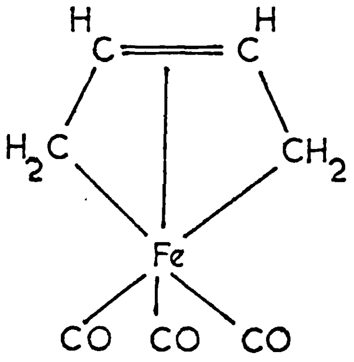
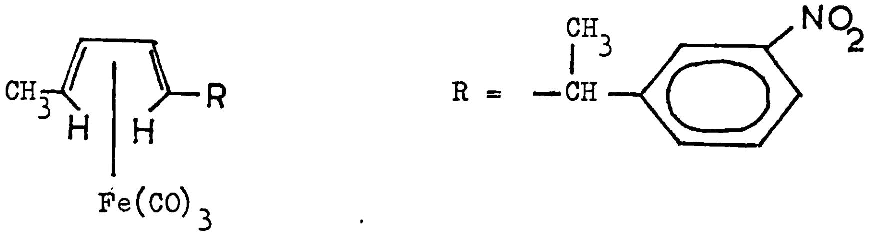


(1.6)

A further structure has been proposed where the free olefin in (1.2) was also π-bonded to the iron to form a tridentate ligand.[6] This was on the basis of the proton n.m.r. spectrum of the complex, which showed two protons at 5.85δ in the normal olefinic region and four at 1.68δ and 0.22δ in the aliphatic region. This interpretation assumes that the presence of the iron atom does not alter the chemical shifts of the protons by anisotropic effects. In the carbon-13 n.m.r. spectrum,[7] both the shifts and the ^{13}C-H coupling constants have values consistent with sp^2 rather than sp^2 and sp^3 hybridised carbon atoms and so tend to favour (1.5). Long range coupling constants in the proton n.m.r. spectrum have recently been calculated,[8] which were interpreted as evidence that all the diene protons are coplanar, as in (1.5). However, it has recently been shown by an X-ray diffraction technique that the C-H bonds can deviate by as much as 30° from the diene plane in substituted complexes.[9] The deviations measured in (2-[(m-nitrophenyl) amino]-trans,trans-3,5-heptadiene)iron tricarbonyl (1.7) are shown in (1.8). Angles below the diene plane (i.e. towards the metal) are indicated by a negative sign. Thus, all substituents except those at the



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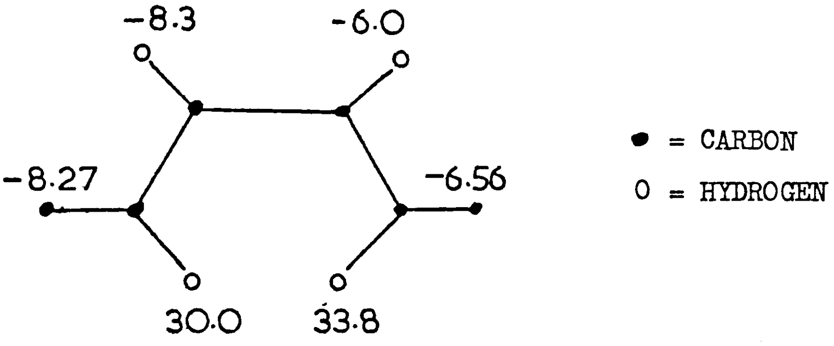


(1.8)

anti positions lie below the diene plane.

It has been suggested[10] that the degree to which the actual structure approaches the extremes of bonding may be judged by the lengths of the carbon-carbon bonds: (1.5) would have a short-long-short pattern as would free butadiene in its ground state, but (1.6) would have a long-short-long pattern as would butadiene in its first excited state. This has been interpreted by an examination of the molecular orbitals of butadiene:

When butadiene becomes bonded to a metal, electron density is donated from the highest occupied m.o. of butadiene to the metal, which in turn donates electron density to the lowest unoccupied m.o. of butadiene. These two shifts have a similar effect on the

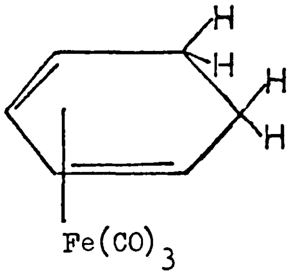
π- bonding of butadiene as does promotion of butadiene from the ground state to its first excited state. This means that an increase in the strength of the bond between butadiene and the metal would tend to change the short-long-short pattern to a long-short-long pattern. In(butadiene)iron tricarbonyl, the effect of the bonding of butadiene to iron has tended to equalize the carbon-carbon bond lengths, and so the bonding in the diene can be regarded as being composed of a mixture of the ground and first excited states.[11]

The bonding in(butadiene)iron tricarbonyl has also been discussed by Connor et al who also performed an ab initio self consistent field molecular orbital calculation and measured the He(I), He(II) and X-ray photoelectron spectra.[12] The calculated electron density was higher on C_1 and C_4 than on C_2 and C_3. This is consistent with the experimental evidence that electrophilic substitution occurs at the C_1 position.[13] Competitive acylation showed that(butadiene)iron tricarbonyl reacted much faster than benzene and cyclopentadienyl manganese tricarbonyl but at a similar rate to ferrocene, indicating an electron density greater than unity on C_1.

The chemistry of(diene)iron tricarbonyl complexes has been reviewed.[14] Derivatives of(butadiene) iron tricarbonyl show typical reactions of the functional groups. The coordinated sorbic acid was found to be slightly weaker than the free acid indicating the (butadiene)iron tricarbonyl group to be electron donating. This property was also indicated by the ease of acetylation of

(1-phenylbutadiene) iron tricarbonyl by acetyl chloride and tin tetrachloride.

The first (dienyl) iron tricarbonyl complex was isolated by E.O. Fischer in 1960.[15] This was formed by abstraction of a hydride ion from (cyclohexadiene) iron tricarbonyl (1.9) with triphenylmethyl tetrafluoroborate. Its structure is shown in (1.10). The corresponding acyclic complex (1.11) was made by an analogous method from (*anti* 1-methyl butadiene) iron tricarbonyl (1.12).[16] However, attempts to repeat the reaction with (*syn* 1-methyl butadiene) iron tricarbonyl (1.13) failed. It was suggested that this was due mainly to kinetic rather than thermodynamic control of the reaction.



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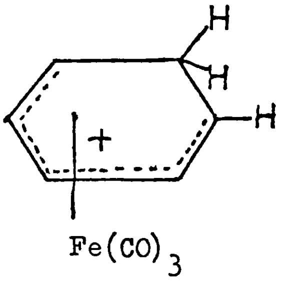

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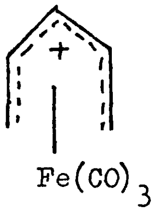

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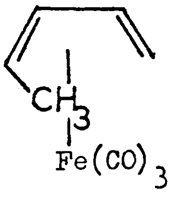

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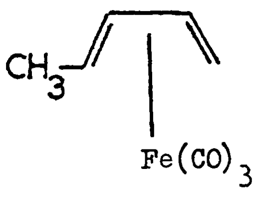
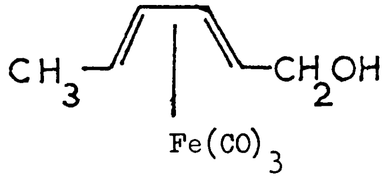


(1.13)

The acyclic pentadienyl iron tricarbonyl (P.I.T.) complexes have usually been prepared from the corresponding substituted (butadiene) iron tricarbonyl complex with an alcohol group on the carbon adjacent to the diene unit, by addition of a strong acid.[16,17] For instance (hexa-2, 4-dien-1-ol) iron tricarbonyl (1.14) gave (1-methyl) P.I.T. (1.15) when treated with tetrafluoroboric acid in acetic anhydride. The complex was isolated as its tetrafluoroborate salt. The reaction is thought to proceed by initial protonation of the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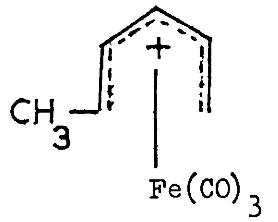
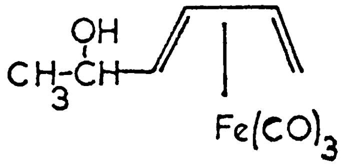

(1.15)

alcohol, followed by loss of water and a rearrangement of the pentadienyl system to yield the observed cis cation.

The acyclic pentadienyl system was found to be readily attacked by nucleophiles, forming substituted diene complexes. Reaction with water afforded an alcohol, and methanol a methyl ether. Attack always occurred on the most substituted terminal carbon of the system, only (1.16) being formed from (1-methyl) P.I.T. (1.15) on reaction with water, and only (1.17) with methanol. None of the original alcohol complex (1.14) was found in the reaction products.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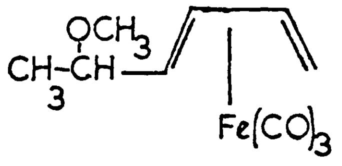
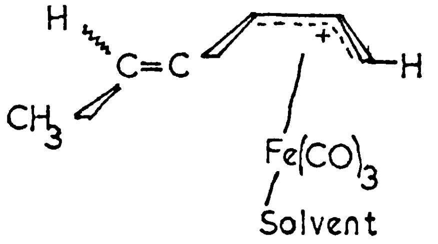

(1.17)

The mechanism proposed for this reaction suggested the intervention of an intermediate trans ion in the scheme. This was formed from the cis P.I.T. complex by a rotation of the C_2–C_3 bond. The two trans ions which could be generated from the asymmetric complex (1.15) are (1.18) and (1.19). These are shown as π-allyl complexes, though several other resonance structures can be drawn. The more likely intermediate was thought to be (1.18) as it had the more substituted olefin and the less sterically crowded solvated π-allyl iron tricarbonyl cation. Also, the other trans ion (1.19) would be destabilized by the inductive effect of the methyl group reducing the bonding via back-donation from iron to the π-allyl system.



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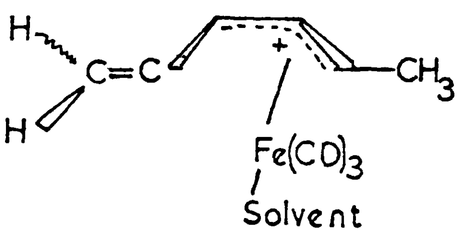
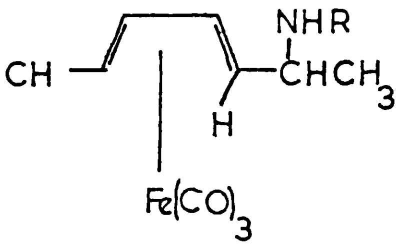


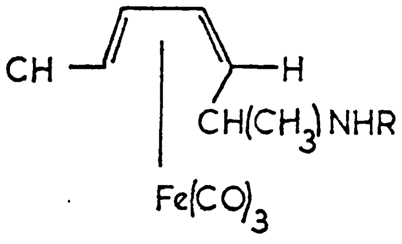
(1.19)

The cations were also found to react with primary amines to give two possible products.[18,19] The isomer isolated was a function of the basicity of the amine. Weakly basic amines (pK_b 10–13) such as 3-nitroaniline gave (1.20), analogous to the product with water, with (1,5-dimethyl) P.I.T.. However, strongly basic amines (pK_b 3–6) such as ethylamine and methylbenzylamine gave a cis substituted product (1.21).



Fe(CO)$_3$

(1.20)

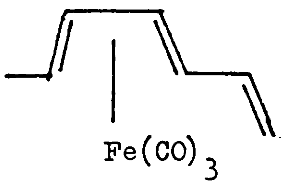


Fe(CO)$_3$

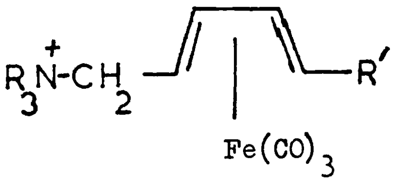
(1.21)

The mechanism suggested was that strongly basic amines attacked the cis P.I.T. complex directly, but weakly basic amines attacked only the trans ion intermediate. Amines with an intermediate basicity (e.g. aniline - pK$_b$ 9.4) gave either (1.20) or (1.21) or mixtures of the two depending on the conditions used.

Two types of products have been found from the reaction of tertiary amines with P.I.T. derivatives. Trimethylamine and triethylamine abstracted a proton from (1,5-dimethyl) P.I.T. to yield a triene (1.22), but under similar conditions reaction with (1-methyl) and (1-ethyl) P.I.T. gave quaternary ammonium salts (1.23).[20] This difference was ascribed to steric rather than electronic effects.



(1.22)

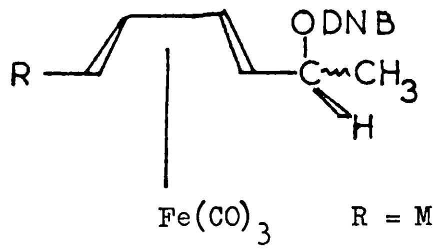


(1.23)

R = Me,Et
R′ = Me,Et

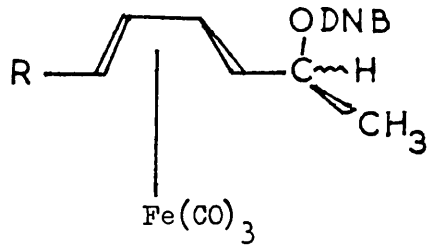
However, a compound analogous to (1.22) was isolated from the reaction of (1-methyl)P.I.T. with basic alumina under heterogeneous conditions.[21]

Further evidence for the involvement of trans ions in the reactions of (diene) iron tricarbonyl complexes was obtained from the kinetics of solvolysis of the 2,4-dinitrobenzoate esters of (6-phenyl hexa-3,5-dien-2-ol) iron tricarbonyl and (hepta-3,5-dien-2-ol) iron tricarbonyl.[22-25] Both the ψ endo and the ψ exo isomers were isolated in each case, and were drawn as (1.24) and (1.25) respectively, though this assignment has been questioned by Foreman[26] from an n.m.r.



R = Me,Ph

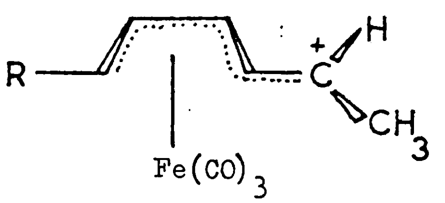
(1.24) endo



(1.25) exo

spectroscopic study of the alcohols, using lanthanide shift reagents to determine the stereochemistry of the molecules. The rates of solvolysis in 80% aqueous acetone of the ψ endo isomers were found to be slower than the ψ exo isomers by a factor of almost ninety for both R = Me and R = Ph, though the rates were faster in the methyl derivatives. There was complete retention of configuration in the products, except for the phenyl substituted ψ endo isomer when 92.5 - 95.0% retention was observed. The reaction was shown to be governed by an SN1 mechanism by the salt and common ion effects - sodium fluoroborate increased the rate of solvolysis, and sodium 3,5-dinitrobenzoate decreased it.

This led to the conclusion that the isomers of each ester gave rise to different ions which interconverted at a slower rate than the rate of attack of water to give the products. These were drawn as the two trans ions formed by alkyl oxygen fission of the ester, followed by loss of 2,4-dinitrobenzoate ion exo to the iron tricarbonyl group. The endo isomer produced cation (1.26) and the exo isomer (1.27). To account for the stability of these ions as reactive intermediates,



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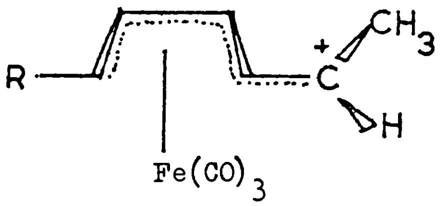
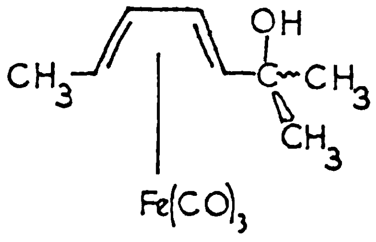


(1.27)

direct participation of the iron atom was suggested.

Subsequent experiments using n m r spectroscopy led to the observation of a trans ion in equilibrium with a cis ion at low temperature.[27] (2-methyl hepta-3,5-dien-2-ol) iron tricarbonyl (1.28) was converted to a trans ion (1.29) and a cis ion (1.30) on treatment



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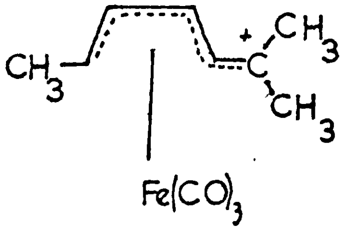

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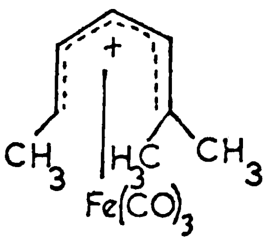
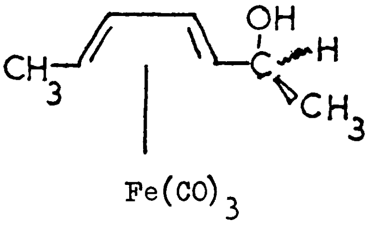
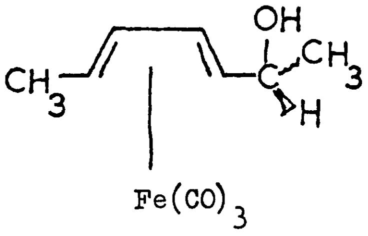


(1.30)

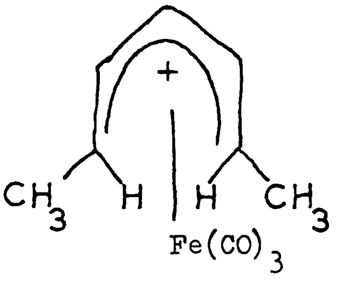
with fluorosulphonic acid at -78°. The equilibrium constant for the *cis*-*trans* conversion was 3.0 ± 0.3 at -50° on the side of the *trans* form, and the rate of conversion from *trans* to *cis* was 0.75 sec^{-1} at -32.5°C with an energy barrier in the order of 55 kJ mol^{-1}. However, no *trans* isomer was detected under the same conditions with either the ψ *exo* (1.31) or the ψ *endo* (1.32) isomer of (hepta-3,5-dien-2-ol) iron tricarbonyl. Each was converted to a different *cis* ion, the ψ *exo* complex forming *cis*,syn,syn (1,5-dimethyl) P.I.T. (1.33) and the ψ *endo* complex forming *cis*,syn,anti (1,5-dimethyl) P.I.T. (1.34).



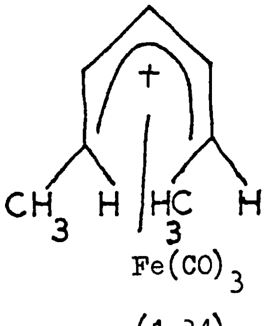
(1.31)



(1.32)



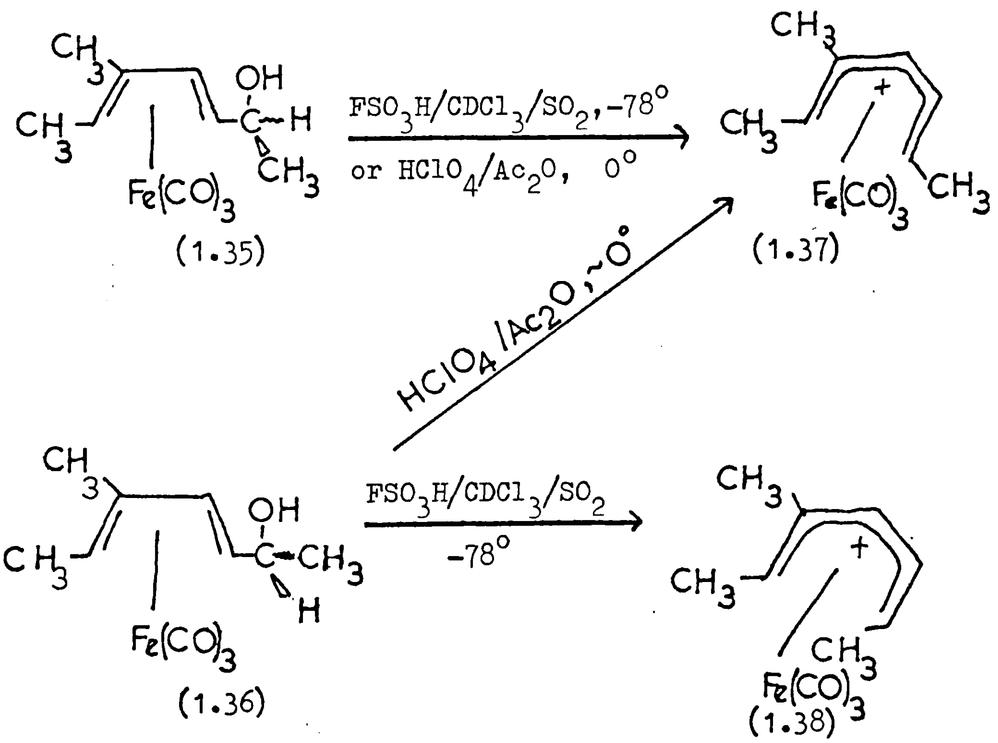
(1.33)



(1.34)

It was concluded that P.I.T. complexes could adopt either a *cis* or a *trans* structure, and that the *trans* form could be made more stable by suitable substitution. Steric effects alone could not explain the stability of (1.29) because the situation in (1.30) would be expected to be very similar to that in (1.34). However, n m r evidence tended to suggest that the charge on C_1 was greater in the trans form than the cis, as greater stabilization would result in (1.29), with a tertiary carbon at C_1, than in a trans ion form (1.31) with a secondary carbon at C_1.

Similar results were obtained[28] in a study of the reaction of fluorosulphonic acid in liquid sulphur dioxide with (5-methyl-3,5-heptadien-2-ol) iron tricarbonyl at -78°. It was again found that the Ψ exo (1.35) and the Ψ endo (1.36) isomers were converted stereospecifically to isomeric cis cations which had syn,syn (1.37) and syn, anti (1.38) structures respectively. Trans ions were not observed in the n m r spectra. Treatment of either alcohol with perchloric acid in acetic anhydride at room temperature gave only (1.37). The results are shown in scheme 1,1, and are consistent with protonation of the alcohol, followed by loss of water exo to the metal to form a trans ion.



SCHEME 1.1

This can rearrange by rotation of the $C_2 - C_3$ bond to the cis configuration at low temperature. The thermodynamically more stable cis, syn,syn cation is obtained from the ψ endo alcohol at higher temperatures either by direct isomerisation of the cis,syn,anti cation or through a small equilibrium concentration of a trans species.

Despite the large expansion of the field of organometallic chemistry over the last decade, there has been little use of kinetic studies as a probe for reaction mechanisms when compared with their extensive use in organic chemistry. This may be to some extent due to experimental difficulties involved in the handling of air - or moisture - sensitive compounds, which have been partially overcome by determining relative rates of reaction by examination of products from competitive experiments rather than measuring the rates individually. e.g. 13, 29

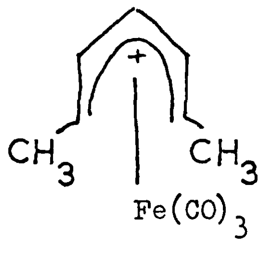
The purpose of this work was to investigate the mechanism of reaction of a ligand coordinated to a metal by use of kinetics. Pentadienyl iron tricarbonyl complexes were chosen in particular in order to throw some light on the role of the trans ion in their chemistry. Furthermore, they are relatively air stable solids capable of being prepared in a high state of purity, and so lend themselves to this method of examination.

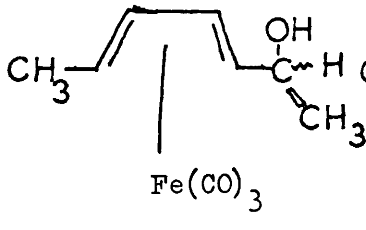
CHAPTER 2

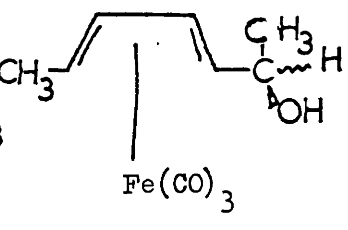
Formation of Pentadienyl Irontricarbonyl complexes from coordinated alcohols

A: INTRODUCTION

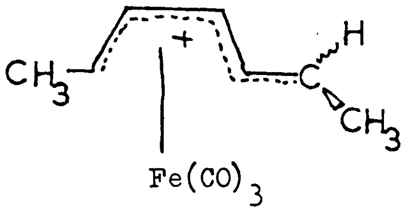
The two diastereoisomers of (hepta-3,5-dien-2-ol)irontricarbonyl were first isolated by Mahler and Pettit,[16] and had very similar properties except for their melting points. The complex made by reaction of (hexa-2,4-dien-1-ol)iron tricarbonyl with methyl magnesium iodide had a melting point of 70°. However, direct combination of hepta-3,5-dien-2-ol with iron pentacarbonyl gave the other isomer, with a melting point of 85°. Treatment of either compound, or a mixture of the two, with fluoroboric acid afforded only one compound in almost quantitative yield. This was shown to be syn,syn(1,5-dimethyl-pentadienyl)iron tricarbonyl tetrafluoroborate (2.1). Reaction of this compound with water yielded only the higher melting isomer, which was later assigned[23] the ψ exo structure (2.2). The ψ endo isomer is shown in (2.3).


(2.1)

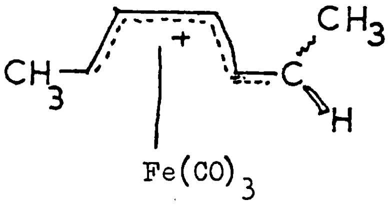

(2.2)


(2.3)

Although the kinetics of solvolysis of 3,5-dinitrobenzoate esters of (2.2) and (2.3) in 80% aqueous acetone were found to be consistent with an SN1 mechanism, the products had retained configurations. This implies that the cis cation (2.1) is not an intermediate as this this would lend to the formation of (2.2) only. Hence, the esters gave different cationic intermediates which either did not exchange or did so slower than the rate of formation of the alcohols. *Trans* ion structures were proposed for these - (2.4) being derived from (2.2) and (2.5) from (2.3) by the loss of 2,4-dinitrobenzoate ion *exo* to the iron tricarbonyl group. Subsequent *exo* attack of water gave the products without loss of configuration.



(2.4)



(2.5)

It was thought that the trans ions may also be intermediates in the formation of *cis* P.I.T. from the reaction of acid with the Ψ *exo* and Ψ *endo* diastereoisomers of (3,5-dien-2-ol) iron tricarbonyl complexes. This reaction was studied kinetically.

B: RESULTS

(i) Kinetics of formation at room temperature

The reaction of Ψ exo and Ψ endo (6-phenylhexa-3,5-dien-2-ol) iron tricarbonyl with an excess of trifluoroacetic acid in nitromethane was chosen for study. There were several reasons for using this particular system. Both isomers were known and were well defined crystalline solids, giving almost quantitative yields of (1-methyl, 5-phenyl) P.I.T. on treatment with fluoroboric acid. The choice of solvent was restricted to dry nitromethane as P.I.T. complexes would precipitate out of non-polar solvents, so causing an heterogeneous system. Other more polar solvents such as methyl cyanide and alcohols were found to react with P.I.T. as it formed. The acid was limited to one which was soluble in nitromethane but which did not react with P.I.T. . The former condition excluded acids normally available in aqueous solution such as tetrafluoroboric acid and hexafluorophosphoric acid, and the latter excluded p toluene sulphonic acid and sulphuric acid which precipitated a brown material with loss of carbon monoxide from solutions of P.I.T.. Trichloroacetic acid decomposed the P.I.T. complex slowly, while acetic acid was too weak to react with either alcohol complex. Trifluoroacetic acid (TFA) was found to be suitable. There was some reaction with P.I.T. though at a much slower rate than the rate of its formation from either dienol complex under experimental conditions.

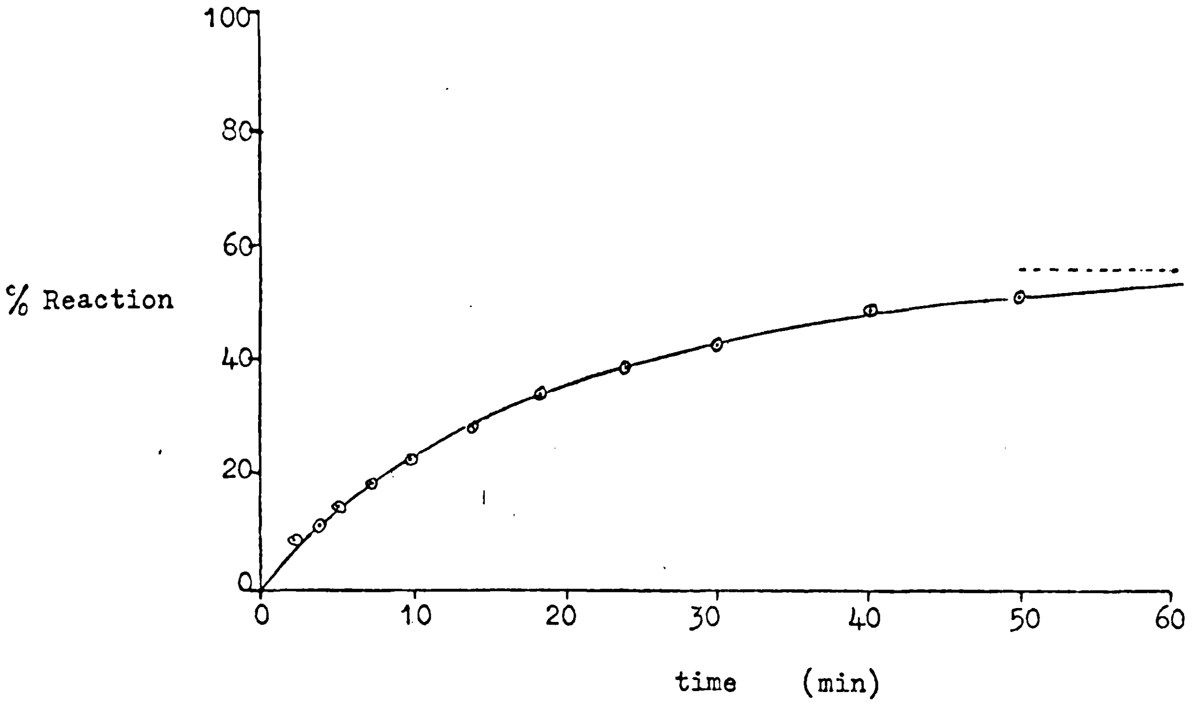
Reactions were followed by observing changes on the carbonyl region (2200 - 1900 cm^{-1}) of the infrared spectrum as a function of time. The concentration of (1-methyl, 5-phenyl) P.I.T. could be determined directly in solution from the intensity of the 2105 cm^{-1} carbonyl bond, which was found to obey Beer's Law.

Preliminary work showed that the kinetic runs were too fast to follow by a sampling technique, the half life being generally less than 15 mins. They were therefore carried out in a thermostatted cell in the i.r. spectrometer and the intensity of the 2105 cm^{-1} carbonyl band measured at intervals.

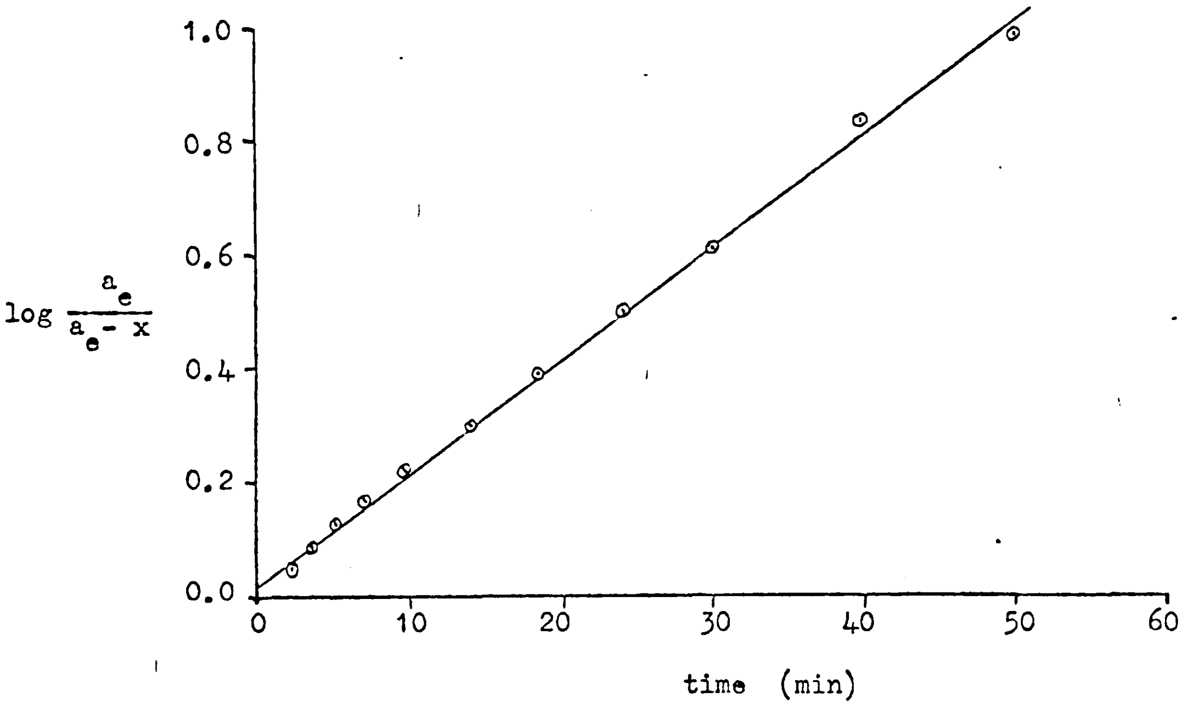
The reaction of ψ endo (6-phenylhexadien-2-ol) iron tricarbonyl with a ten-fold excess of TFA in nitromethane was found to proceed to an equilibrium. A plot of concentration of P.I.T. against time is shown in graph 2.1. The position of equilibrium was estimated at a concentration of 0.00575M P.I.T. - i.e. 57.5% reaction. This was a true equilibrium, as it could be shifted towards completion by addition of more acid, and towards the dienol by addition of water. However, the exact position could not be determined owing to a slow reaction of TFA with P.I.T., which reduced its concentration to only 0.0014M after 22 hours.

The approach to equilibrium obeyed pseudo first order kinetics, as shown in graph 2.2. The quantity x is the concentration of P.I.T. at a particular time, and a_e is the concentration of P.I.T. at equilibrium.

Estimation of the equilibrium concentration of P.I.T. became more difficult when the amount of acid used was increased. This caused a shift of equilibrium towards P.I.T. and a faster rate of decomposition. An iterative method was developed in order to estimate this position, using the computer program in the appendix to this chapter. This was based on the fact that the reaction rate was governed by pseudo-first order kinetics. A minimum value for



GRAPH 2.1 Reaction of ψ endo(6-phenyl hexadien-2-ol)iron tricarbonyl (0.01M) with TFA (0.10M) in CH_3NO_2 at 25°



GRAPH 2.2 Reaction of ψ endo(6-phenyl hexadien-2-ol)iron tricarbonyl (0.01M) with TFA (0.10M) in CH_3NO_2 at 25°

the equilibrium concentration of P.I.T. was guessed - though this was not critical - and a value of the expression (1) calculated for

$$z = \log_{10} (a_e/(a_e - x_t)) \qquad (1)$$

where a_e = estimated equilibrium concentration of P.I.T.
and x_t = concentration of P.I.T. at time t.

each point. The gradient and error for a graph of z against t was then found by application of the least squares method.[30,31] The equilibrium concentration was then increased by 0.0005M, and the process repeated until the maximum estimated value was reached.

This generated a series of gradients and errors. If the estimate was too low, the plot of z against t was curved upwards, as in figure 2.1, with a large error in the computed least squares gradient. On the other hand, if it was too high, the line curved downwards as in figure 2.2. The straight line in figure 2.3 was obtained when the estimated value was close to the experimental one, and was recognised by the gradient having the minimum error. The experimental rate constant k_{obs} expressed in units of sec^{-1} was calculated from this gradient by multiplying by the conversion factor 2.303/60.

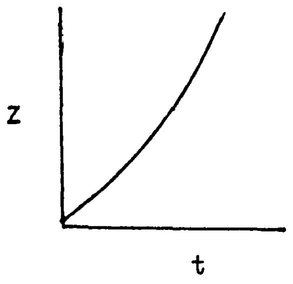


figure 2.1

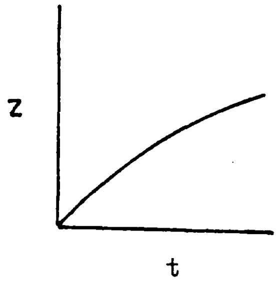


figure 2.2

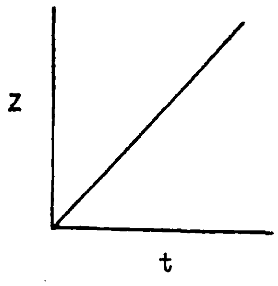


figure 2.3

The results from four kinetic runs under similar conditions are shown in table 2.1. The calculated equilibrium concentration varied slightly between runs, but the calculated rate constants were reasonably consistent. The average value was 7.9×10^{-4} sec^{-1}, with a standard deviation of ± 0.26. The percentage error at two standard deviations was 6.6%.

Run No.	k_{obs} $sec^{-1} \times 10^4$	equilibrium concentration $M \times 10^2$
1	8.3	0.56
2	7.7	0.575
3	7.8	0.635
4	7.8	0.630

TABLE 2.1.

In order to establish the order of reaction with respect to TFA, further runs were done with fifteen and twenty times excess of acid. These results were also calculated using the iterative method and are shown in table 2.2. The overall error was estimated to be within ± 10% of the value quoted. This data showed that the

Excess of TFA	Average $k_{obs} \times 10^4 (sec^{-1})$
10	7.9
15	12.1
20	14.6

TABLE 2.2

rate of reaction increased linearly with the concentration of TFA, and so was first order in acid. The rate equation for the reaction is in equation 2, where the second order rate constant

$$\text{rate} = k[\psi\ \underline{\text{endo}}\ (6\text{-phenylhexa-3,5-dien-2-ol})\text{iron tricarbonyl}][\text{TFA}] \qquad (2)$$

k is 7.9×10^{-3} mol^{-1} sec^{-1} at 24.5°.

When the Ψ exo dienol was used, the approach to equilibrium was too fast to follow at 24.5° even in the i.r. cell. With a twenty-fold excess of TFA, the concentration of P.I.T. reached a maximum value of 0.0085M in less than 4 minutes. This then slowly decreased owing to decomposition, reaching 0.0062M after two hours. Under similar conditions, the ψ endo dienol reached a maximum concentration of 0.0081M after about an hour. In order to slow down the reaction with the ψ exo dienol, it was repeated at 10°. However, the approach to equilibrium still could not be observed.

Assuming the reaction reached approximately 95% completion in 100 seconds, a minimum value of the rate constant was calculated to be 3×10^{-1} $\text{mol}^{-1}\text{sec}^{-1}$ if the kinetic equation was of a similar form to the Ψ endo case. Hence, the Ψ exo/ Ψ endo rate ratio was greater than forty.

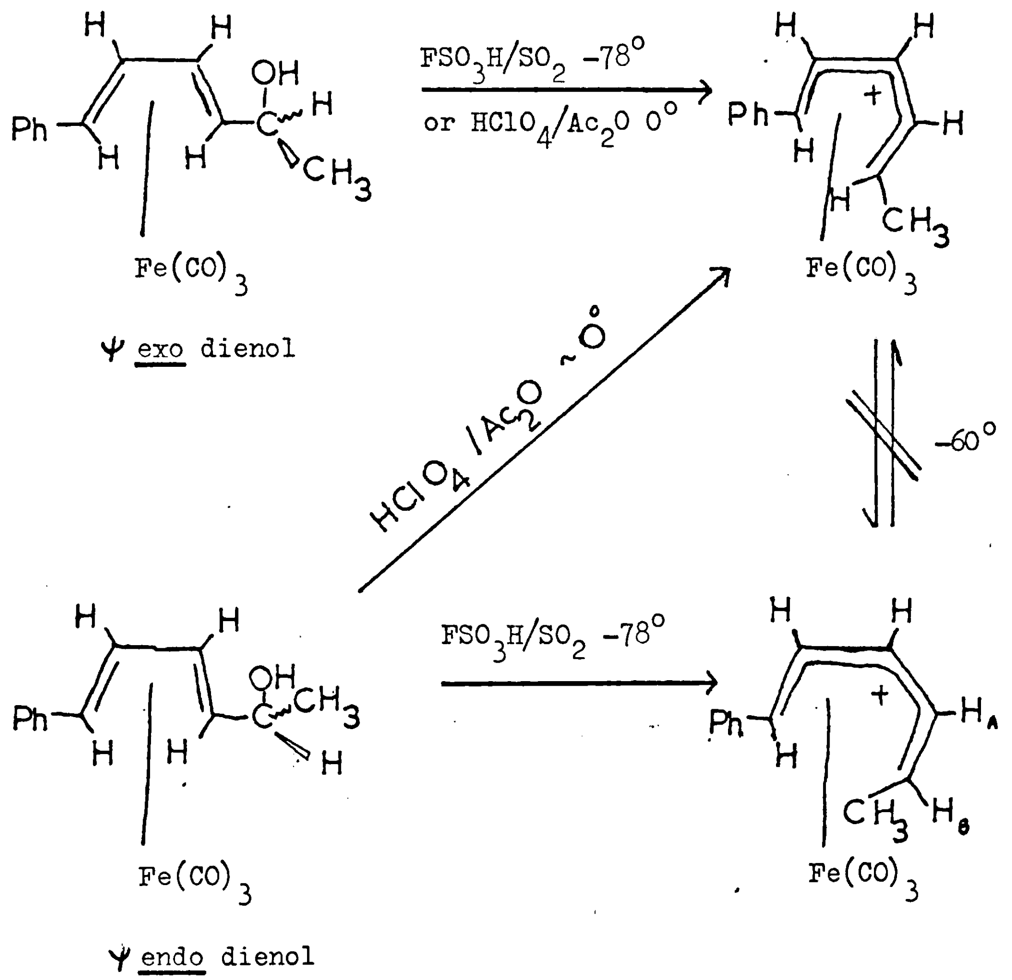
(ii) Formation at low temperature

The behaviour of the isomers of (6-phenylhexa-3,5-dien-2-ol) iron tricarbonyl towards a strong acid at low temperature was investigated by use of n m r spectroscopy. In contrast to the reaction at room temperature when only one product, (1-methyl, 5-phenyl) P.I.T., was isolated, each isomer gave a different cationic species at -78°.

Each complex was first dissolved in liquid sulphur dioxide to which a solution of fluorosulphonic acid in liquid sulphur dioxide containing TMS was added. During and after mixing, care was taken to prevent the temperature from rising above -78°. N M R. spectra were recorded within ten minutes to avoid possible decomposition. These are shown as spectrum 4.1 and spectrum 4.2 which were from the ψ exo and ψ endo isomers respectively. No change in either spectrum was found after standing for 1 hour at -60°. On warming above -20°, both solutions darkened due to decomposition, and the n m r signals became broad owing to the presence of paramagnetic species.

Spectrum 4.1 was identical to the spectrum of a solution of cis,syn,syn(1-methyl,5-phenyl) P.I.T.. However, spectrum 4.2 had two notable differences. Firstly, the methyl group at 1.57 δ was in accord with an anti rather than a syn configuration[25] and secondly, the low field proton at 4.61 δ was characteristic of a anti hydrogen. This is consistent with a cis,syn,anti pentadienyl structure as shown in (2.6). This was confirmed by double resonance experiments, and by the magnitude of the coupling constants. For instance J_{H_A,H_B} was 7.5 Hz,which is a typical value for a cis olefinic coupling constant. No additional lines were observed in the spectrum.

The results of these experiments are summarized in scheme 2.1.



SCHEME 2.1

C: DISCUSSION

The mechanism of formation of pentadienyl iron tricarbonyl species from the reaction of (6-phenylhexa-3,5-dien-2-ol) iron tricarbonyl with trifluoroacetic acid in nitromethane must be consistent with the following observations:

1) The reaction of the ψ endo isomer in a second order process, first order in dienol and first order in TFA.

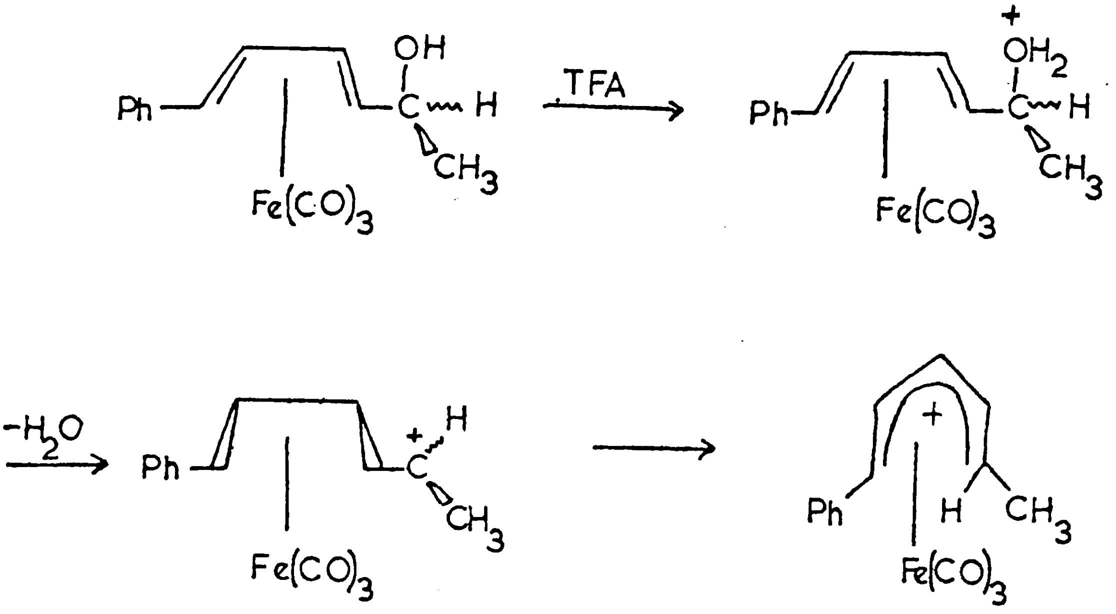
2) The reactions of both isomers proceed to the same equilibrium position under similar conditions.

3) The ψ exo isomer reacts at a faster rate than the ψ endo isomer.

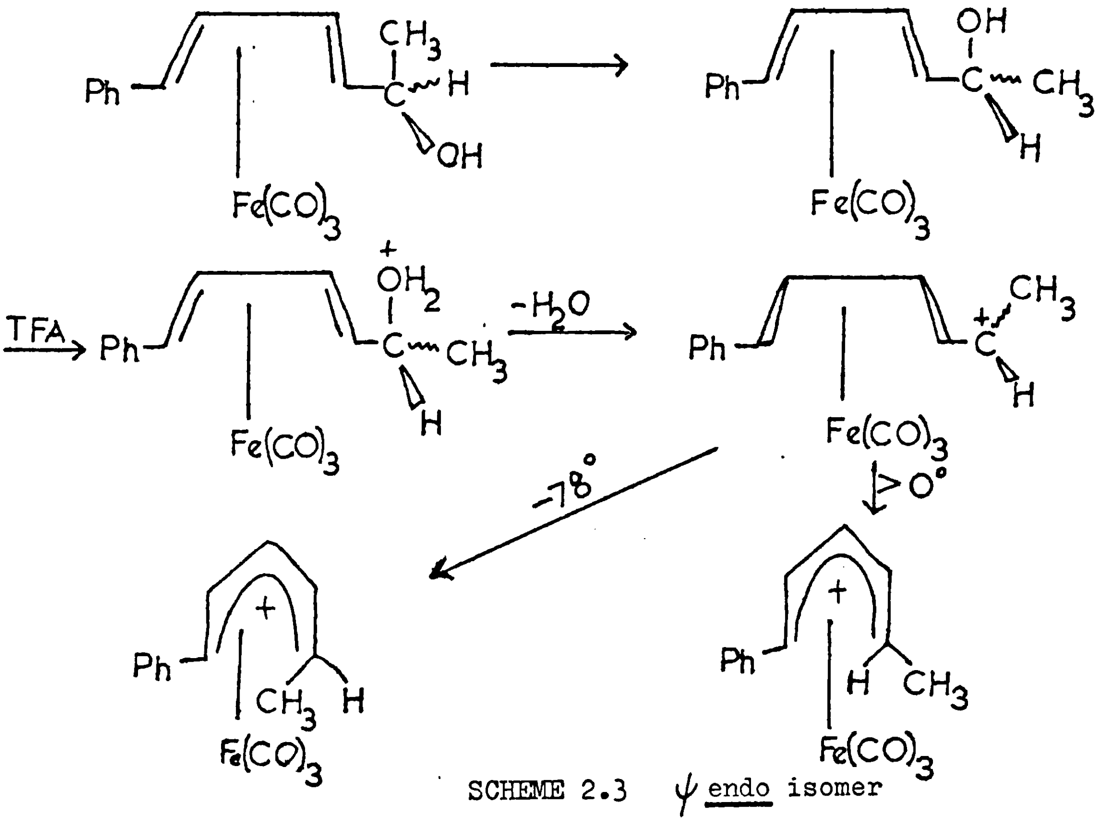
4) At low temperature, each isomer is converted stereospecifically to a different dienyl cation, but at room temperature, only one product is formed.

On the basis of the above results, a mechanism is proposed for the reaction of each isomer. These are shown in scheme 2.2 and in scheme 2.3 for the ψ exo and ψ endo isomers respectively. The first step in each case is the protonation of the alcoholic oxygen atom exo to the $Fe(CO)_3$ group. Loss of water generates a different trans ion in each case. These rearrange by rotation of the C_3–C_4 bond to form the observed cis pentadienyl cations at low temperature. At higher temperatures, the trans ion from the ψ endo complex rearranges to the more stable trans ion from the ψ exo complex. Hence, under these conditions, only one product, the cis,syn,syn pentadienyl cation, is observed.

In discussing the above mechanism, it is convenient to examine first the stereochemistry of the (dienol) iron tricarbonyl complexes. The steric interactions in these compounds have been

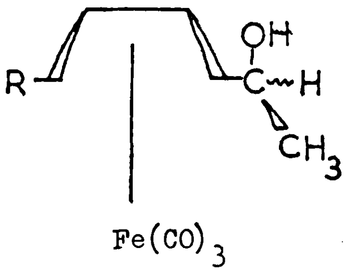


SCHEME 2.2 ψ exo isomer

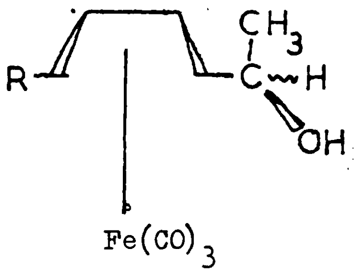


SCHEME 2.3 ψ endo isomer

considered in some detail by Clinton and Lillya,[23] who suggested that steric interactions involving the dienol ligand and terminal carbonyl groups on iron were of primary importance in determining conformation. By use of scale models, the most stable conformation of each isomer was found, and these are shown as (2.7) and (2.8) for ψ exo and ψ endo respectively.



(2.7)

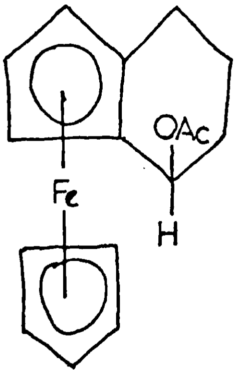


(2.8)

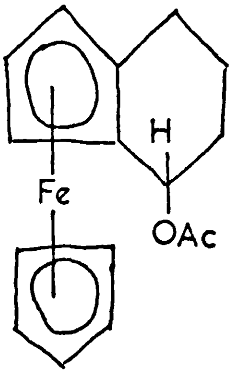
The existence of a preferred stereochemistry was demonstrated by the rates of solvolysis of the 3,5-dinitrobenzoate esters of (2.7) and (2.8) which showed large ψexo-/ ψ endo-rate ratios in the order of 100 for both methyl and phenyl substituted complexes.[22,23,24] The products showed complete retention of configuration in all cases except for 2.8 (R = Ph) where 3% inversion occurred. The mechanism proposed suggested that the 3,5-dinitrobenzoate ion departs exo to the iron after S_N1 alkyl oxygen fission, thus requiring (2.8) to rotate to a less stable conformation for solvolysis to take place. The cationic intermediates, drawn as trans ions similar to those in schemes 2.2 and 2.3, were then attacked by water exo to the iron to give alcohols without loss of configuration. Further results[25] from the solvolysis of the sterically more restricted ester of (4-methylhepta-3,5-dien-2-ol) iron tricarbonyl showed an even larger ψ*exo*-/ ψ *endo* rate ratio of 2500, providing more evidence for restricted rotation in the C_2-C_3 bond of the dienol complexes.

It has been suggested that the original stereochemical assignment in the dienol esters made by Clinton and Lillya is incorrect. An n m r spectroscopic study of the corresponding alcohols using lanthanide shift reagents gave results which were more consistent with a reversal of the ψ *exo* and ψ *endo* labels.[26] However it was stressed that as the application of these reagents to organometallic compounds was novel, the interpretation of the data may be in question and that only an X-ray structure determination would decide the stereochemistry unequivocally. If Foreman's assignment is indeed correct, then the ψ *endo* ester is the more reactive isomer. Protonation of the alcohol complexes could proceed via the iron atom to give *endo* protonation. To preserve the known stereochemistry of the cationic product, loss of water must also be *endo* to iron rather than a more usual *exo* departure of the leaving group.

Departure of the leaving group *exo* to the metal atom has been confirmed in cyclic systems, where the stereochemistry is more rigid. For instance, in the hydrolysis of the *exo* and *endo*-isomers of (α acetoxy 1,2-tetramethylene) ferrocene (2.9 a,b), the *exo* isomer was more readily solvolysed by a factor of 2500.[32] The product in each case was exclusively the *exo* alcohol, indicating that it is necessary for the iron atom to interact directly with the α-position.

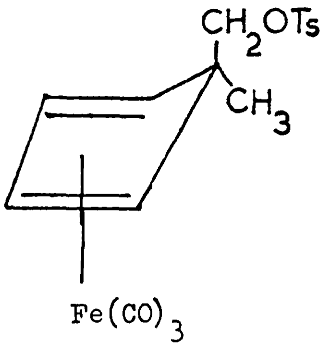


(2.9a)

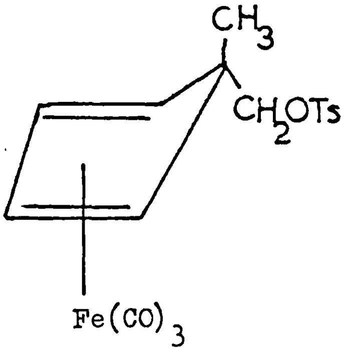


(2.9b)

A more extreme case was observed in the heterolysis of [5-endo-methyl-5-exo-(tosyloxymethyl) cyclopentadiene] iron tricarbonyl (2.10a) in a solution of tetrafluoroboric acid in acetic anhydride. Loss of tosylate ion, followed by ring expansion yielded (1-methyl cyclohexadienyl) iron tricarbonyl. In contrast, the geometrical isomer [5-exo-methyl-5-endo (tosyloxymethyl) cyclopentadiene] iron tricarbonyl (2.10b) did not undergo ring expansion, but decomposed slowly to iron II salts with the loss of carbon monoxide.[33]

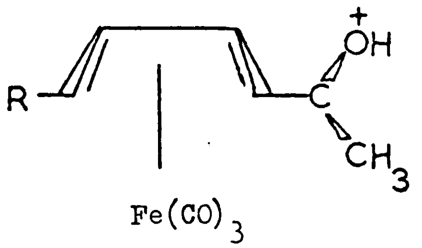


(2.10a)

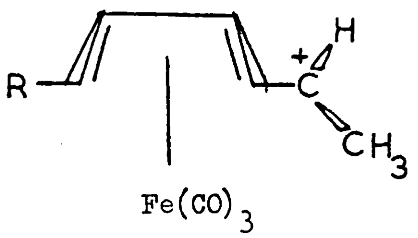


(2.10b)

It has been suggested that the esters of trans,trans(dienol) iron tricarbonyl complexes exhibit reactivity similar to that of ferrocenyl carbinyl esters.[34] The solvolysis reactions proceed by departure of the leaving group exo to iron and with retention of configuration in each case. The mechanisms of stabilization of the cationic intermediates in the reaction were discussed with reference to the n.m r spectra of the corresponding protonated ketones. For instance the protonated dienone (2.11) was used as a model for the trans ion (2.12). The n m r. shift data were interpreted as

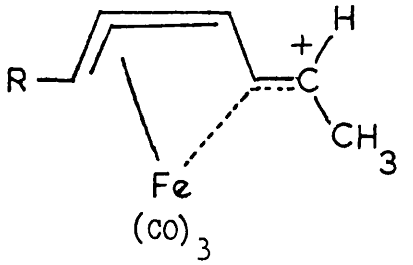


(2.11)

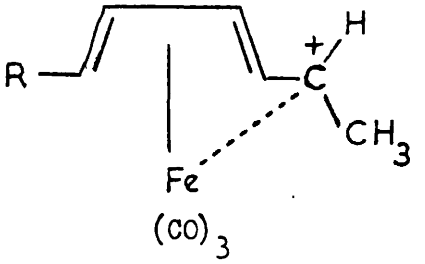


(2.12)

favouring iron-carbon hyperconjugation as in (2.13a) rather than direct overlap of the empty p orbital on the terminal carbon with a non-bonding orbital on iron (2.13b) for both diene and ferrocenyl complexes.

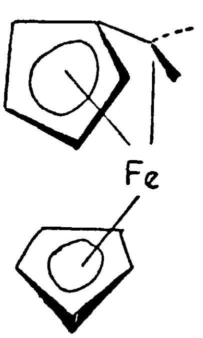


(2.13a)

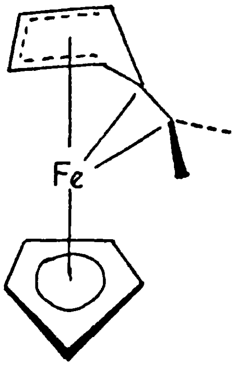


(2.13b)

The mode of bonding in ferrocenylalkylium ions was also discussed in some detail by Turbitt and Watts,[35,36] who tended to favour a distorted ring system with some degree of direct bonding between iron and the terminal carbon as in (2.14a,b). The ions were generated stereospecifically from 1-hydroxyalkylferrocenes in trifluoroacetic acid solution. The two isomers of (1-methylferrocenyl)

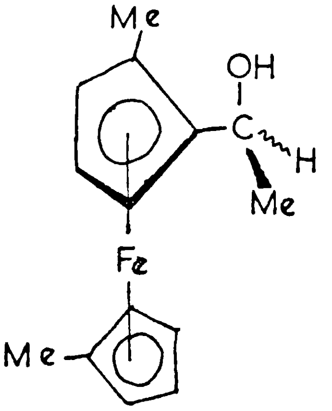


(2.14a)

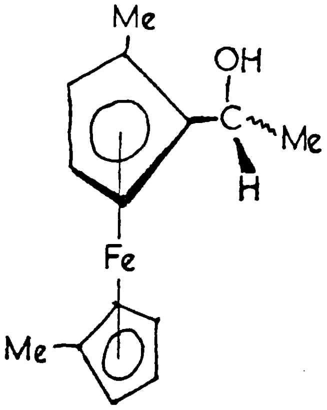


(2.14b)

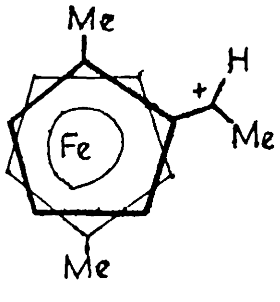
ethanol (2.15a, b) generated different ferrocenyl cations (2.16 a,b) in equilibrium. The equilibrium constant was greater than 32 favouring (2.16a). This strongly resembles the reaction of



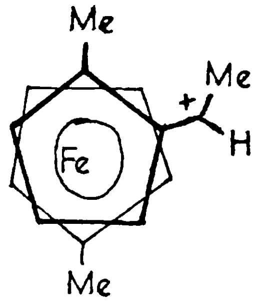
(2.15a)



(2.15b)



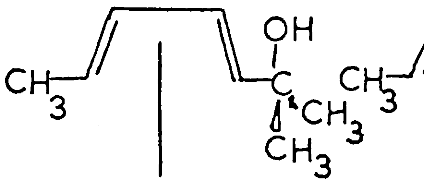
(2.16a)



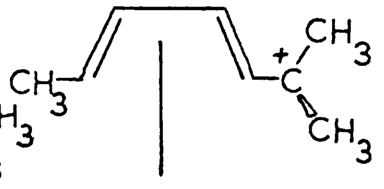
(2.16b)

(2-methylhepta-3,5-dien-2-ol) iron tricarbonyl (2.17) with fluorosulphonic acid at low temperature,[27] except that in this case, the <u>trans</u> ion (2.18) could rearrange to a <u>cis</u> pentadienyl cation (2.19).

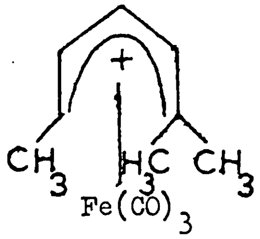
The equilibrium position lay on the side of the trans ion at -50°. Such a rearrangement is not possible in the cyclic system (2.16).



(2.17)

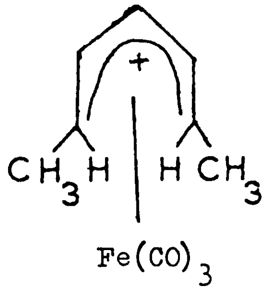


(2.18)

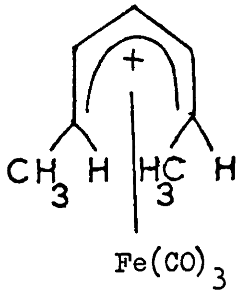


(2.19)

The difference between the stability of the cis and the trans pentadienyl cations was increased in the ions formed from (hepta-3,5-dien-2-ol) iron tricarbonyl where no trans ion was detected at low temperature. This was attributed to two main factors. Firstly, steric effects of the anti methyl group would tend to destabilize (2.19) over a cis ion containing only syn substitutents. This has been demonstrated by the two ions (2.20 a,b), differing only in the syn,anti configurations of the methyl substituents, which were both stable at low temperature but only



(2.20a)



(2.20b)

(2.20a) was stable at room temperature.[27] Secondly, if the charge density at C_2 is greater in the *trans* ion than in the *cis* ion, then greater stabilization results in (2.18) with a tertiary carbon at the 2 position than in a *trans* ion from (hepta-3,5-dien-2-ol) with a secondary carbon at the 2 position.

Thus, it is reasonable to expect that the two *trans* ions postulated in the protonation of the isomers of (6-phenylhexa-3,5-dien-2-ol) iron tricarbonyl would not be detected at low temperature, but would form two different *cis* pentadienyl cations. At higher temperatures, only the thermodynamically more stable *cis* syn,syn cation would be isolated from both isomeric alcohols. Formation of this cation from the ψ *endo* alcohol could be via two possible mechanisms - from interconversion of the *trans* ions or from a small concentration of the *cis*,syn,anti cation.

In conclusion, the kinetic data and products formed in the reaction of the ψ *endo* and ψ *exo* isomers of (6-phenylhexa-3,5-dien-2-ol) iron tricarbonyl with acid are consistent with initial protonation of the alcoholic oxygen, followed by stereospecific elimination of water *exo* to iron to generate two *trans* pentadienyl cations. These ions are stabilized by direct participation of iron and are reactive intermediates, rapidly forming two *cis* pentadienyl cations at low temperature. At room temperature, only the thermodynamically more stable *cis*,syn,syn(1-methyl,5-phenyl pentadienyl)iron tricarbonyl complex is isolated. As each step is reversible, the reaction tends to an equilibrium position determined by the concentration of acid in solution.

D: EXPERIMENTAL

(i) Materials.

ψ exo and ψ endo (6-phenylhexa-3,5-dien-2-ol) iron tricarbonyl. Both complexes were prepared by the method of Clinton and Lillya.[23] Purification was by repeated recrystallization from 60–80° petroleum ether.

Nitromethane

Nitromethane (B.D.H.) was purified by a method based on that of Olah.[37] Nitromethane (1 dm^3) was washed three times with 100 cm^3 aliquots of a solution containing sodium hydrogen carbonate (25 g) and sodium metabisulphite (25 g) in water (1 dm^3) followed by water (100 cm^3), 5% sulphuric acid (100 cm^3), water (100 cm^3) and sodium hydrogen carbonate solution (25 g dm^{-3}, 100 cm^3). The wet nitromethane was dried with anhydrous sodium sulphate followed by magnesium sulphate (dried). Final removal of water was with activated "Drierite" followed by filtration through a 60 cm column of 1/8" activated molecular sieves (4 Å). The dried solvent was distilled at reduced pressure through a 500 cm Vigreux column under an atmosphere of dry nitrogen. b.p. 57°/156 mm Hg.

Trifluoroacetic acid

Trifluoroacetic acid (Koch Light) (100 cm^3) and trifluoroacetic anhydride (Koch Light) (20 cm^3) were stood under nitrogen overnight before being fractionated through a 150 cm Vigreux column. The fraction 70.5 – 71.0° was collected, and stored under nitrogen in greaseless apparatus. [lit. b.p. 71°/741 mm Hg].

Fluorosulphonic acid

Fluorosulphonic acid (Merck) was purified by distillation into a cold trap in liquid nitrogen in vacuo using greaseless apparatus. Manipulations with the compound were performed in a glove box under an atmosphere of dry nitrogen.

(ii) Kinetic Procedure.

Fresh solutions of the dienol complexes and of trifluoroacetic acid in dry nitromethane were made prior to each kinetic run. Particular attention was paid to ensure that all glassware was dry. An aliquot (5 cm^3) of each reactant was pipetted into a 10 cm^3 volumetric flask. The solution was mixed and a sample quickly placed in an infrared cell fitted with calcium fluoride windows. (In preliminary experiments, it was found that potassium bromide cell windows were unsatisfactory as the surface slowly became coated with potassium tetrafluoroborate on contact with solutions of *cis*, syn,syn (1-methyl, 5-phenyl) pentadienyl iron tricarbonyl tetrafluoroborate in nitromethane). The reference solution was trifluoroacetic acid in nitromethane,at the same concentration as the reaction solution. The infrared spectrum was repeatedly scanned across the region 2200-1900 cm^{-1} using a Perkin Elmer 337 double beam spectrometer. The concentration of *cis*,syn,syn (1-methyl, 5-phenyl) pentadienyl iron tricarbonyl trifluoroacetate in solution was determined directly from the intensity of the 2105 cm^{-1} carbonyl band as this complex was found to obey Beer's Law.

(iii) Low temperature preparation of pentadienyl complexes.

Solutions of each isomer of (6-phenylhexa-3,5-dien-2-ol) iron tricarbonyl were prepared at low temperature using the apparatus shown in figure 2.4. Fluorosulphonic acid (2.5 g, 25 mmol) was placed in the n m r tube by syringe, and a phial containing the dienol complex (0.20 g, 0.64 mmol) placed in the large tube, followed by a small amount of tetramethylsilane (~ 0.1 ml). The apparatus was immersed in a solid CO_2/acetone bath, and evacuated. Sulphur dioxide (~ 5 ml) was condensed into the apparatus. The reagents were rapidly mixed at -78° by tipping the acid from the side arm. The n.m r. tube was finally filled by decantation and sealed off at -60°. The n m r. spectrum was recorded at -60° within about 5 minutes of mixing in a Varian HA-100 spectrometer fitted with a variable temperature probe.

(iv) Computer Program

A Fortran computer program was used to calculate the equilibrium position and rate of attainment of equilibrium in the kinetic experiments. This is shown below.

```
         PROGRAM FSTP (INPUT,OUTPUT)
C             CALC OF FIRST ORDER PLOT
         DIMENSION X(75),Y(75),Z(75),YOB (75)
         READ (1,1) NO
         DO 25 NUT = 1,NO
         READ (1,1)N
1        FORMAT (I2)
         WRITE (3,10)N
10       FORMAT(//15X,*NUMBER OF POINTS IS*,I2)
         DO 55  I=1,N
         READ (1,2) X(I),Z(I)
2        FORMAT (2F10.0)
55       CONTINUE
         READ (1,4) CON
         READ (1,4)CONMAX
4        FORMAT (F10.0)
75       CONTINUE
         WRITE (3,5) CON
5        FORMAT(//15X,*EQUILIBRIUM POSITION IS *,E10.4)
         DO 15 I=1,N
         DENS=2.0-ALOG10(Z(I))
         CONC=DENS/ 1.155
         YOB(I)=CON/(CON-CONC)
         IF (YOB(I)).LE.0.0 ) GO TO 85
         Y(I)=ALOG10(YOB(I))
15       CONTINUE
C        LEAST SQUARES ANALYSIS
         SX=0.0
         SY=0.0
         SXY=0.0
         SX2=0.0
         XN=N
         DO 35 I = 1,N
         SX=SX+X(I)
         SY=SY+Y(I)
         SXY=SXY+X(I)*Y(I)
         SX2=SX2+X(I)**2
35       CONTINUE
         A=(SX*SXY-SY*SX2)/(SX**2-XN*SX2)
         B=(SX*SY-XN*SXY)/(SX**2-XN*SX2)
         WRITE (3,30)A
         WRITE (3,40)B
30       FORMAT (15X,*INTERCEPT=*,E14.6)
40       FORMAT (15X,*GRADIENT=*,E14.6)
         E=0.0
         DO 45 I =1,N
         YCALC=A+B*X(I)
         E=E+(Y(I)-YCALC)**2
45       CONTINUE
         ERR=SQRT(F/(XN-1.0))
         ERRA=ERR*SX2/(XN*SX2-SX**2)
         G=ABS(XN*SX2-SX**2)
         ERRB=ERR*XN**0.5/SQRT(G)
         WRITE (3,50)ERRA,ERRB
```

```
50      FORMAT (15X,*ERROR IN INTERCEPT=*,F9.6,5X,*ERROR*
       C* IN GRADIENT = *,F9.6
        ERRC=ABS(ERRB*200.0/B)
        WRITE(3,60)ERRC
60      FORMAT (15X,*PERCENT ERROR IN GRADIENT=*F10.6)
85      CONTINUE
        CON=CON+0.005
        IF(CON.G.E.CONMAX)GO TO 25
        GO TO 75
25      CONTINUE
        STOP
        END.
```

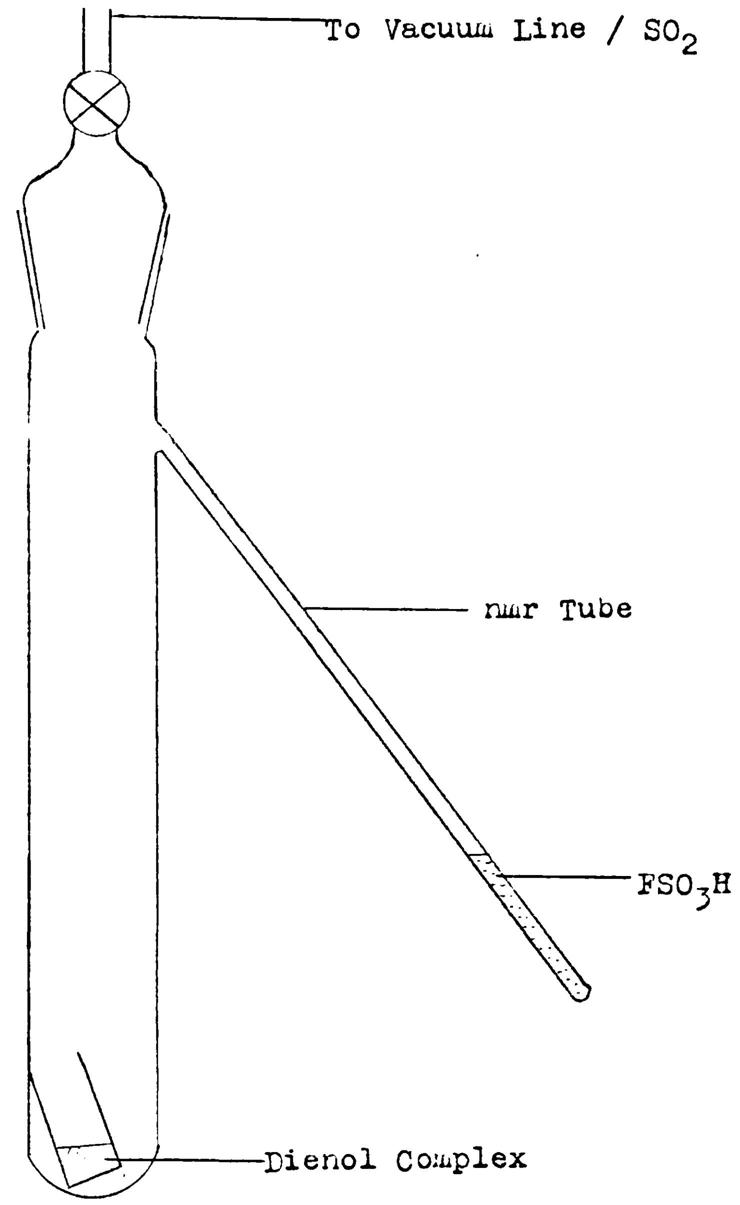


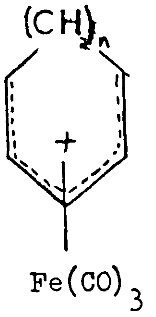
FIG 2.4 Low Temperature Reaction Vessel

CHAPTER 3

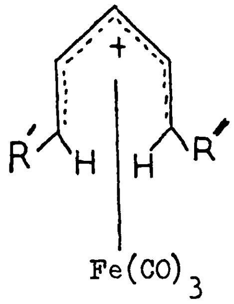
Kinetics of the reaction of Pentadienyl iron tricarbonyl cations with nucleophiles

A: INTRODUCTION

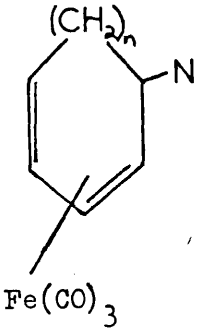
Both cyclic (3.1) and acyclic (3.2) (dienyl) iron tricarbonyl cations are susceptible to attack by nucleophiles (N) to yield substituted diene complexes (3.3) and (3.4).



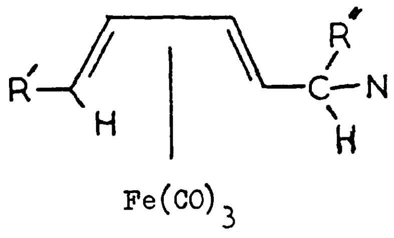
(3.1)



(3.2)



(3.3)



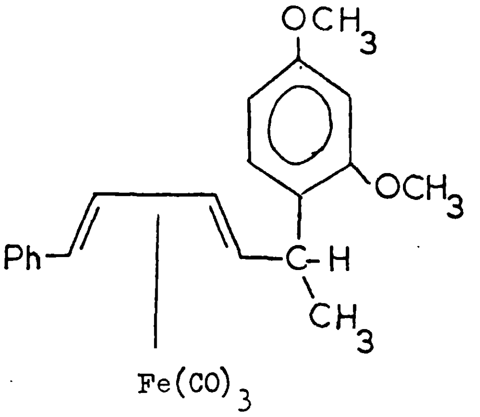
(3.4)

In the case of cyclic ligands, reaction with cyanide, alkoxide, hydride and the acetylacetonate anion[38,39] have been reported. The last reaction has also been studied kinetically,[40] and a mechanism was proposed which involved attack on the coordinated ligand by the anion. Analogous reactions for complexes with acyclic ligands have been outlined in Chapter 1.

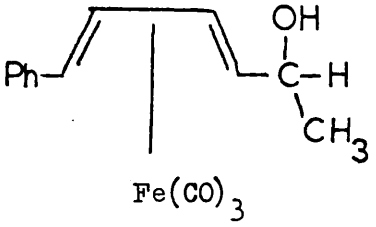
B: RESULTS

I Reaction of Pentadienyl Iron Tricarbonyl Complexes with Activated Arenes.

The (1-methyl, 5-phenyl) derivative of (3.2) reacted with 1,3-dimethoxybenzene to give a complex (3.5) which was isolated in low yield. The trans, trans structure was confirmed by nmr



(3.5)



(3.6)

spectroscopy and by elemental analysis. The product from reaction with water (3.6) also had a trans, trans structure. Substitution on the arene ring took place exclusively at the 4 position, ortho to one methoxy group and para to the other. This is consistent with the normal ortho, para directing properties of methoxy benzenes.[41] Under forcing conditions, using an excess of P.I.T., another complex was observed on trace amounts with thin layer chromatographic analysis. By using preparative tlc, a sufficient quantity of sample was isolated for its nmr spectrum to be recorded. This was very similar to the spectrum of (3.5), though an integral indicated that the complex contained 4,6-disubstituted arene ring formed from attack of (3.5) by a further molecule of P.I.T. No 2- or 5-substituted dimethoxybenzene derivatives were observed.

Products analogous to (3.5) were isolated with (1,5-dimethyl) P.I.T. and (1,5-diphenyl) P.I.T. The structures were again confirmed by elemental analysis and by nmr spectra. The yields were low (15-20%) because of losses in working up of the products, as separation of 1,4-dimethoxybenzene from (3.5) proved difficult, except with the 1,5-diphenyl derivative, when the yield was 55%. However, the reaction appeared to go to completion and give only one product when carried out with dilute solutions in nitromethane, though separation of this mixture proved impractical.

A simple test was used to determine whether an arene was attacked by P.I.T. complexes. The complex used was (1-methyl, 5-phenyl) P.I.T. because it was found to react quickly with 1,3-dimethoxybenzene A 10^{-2}M solution in dry nitromethane was added to a ten-fold excess of arene and the solution degassed. The infrared spectrum between 2200 and 1900 cm^{-1} was measured periodically, and the concentration of P.I.T. found from its carbonyl stretching frequency at 2105 cm^{-1}. If a reaction occurred, new carbonyl bands characteristic of (diene) iron tricarbonyl complexes appeared at 2000 and 1900 cm^{-1}. No reaction was observed with methoxybenzene or 1,3,5-trimethylbenzene. 1,2-Dimethoxybenzene reacted approximately sixty times slower than 1,3-dimethoxybenzene and 1,4-dimethoxybenzene slower still by a factor of at least two. This is consistent with the structures of these aromatic compounds, 1,2-dmb having two ortho, meta and two para, meta positions compared with 1,4-dmb with four ortho, meta positions. As would be expected, 1,3,5-trimethoxybenzene reacted somewhat faster than 1,3-dmb (see p.79). With indole, formation of the products was very rapid, and reached 95% completion in only two minutes.

Kane-Maguire has recently reported similar electrophilic substitution with (cyclohexadienyl) iron tricarbonyl tetrafluoroborate.[42,43] It attacked a number of activated arenes including indole derivatives, pyrrole and thiophene to give products of the type (3.3). Indole was shown by 'H nmr spectroscopy to be substituted at the 3 position which is the most active site for electrophilic attack. 1,3,5-Trimethoxybenzene and 1,3-dimethoxybenzene also reacted with the cyclic dienyl salt.[43] The kinetics of substitution were also investigated and found to be first order in each reactant.

The reaction of open chain P.I.T. complexes with arenes was studied kinetically in order to throw some light on the reactivity of these compounds. The main effort was on measuring the rates of reaction of different P.I.T. complexes with 1,3-dmb to investigate the effect of substituents. This particular substrate was used as it reacted with the P.I.T. complexes at a reasonable rate to follow by infrared spectroscopy. In each case, dry nitromethane was the solvent for the reaction, as it dissolved both the P.I.T. complexes and the arenes without decomposition. Other solvents were unsatisfactory as they either did not dissolve the reagents or reacted with them. For instance, solvents of low polarity such as petroleum ether and diethyl ether were in the former category while methanol and methyl cyanide were in the latter.

The kinetic results are divided into five sections. Reactions obeying similar rate laws are grouped together.

(a) Reaction of 1,3-dimethoxybenzene with (1,5-dimethyl)- and (1,3,5-trimethyl) pentadienyl iron tricarbonyl tetrafluoroborate.

The reactions were followed under pseudo first order conditions with at least a ten-fold excess of dimethoxybenzene. The concentration of P.I.T. complex was 0.01M in order to give an optical density of about one for the 2105 cm^{-1} carbonyl peak when measured in an i.r. cell with a path length of 0.5 mm. The rate of reaction was determined by the disappearance of this peak. The product in each case had a strong carbonyl peak at 2035 cm^{-1} and a broader peak at 1960 cm^{-1}. As nitromethane absorbs at ca. 2000 cm^{-1}, the product peaks could not be used to monitor the reaction.

Preliminary measurements with (1,5-dimethyl) P.I.T. and 0.5M 1,3-dmb indicated a half-life of only 24 minutes for the reaction. As this was too fast to follow by a sampling technique, a thermostatted i.r. cell was used as the reaction vessel. The concentration of P.I.T. was determined directly by running an i.r. spectrum between 2200 and 1900 cm^{-1}. The technique used is described in the experimental section as "method A".

The results were found to fit a pseudo first order rate equation, giving a straight line graph for $\log_{10}(a/(a-x))$ against time, where a is the initial concentration of P.I.T., and x is the concentration at time t. A noteworthy feature of the graph was that it did not go through the origin. A small intercept on the y axis was found in every kinetic run. This represented a concentration of approximately 0.0095M P.I.T., though this varied between runs. A typical plot is shown in graph 3.1. The intercept was not removed by further drying of solvents or purification of materials, and appeared a genuine feature of the reaction. It was interpreted by assuming there was an initial rapid reaction which was over in less than two minutes, followed by a slower one which was observed.

The order of reaction was determined by carrying out a series of kinetic runs with different concentrations of 1,3-dmb. Good first order plots were obtained when the excess of arene over P.I.T. complex was between ten and sixty times. Runs were done in duplicate and were reproducible to within 5%. Gradients were computed by a least squares analysis and were used to calculate the pseudo rate constants (k_{obs}). Values of k_{obs} found at each concentration of 1,3-dmb are shown in Table 3.1.

TABLE 3.1

Reaction of (1,5-dimethyl) P.I.T. (0.01M) with 1,3-dmb in nitromethane at 25.0°C

Concentration of 1,3-dmb [M]	k_{obs} $sec^{-1} x 10^4$
0.10	0.98
0.20	2.1
0.40	4.6
0.50	4.9
0.60	6.4

The linear dependence of the rate on the concentration of 1,3-dmb is shown in graph 3.2. The slope of this graph was used to calculate the second order rate constant of the reaction. The overall rate equation of the reaction was consistent with:

$$\text{RATE} = k_2[\text{1,3-dmb}][\text{(1,5-dimethyl)P.I.T.}]$$

$$\text{where } k_2 = 1.1 \times 10^{-3}\ \text{dm}^3\text{mol}^{-1}\text{sec}^{-1}$$

(1,3,5-Trimethyl) P.I.T. was found to be less reactive than (1,5-dimethyl) P.I.T. towards 1,3-dmb. The half-life for the reaction of (1,3,5-trimethyl) P.I.T. (0.01M) with 1,3-dmb (0.5M) in nitromethane at 25.0° was almost 12 hrs. The rate of reaction was found by taking samples of solution and immediately running the i.r. spectra in order to determine the concentration of (1,3,5-trimethyl) P.I.T. This technique is described in the experimental section in "method B".

When a fifty-fold excess of 1,3-dmb was used, the reaction obeyed pseudo first order kinetics up to at least 75% reaction. However, because of a slight decomposition of (1,3,5-trimethyl) P.I.T. in nitromethane over a long period of time, only the first 40% reaction was followed with a ten-fold excess of 1,3-dmb. A typical pseudo first order plot is shown in graph 3.3. The main difference between this and the graph for (1,3-dimethyl) P.I.T. was that the line went through the origin.

The activation energy and activation entropy for this reaction were determined by observing the reaction rate at different temperatures. The reaction with a fifty-fold excess of 1,3-dmb was performed at 25.0°, 35.0° and at 45.0°. The order of reaction was found by using ten times excess of 1,3-dmb at 25.0° and 45.0°. Straight lines passing through the origin were observed at both temperatures (graph 3.4), indicating that the order did not change with temperature. Values of k_{obs} for each reaction are summarised in table 3.2. The error limit in these cases was estimated to be within 10% of the value quoted. Each run was done in duplicate, and the gradient of the pseudo first order plot calculated by using the method of least squares.

The activation energy of the reaction was calculated from the second order rate constants (k_2) derived from the data in table 3.2. The Arrhenius plot is shown in graph 3.5, where T is the absolute temperature. Least squares analysis of the points gave a gradient of -2.30×10^3 with an error of 12.6, which is equivalent to an

TABLE 3.2

Reaction of (1,3,5-trimethyl) P.I.T. (0.01M) with 1,3-dmb in nitromethane

Concentration of 1,3-dmb [M]	Temperature °C	k_{obs} $sec^{-1} \times 10^5$
0.10	25.0	0.33
0.50	25.0	1.6
0.50	35.0	3.1
0.10	45.0	1.1
0.50	45.0	4.9

activation energy of 44.0 ± 5.6 kJ mol^{-1}.

The activation entropy was calculated by using the equation:[44]

$$k_2 = \frac{kT}{h} \exp\left(-\Delta H^{\ddagger}/RT\right) \exp\left(\Delta S^{\ddagger}/R\right) C_B$$

where k_2 = second order rate constant.

C_B = concentration of 1,3-dmb.

T = absolute temperature

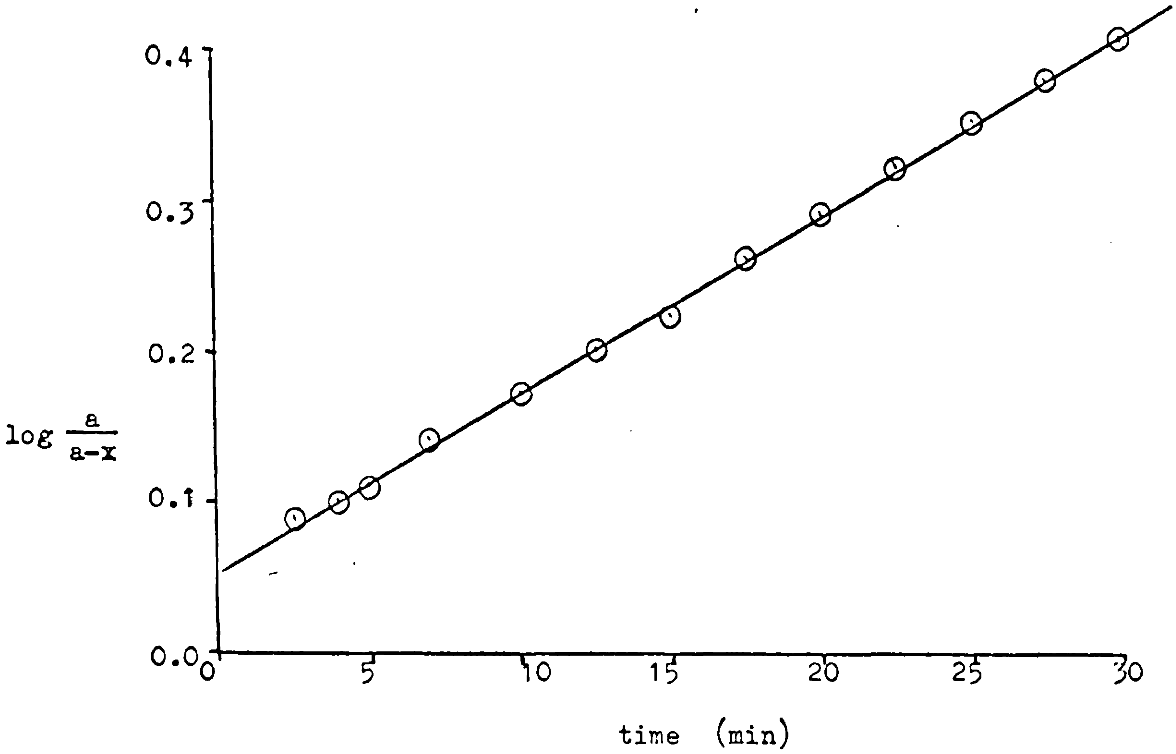
h = Planck's constant.

k = Boltzmann's constant.

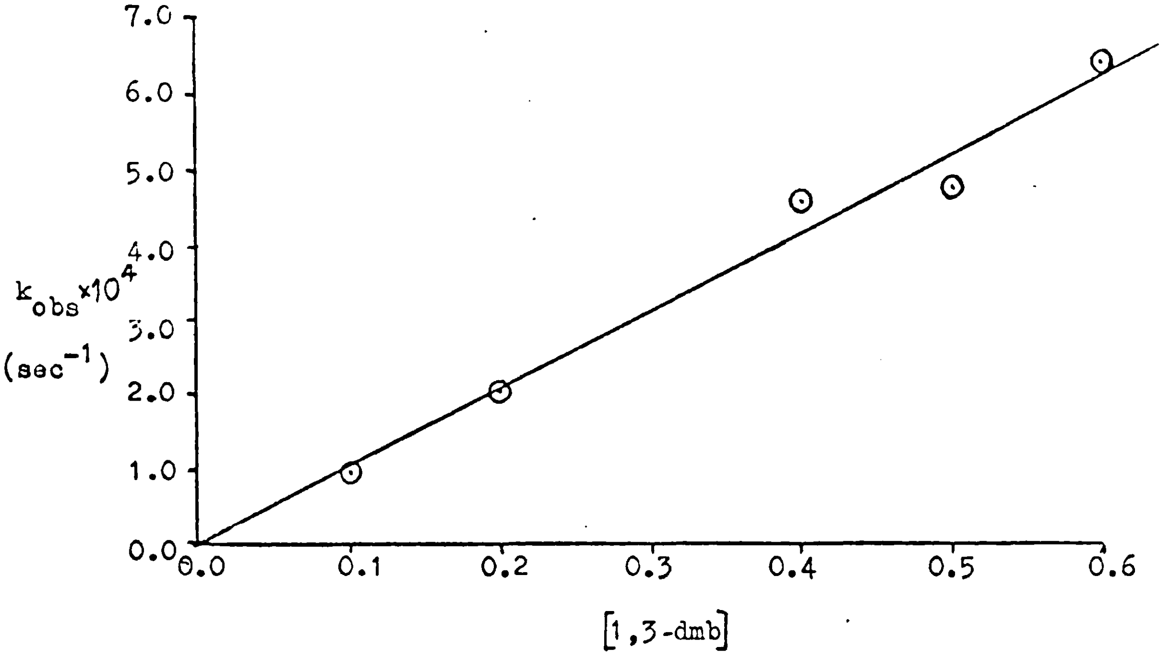
$\Delta H^{\ddagger}$ = Activation enthalpy.

$\Delta S^{\ddagger}$ = Activation entropy.

Using the data for the reaction at 25.0°C, the activation entropy $\Delta S^{\ddagger}$ was calculated as -189 ± 18 $JK^{-1}mol^{-1}$. The error was estimated from the error on the gradient of the Arrhenius plot.

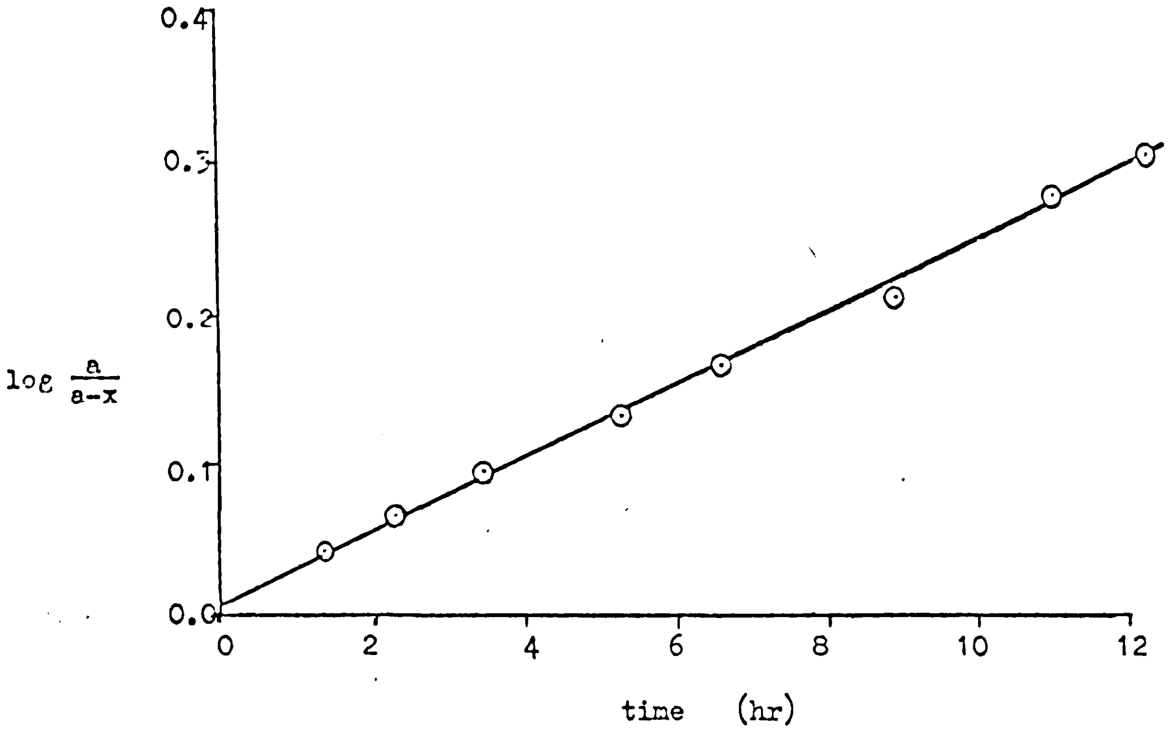


GRAPH 3.1 Reaction of (1,5-Dimethyl)P.I.T. (0.01M) with 1,3-dmb (0.50M) in nitromethane at 25.0°

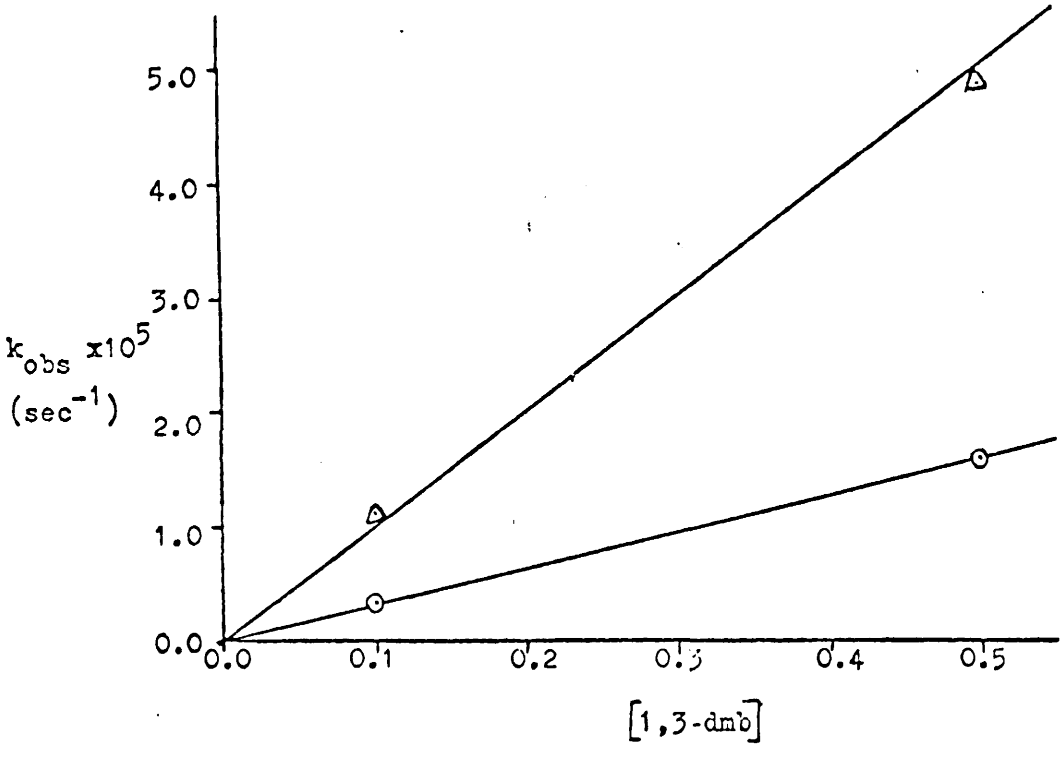


GRAPH 3.2 Reaction of (1,5-Dimethyl)P.I.T. (0.01M) with 1,3-dmb

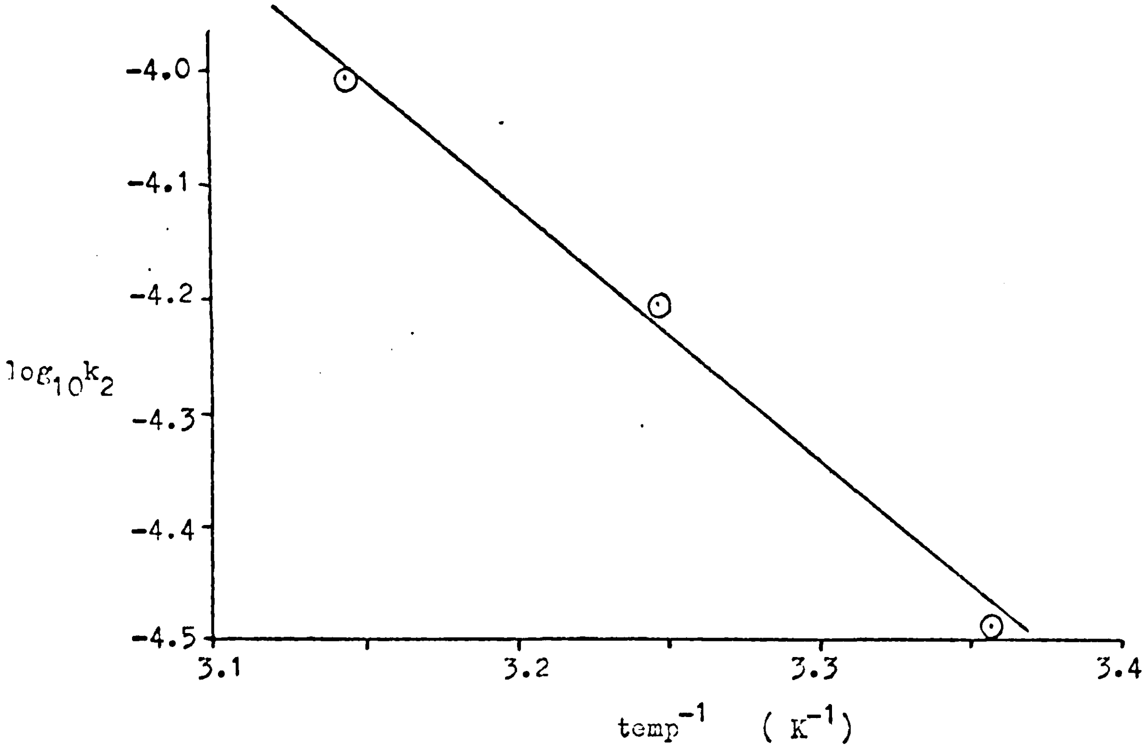
k_{obs} vs. [1,3-dmb]



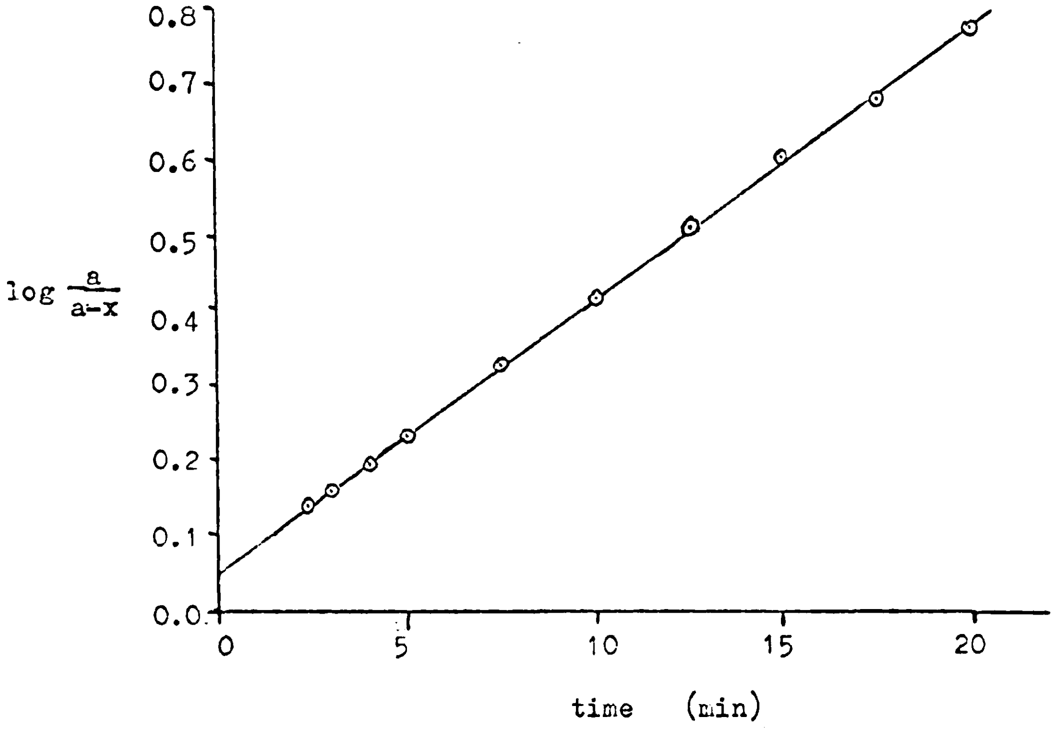
GRAPH 3.3 Reaction of (1,3,5-Trimethyl) P.I.T. (0.01M) with 1,3-dmb (0.50M) in nitromethane at 25.0°



GRAPH 3.4 Reaction of (1,3,5-Trimethyl) P.I.T. (0.01M) with 1,3-dmb at 25°(⊙), and at 45°(△)



GRAPH 3.5 Reaction of (1,3,5-Trimethyl) P.I.T. (0.01M) with 1,3-dmb
Arrhenius plot of $\log_{10}k_2$ against $temp^{-1}$



GRAPH 3.6 Reaction of (1-methyl,5-phenyl) P.I.T.(0.01M) with
1,3-dmb (0.50M) in nitromethane at 25°

(b) Reaction of 1,3-dimethoxybenzene with (1-methyl, 5-phenyl); (1,4-dimethyl, 5-phenyl) and (1-methyl)pentadienyl iron tricarbonyl tetrafluoroborate.

The reactions with all three complexes were fast, and so were followed by "method A" in the experimental section. They all gave good pseudo first order kinetics up to at least 70% reaction with an excess of 1,3-dmb. A typical plot for the reaction of (1-methyl, 5-phenyl) P.I.T. with fifty times excess of 1,3-dmb is shown in graph 3.6. The line did not go through the origin as was found with the kinetics of (1,5-dimethyl) P.I.T.

The order of reaction was more complex than those in section (a). A plot of k_{obs} against concentration of 1,3-dmb for the (1-methyl, 5 phenyl) cation was not a straight line characteristic of second order equations, but was a curve (graph 3.7). This suggests a series reaction, where a small quantity of intermediate reacts with the substrate, such that if the concentration of substrate is increased, the rate tends to a limit, as with enzyme kinetics[45] i.e.

$$A \underset{k-1}{\overset{k_1}{\rightleftharpoons}} B$$

$$B+C \xrightarrow{k_2} D$$

where A is the cation, which is in equilibrium with an intermediate B. B then reacts with C in a second order reaction to give D - the product . The differential rate equations are

$$\frac{d[A]}{dt} = -k_1[A] + k_2[B] \qquad (1)$$

$$\frac{d[B]}{dt} = k_1[A]-k_{-1}[B]-k_2[B][C] \qquad (2)$$

$$\frac{d[D]}{dt} = k_2[B][C] \qquad (3)$$

Assuming [B] reaches a steady state,

$$\frac{dB}{dt} = 0 \quad k_1[A] - k_{-1}[B] - k_2[B][C]$$

$$\therefore \quad [B] = \frac{k_1[A]}{k_{-1} + k_2[C]}$$

Substituting into equation (3)

$$\frac{d[D]}{dt} = \frac{k_1k_2[A][C]}{k_{-1} + k_2[C]}$$

$$= \frac{k_1\ k_2[A]}{k_{-1}/[C] + k_2} \quad = \text{Reaction rate R}$$

When [C] is very large, $k_{-1}/[C]$ becomes very small

$$\therefore \quad \frac{d[D]}{dt} = \frac{k_1\ k_2[A]}{k_2} = k_1[A] = R_{max.}$$

$$\therefore \quad \frac{d[D]}{dt} = \frac{k_2R_{max}}{k_{-1}/[C] + k_2} = R$$

$$\therefore \quad \frac{1}{R} = \frac{k_{-1}/[C] + k_2}{k_2R_{max.}} = \frac{k_{-1}}{k_2[C]\ R_{max.}} + \frac{1}{R_{max.}}$$

$$\text{i.e.,} \quad \frac{1}{R} \ \alpha \ \frac{1}{[C]}$$

A graph of $1/k_{obs}$ against $1/[C]$ – the concentration of 1,3-dmb was drawn (graph 3.8) for the reaction of (1-methyl, 5-phenyl) P.I.T. with 1,3-dmb in nitromethane and was found to be a straight line. The gradient and intercept were calculated by least squares. This gave a maximum value for k_{obs}, and so a value for $k_1/2.57 \times 10^{3}\ sec^{-1}$.

The error from the least squares calculation was only ± 2.6%, though each kinetic run had an estimated error of less than ± 5%. The ratio k_2/k_{-1} was $2.47M^{-1}$ ± 3.9%.

It was not possible to determine k_2 or k_{-1} separately by the above method, but an estimate was made using non-steady state equations for the series reaction.[46] The first method used k_1 and k_2/k_{-1} together with the k_{obs} values for each concentration of 1,3-dmb to calculate k_2 and so k_{-1}. Another constant K was determined which is the ratio of k_{-1}/k_1 and so is an equilibrium constant for the formation of B from A. The method is outlined in the appendix to this chapter. Though the errors were large, K was estimated to be in the order of 10-20, and k_2 approximately 10^{-1} $dm^3 mol.^{-1} sec^{-1}$.

A second method[47] was employed to check the above calculation. This used the intercept on the y axis at t=0 for the pseudo first order plot of a reaction and gave values of **K** and k_2 which were in close agreement to those derived by the first method.

The reaction of (1-methyl, 5-phenyl) P.I.T. was repeated using 1,3-dmb deuterated in the 2,4 and 6 positions. The rates of reaction were slower than with protio 1,3-dmb. The ratio of rates k_H/k_D was 1.68 with 50 times excess and 1.91 with 10 times excess of arene. This indicates a complex mechanism with one step not involving 1,3-dmb which is consistent with the reaction going via an intermediate which reacts with the arene in a second step.

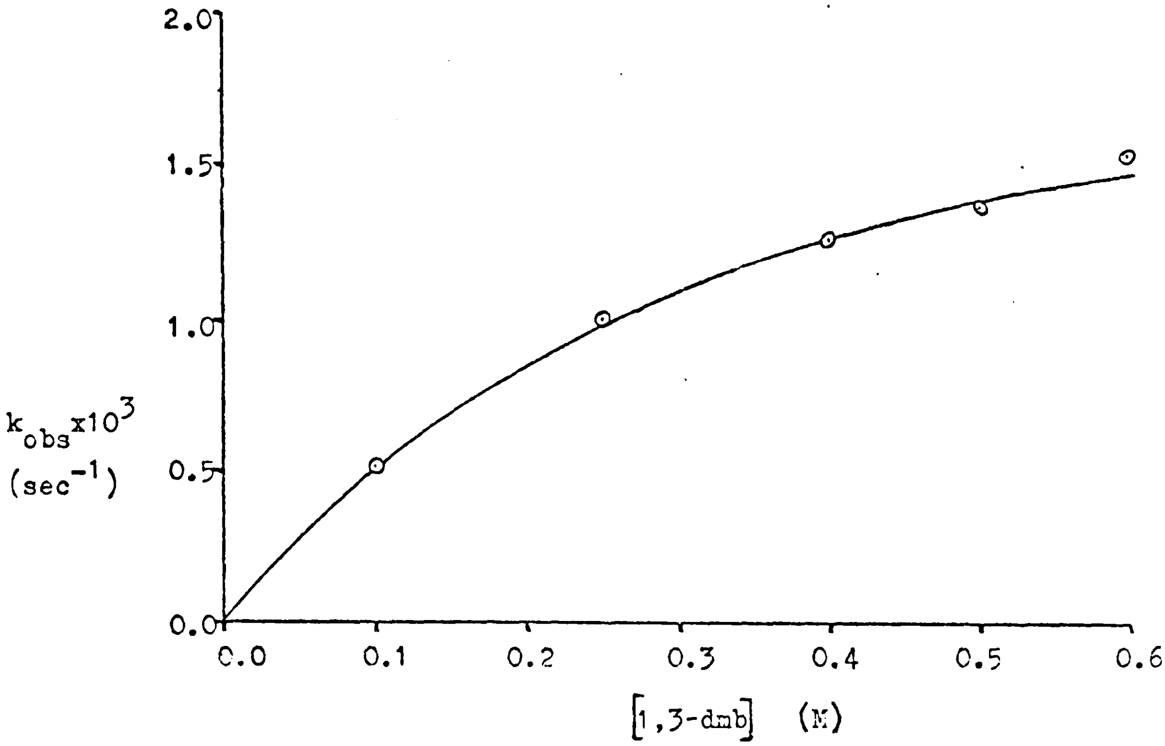
The kinetics of both (1,4-dimethyl, 5-phenyl) P.I.T. and (1-methyl) P.I.T. were very similar to (1-methyl, 5-phenyl) P.I.T. with 1,3-dmb. Reactions were first order in P.I.T. at all concentrations of 1,3-dmb used, and the k_{obs} values for all three complexes are shown in Table 3.3. The order of reaction with respect to 1,3-dmb was again found to be complicated, but reciprocal plots of k_{obs} against concentration of 1,3-dmb gave straight lines. The curve for (1,4-dimethyl, 5-phenyl) P.I.T. is shown in graph 3.9 and was used to calculate the maximum rate k_1 as 2.56×10^{-3} sec^{-1}, and the ratio k_2/k_{-1} as $2.84M^{-1}$. The plot for (1-methyl) P.I.T. is shown in graph 3.10, giving values of 3.22×10^{-3} sec^{-1} for k_1 and 1.43 mol^{-1} for k_2/k_{-1} for this reaction.

TABLE 3.3.

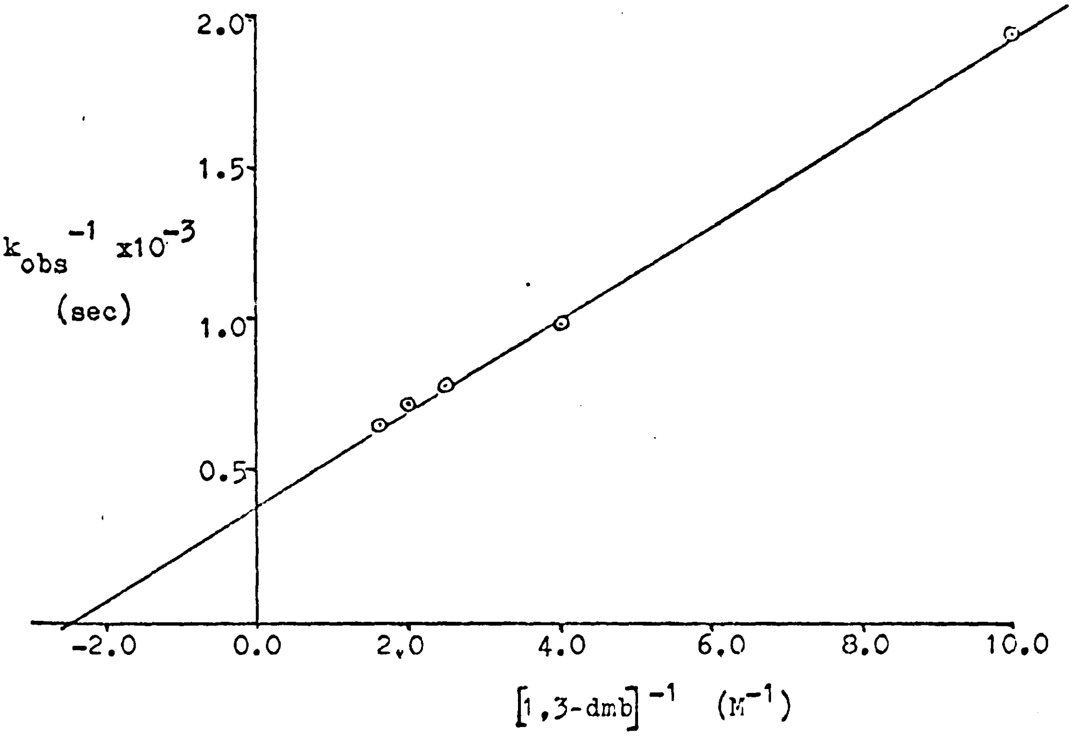
k_{obs} values for reaction of (1-methyl, 5-phenyl), (1,4-dimethyl, 5-phenyl) and (1-methyl) P.I.T. (0.01 mol) with 1,3-dmb in nitromethane at 25.0°

P.I.T. Complex	Concentration of 1,3-dmb [M]	k_{obs} $sec^{-1} \times 10^4$
1-methyl,5-phenyl)	0.10	5.09 (2.67)*
"	0.25	10.0
"	0.40	12.7
"	0.50	13.9 (8.24)*
"	0.60	15.5
(1,4-dimethyl, 5-phenyl)	0.10	5.68
	0.20	9.98
	0.40	14.0
	0.50	14.1
	0.60	15.7
(1-methyl)	0.10	4.00
"	0.20	7.29
"	0.50	12.5
"	0.60	15.6

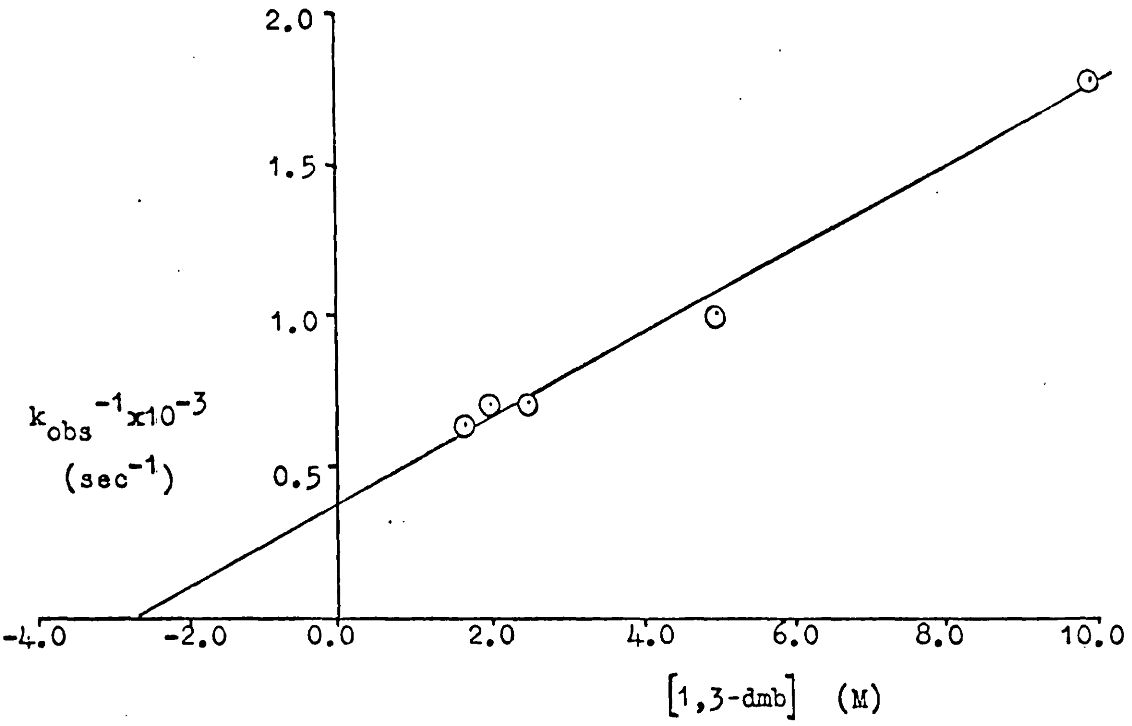
* figures in brackets are values with 2,4,6-deutero 1,3-dmb.



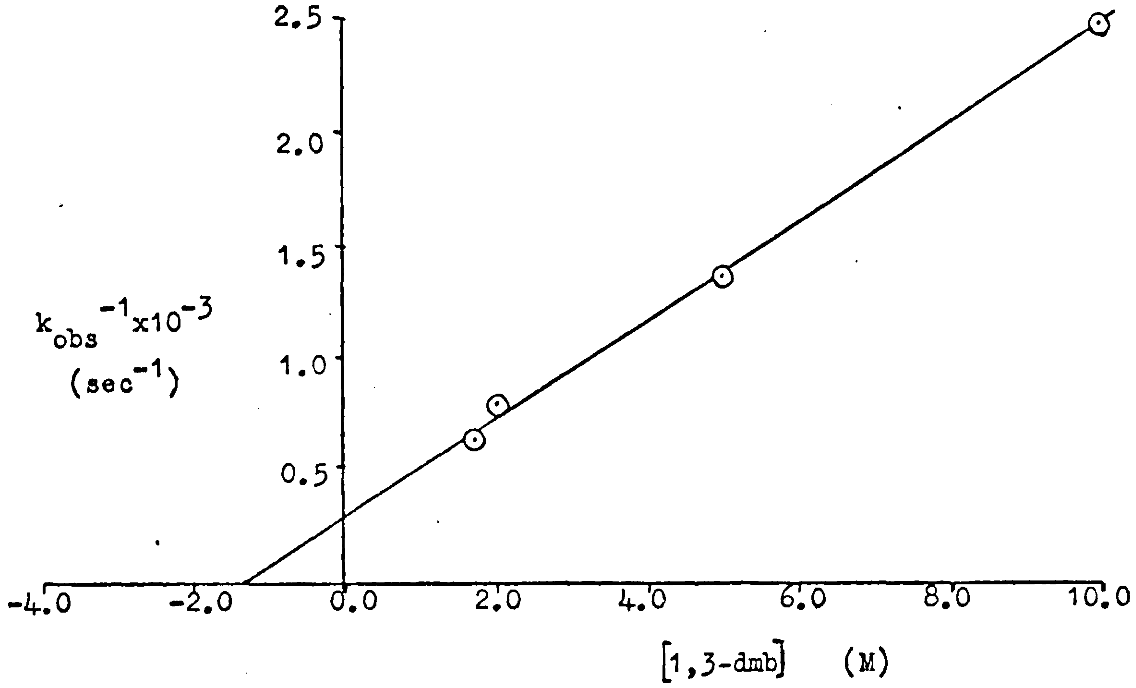
GRAPH 3.7 Reaction of (1-methyl,5-phenyl) PIT (0.01M) with 1,3 dmb: k_{obs} vs. [1,3-dmb]



GRAPH 3.8 Reaction of (1-methyl,5-phenyl) PIT (0.01M) with 1,3 dmb: k_{obs}^{-1} vs. [1,3-dmb]$^{-1}$



GRAPH 3.9 Reaction of (1,4-dimethyl,5-phenyl) PIT (0.01M) with 1,3-dmb: k_{obs}^{-1} vs. [1,3-dmb]



GRAPH 3.10 Reaction of (1-methyl) PIT (0.01M) with 1,3-dmb k_{obs}^{-1} vs. [1,3-dmb]

(c) Reaction of 1,3-dimethoxybenzene with (1,5-diphenyl)pentadienyl iron tricarbonyl tetrafluoroborate.

The kinetics of this reaction were found to be very different from those in sections (a) and (b). Previously, the reactions all went to completion by a process which was first order in P.I.T., but in this system an equilibrium was attained at a rate dependent on the concentration of 1,3-dmb. The position of equilibrium was also dependent on the concentration of 1,3-dmb being moved towards completion when a large excess was used. All reactions were followed in an i.r. cell by "method A".

The concentration/time curves from the reaction of (1,5-diphenyl) P.I.T. with a 20 and a 75-fold excess of 1,3-dmb are shown in graph 3.11 and graph 3.12 respectively. Curves with a similar shape were also obtained with both 10 and 50-fold excess of 1,3-dmb. The equilibrium position was found from the curve by inspection. It was not very sensitive to changes in the concentration of 1,3-dmb, going from 37% completion of reaction with 10 times excess to 31% with 50 times excess.

The reaction appeared to be of the form:-

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C$$

$$\therefore \quad \frac{-dA}{dt} = k_f[A][B] - k_r[C]$$

At $t = 0$ $A=a$, $B=b$, $C=0$.

At equilibrium, $a_e = a - x_e$, $b_e = b - x_e$, $c_e = x_e$.

$$\therefore \quad k_f(a-x_e)(b-x_e) = k_r x_e$$

$$\therefore \quad \frac{dx}{dt} = k_f\left[(a-x)(b-x) - \frac{(a-x_e)(b-x_e)}{x_e}\right]$$

If B is in large excess,

then $b \approx b - x$

$$\therefore \quad \frac{dx}{dt} = k_f b\left[(a-x) - \frac{a - x_e}{x_e}\right]$$

$$bk_f t = \int \frac{dx}{a - a_x/x_{eq}}$$

$$bk_f t = \frac{a}{x_{eq}} \ln \frac{x_{eq}}{x_{eq} - x}$$

A plot of $\log_{10} (x_{eq}/(x_{eq} - x))$ against t gave a straight line passing through the origin for each concentration of 1,3-dmb used. These are shown in graph 3.13 for 10 and 20 times excess and in graph 3.14 for 50 and 75 times excess of 1,3-dmb. The gradients (G) were computed by least squares analysis for each case. The equation above becomes:

$$2.303\ G = bk_f t\ \frac{x_{eq}}{a}$$

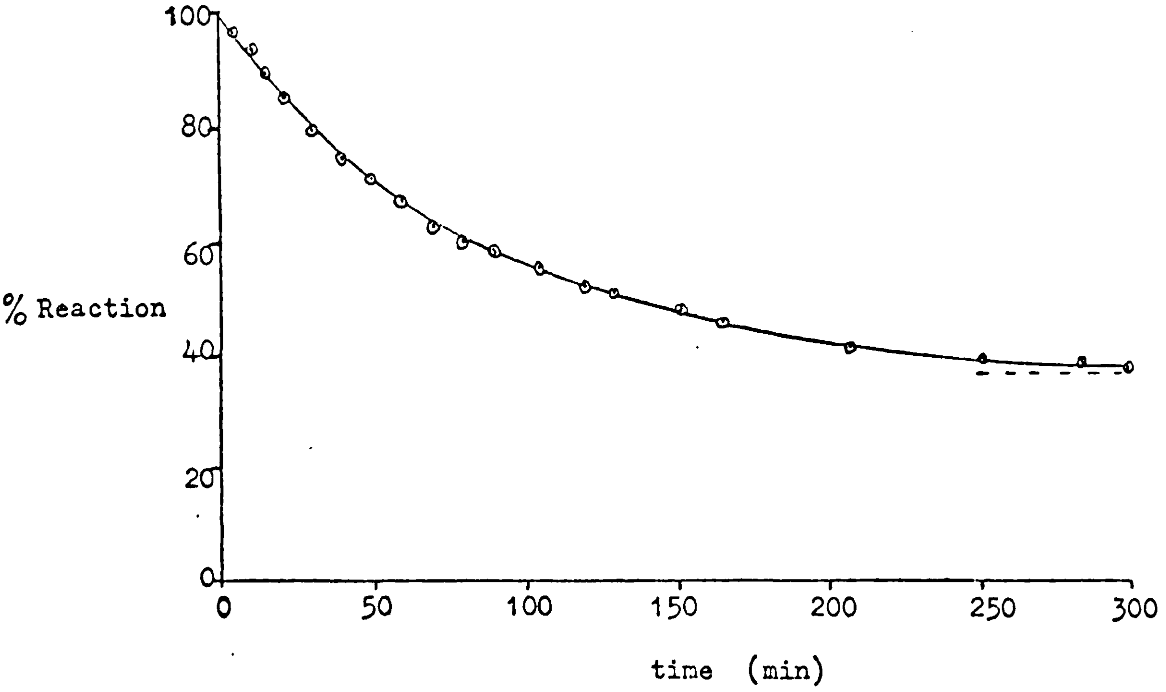
Values of 2.303 G and 2.303 Ga/x_{eq} for each concentration of 1,3-dmb are shown in table 3.4. A plot of 2.303 Ga/x_{eq} against G, the concentration of 1,3-dmb, was a straight line passing through the origin.

TABLE 3.4

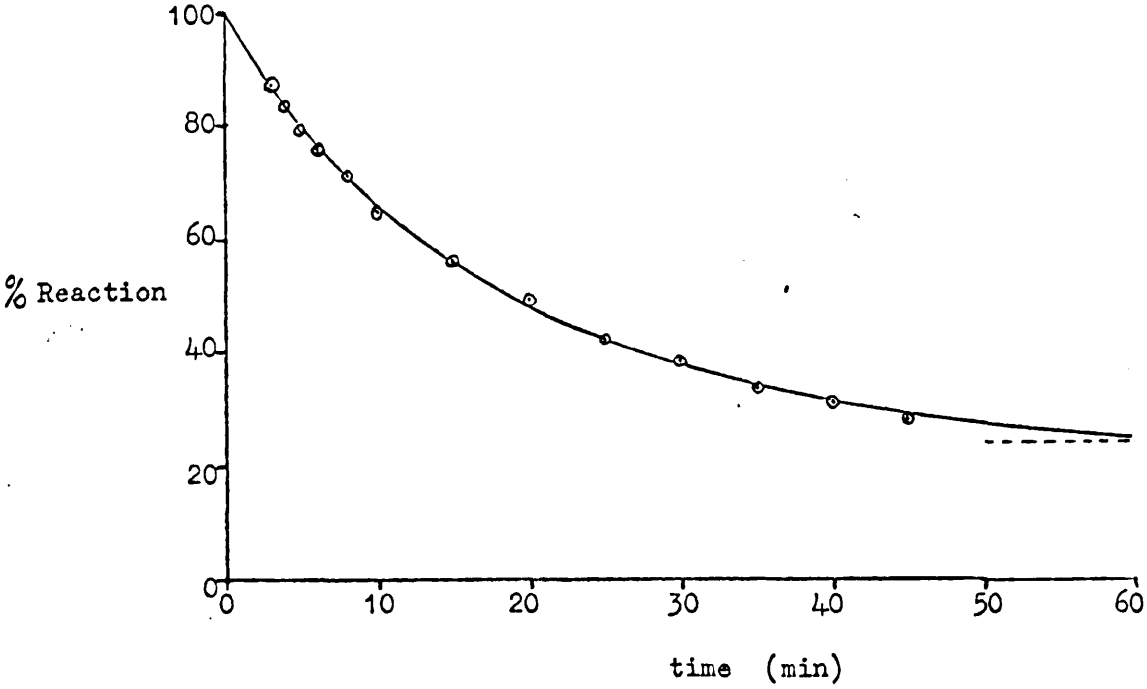
Reaction of (1,5-diphenyl) P.I.T. with 1,3-dmb in nitromethane at 25.0°

[1,3-dmb] mol.	x_{eq}/a	2.303 G $sec^{-1} \times 10^4$	2.303 Ga/x_{eq} $sec^{-1} \times 10^3$
0.10	0.37	2.0	0.54
0.20	0.37	2.7	0.73
0.50	0.31	7.5	2.4
0.73	0.25	9.8	3.9

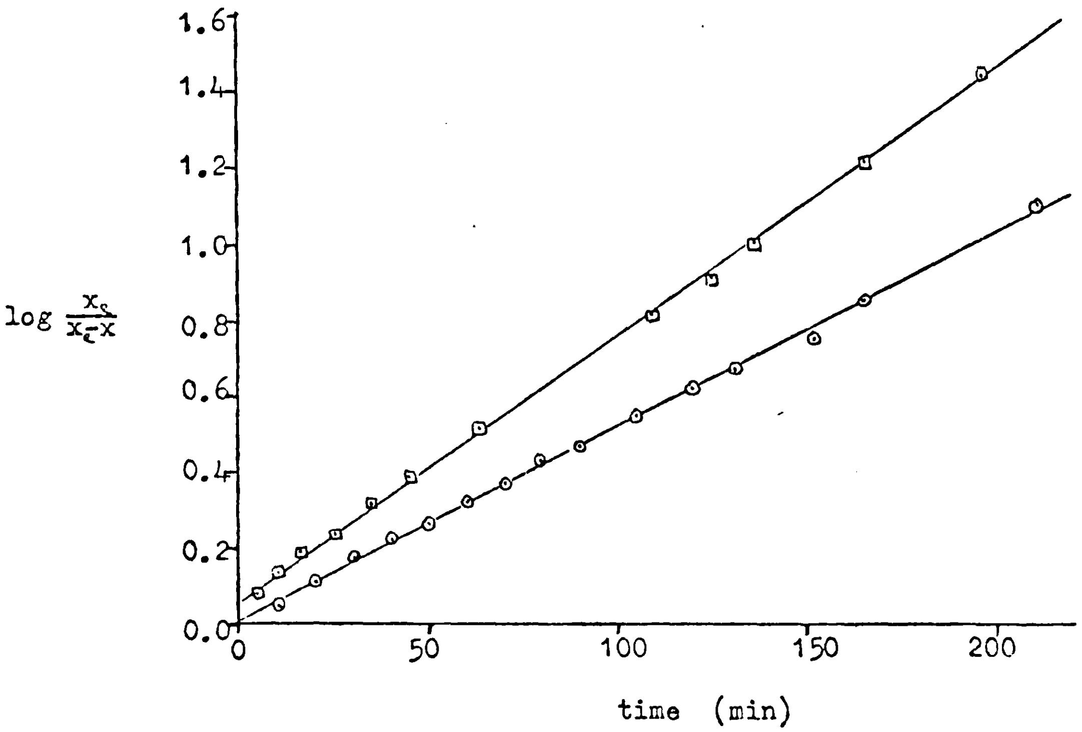
This is shown in graph 3.15. A value for k_f was obtained directly from the gradient and was 4.8×10^{-3} dm $mol^{-1}sec^{-1}$.



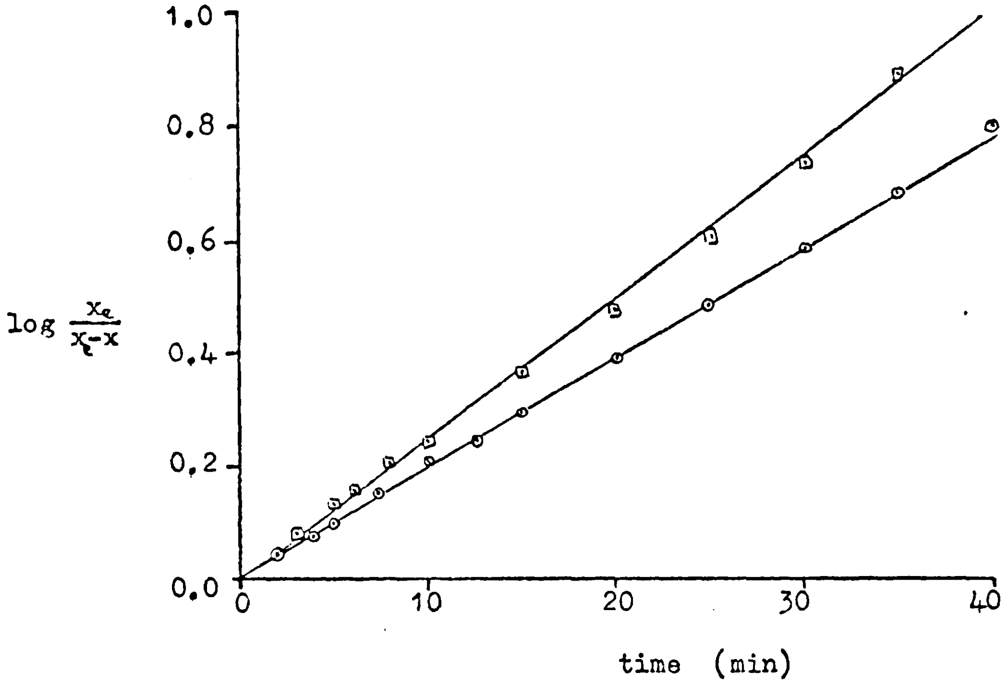
GRAPH 3.11 Reaction of (1,5-dimethyl) P.I.T. (0.01M) with 1,3-dmb (0.10M) in nitromethane at 25°



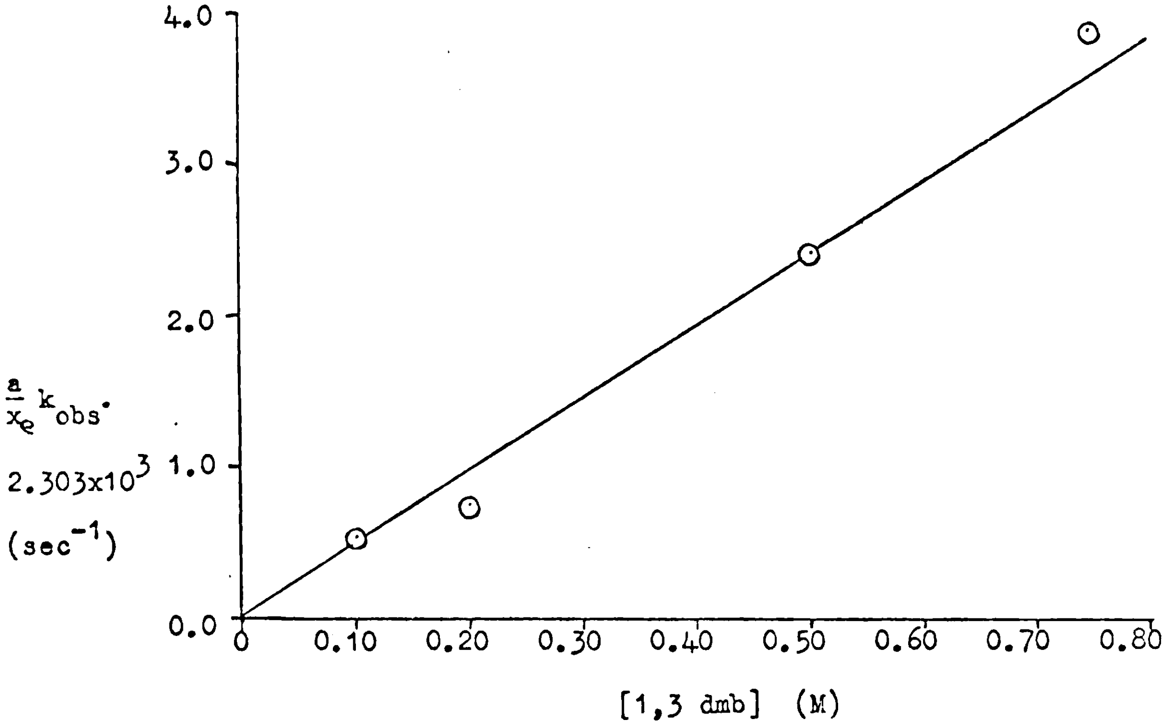
GRAPH 3.12 Reaction of (1,5-diphenyl) P.I.T. (0.01M) with 1,3-dmb (0.75M) in nitromethane at 25°



GRAPH 3.13 Reaction of (1,5-diphenyl)PIT (0.01M) with 1,3-dmb (0.10M)[⊙],(0.20M)[⊡]



GRAPH 3.14 Reaction of (1,5-diphenyl)PIT (0.01M) with 1,3-dmb (0.50M)[⊙],(0.75M)[⊡]



GRAPH 3.15 Reaction of (1,5-diphenyl) P.I.T. (0.01M) with 1,3-dmb

2.303 ak_{obs}/x_e vs. [1,3 dmb]

(d) Reaction of 1,3,5-trimethoxybenzene with (1-methyl, 5-phenyl) and (1,5-dimethyl) pentadienyl iron tricarbonyl tetrafluoroborate

The kinetics of reaction of (1,5-dimethyl) and (1-methyl, 5-phenyl) P.I.T. with 1,3,5-trimethoxybenzene (1,3,5-tmb) were similar to those in the previous section. They both tended to go towards an equilibrium position which was dependent on the concentration of 1,3,5-tmb. However, one notable difference was that the rate of attainment of equilibrium was independent of the concentration of 1,3,5-tmb. All reactions were followed in an i.r. cell by "method A".

The concentration/time curves for the reaction of (1-methyl, 5-phenyl) P.I.T. with a 10 and a 25-fold excess of 1,3,5-tmb are shown in graph 3.16, and for (1,5-dimethyl) P.I.T. with a 25-fold excess of 1,3,5-tmb in graph 3.17. The position of equilibrium for each reaction was found directly from these graphs.

It has been shown that for a reversible first order reaction, the rate of attainment of equilibrium is also a first order process with an effective rate constant the sum of the constants for the forward and reverse directions.[46] i.e.

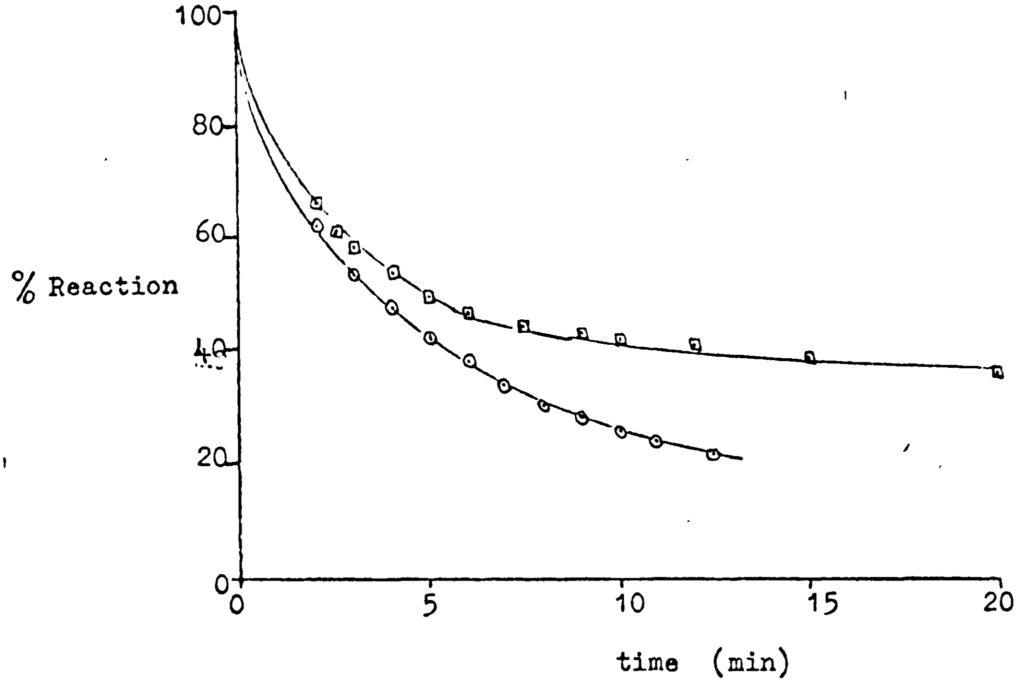
$$\text{for } A \underset{k'}{\overset{k}{\rightleftharpoons}} B$$

$$\ln\left(\frac{A_o - A_e}{A - A_e}\right) = (k + k')\,t$$

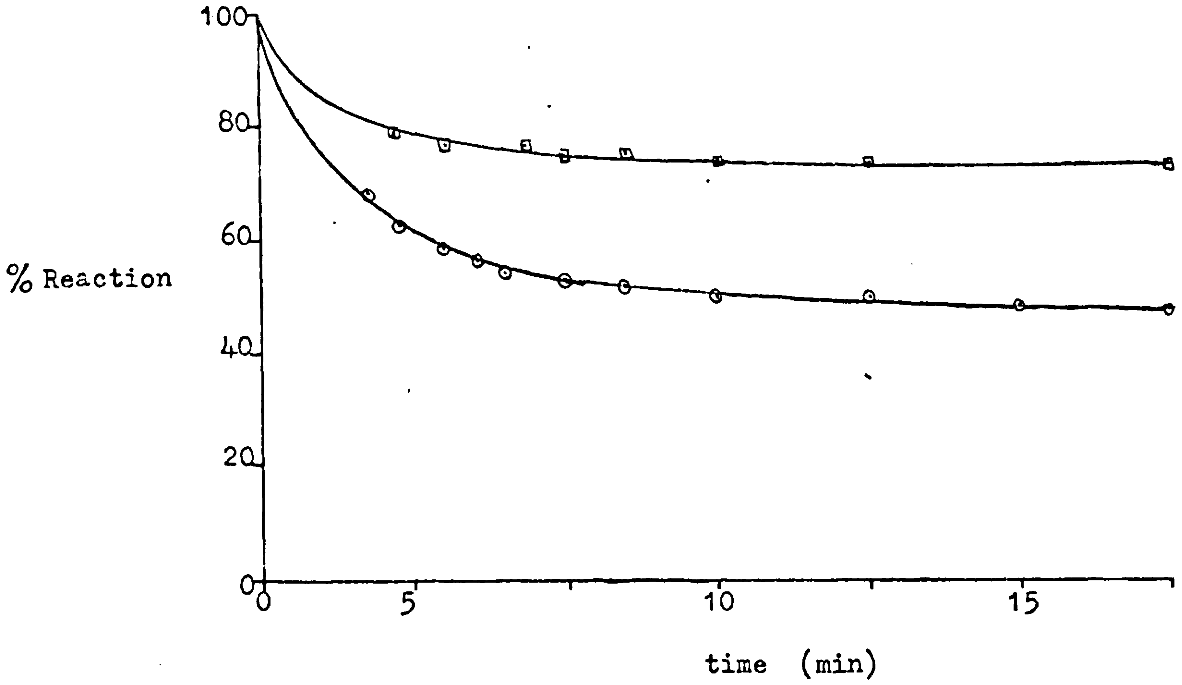
where A_o is the concentration of A at t = 0.

A_e is the concentration of A at equilibrium.

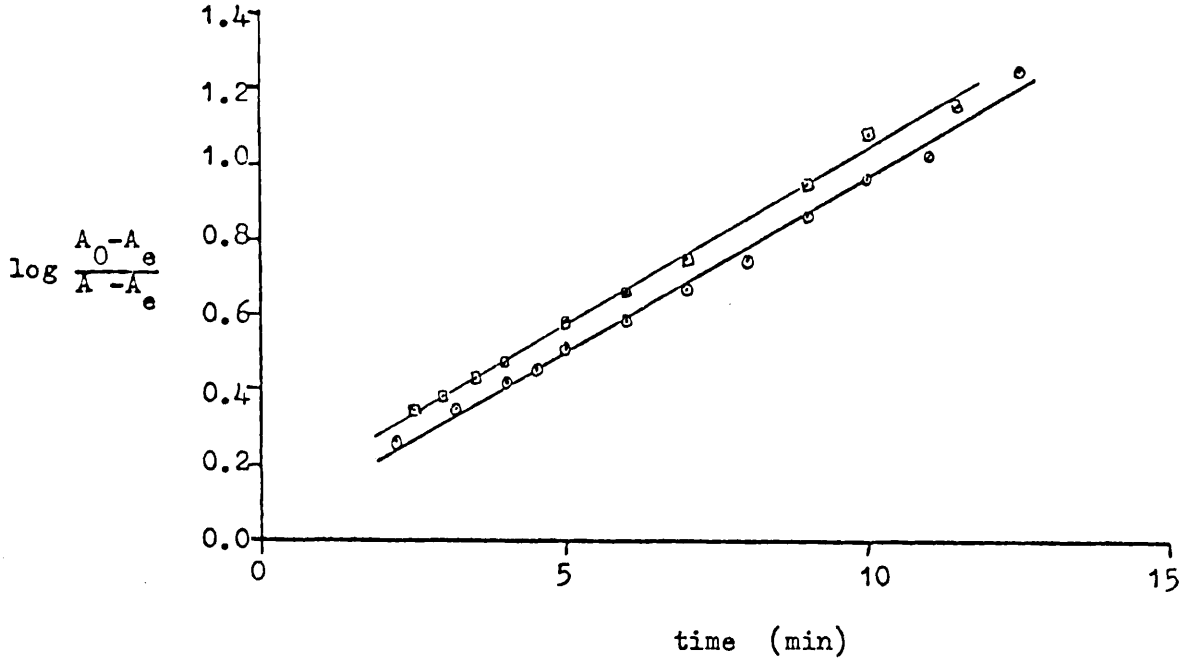
This equation was applied to the reaction with 1,3,5-tmb, substituting the concentration of P.I.T. for A. The plots are shown in graph 3.18 and graph 3.19 for (1-methyl, 5-phenyl) and (1,5-diphenyl) P.I.T. respectively. The gradients with each concentration of 1,3,5-tmb were found to be the same in both cases, indicating that the rate of reaction did not depend on the concentration of 1,3,5-tmb. Hence the overall reaction was a process first order in P.I.T. complex, and zero order in arene. Furthermore, (1-methyl, 5-phenyl) P.I.T. was slower than (1,5-dimethyl) P.I.T., the rates being 2.9×10^{-3} sec^{-1} and 8.3×10^{-3} sec^{-1} respectively. The error on these figures was estimated to be within ± 10% of the values quoted.



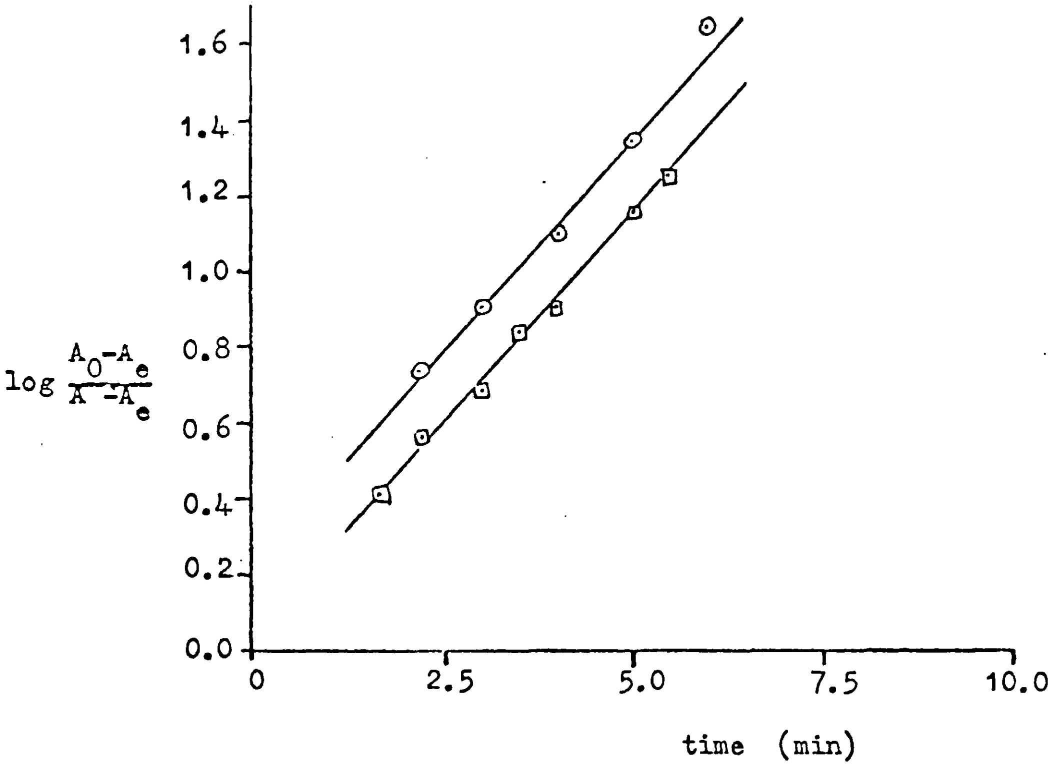
GRAPH 3.16 Reaction of (1-methyl,5-phenyl) P.I.T. (0.01M) with 1,3,5-tmb (0.10M)[□],(0.25M)[⊙]



GRAPH 3.17 Reaction of (1,5-dimethyl) P.I.T. (0.01M) with 1,3,5-tmb (0.10M)[□],(0.25M)[⊙]



GRAPH 3.18 Reaction of (1-methyl,5-phenyl)PIT (0.01M) with 1,3,5-tmb (0.10M)[⊡],(0.25M)[⊙]

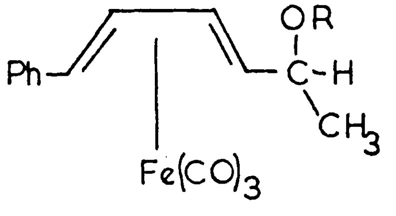


GRAPH 3.19 Reaction of (1,5-dimethyl)PIT (0.01M) with 1,3,5-tmb (0.10M)[⊙],(0.25M)[⊡]

II Reaction of Alcohols with (1-methyl, 5-phenyl) pentadienyl iron tricarbonyl tetrafluoroborate.

The reaction of (1-methyl, 5-phenyl) P.I.T. (0.01M) with methanol (1.0M) was initially very rapid, going to 80% completion in 10 minutes. The pseudo first order rate constant was in the order of 2×10^{-3} sec^{-1}. A slow reaction then took place, with complete conversion after approximately 4 hours. The concentration/time curve is shown in graph 3.20. The reaction was repeated with the addition of trifluoroacetic acid (0.1M) and was somewhat slower, reaching 50% completion after 10 minutes. The slow reaction also observed, but some P.I.T. complex remained after 1 day when the solution had darkened and some decomposition was evident from the intensities of the cation and diene carbonyl bands in the infrared spectrum.

The product of these reactions was isolated, and was exclusively the methyl ether (3.7a). Ethanol and propan-2-ol yielded analogous



(3.7)

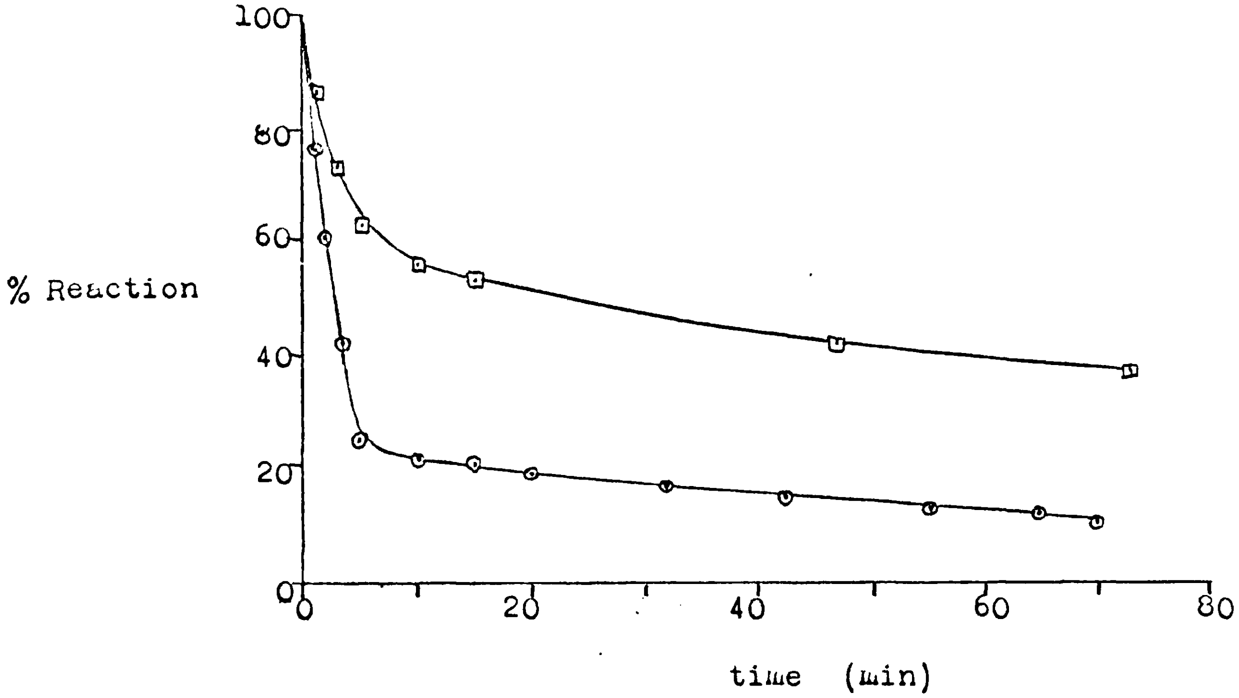
(a) R = Me

(b) R = Et

(c) R = iPr

products (3.7 b,c). The structures were confirmed by nmr spec troscopy and elemental analysis. Each complex generated the original P.I.T. complex on addition of tetrafluoroboric acid.

The results were consistent with the reaction of methanol with the cationic complex rapidly attaining equilibrium, the reverse reaction being the protonation of the methyl ether by tetrafluoroboric acid liberated in the forward reaction. Slow decomposition of the acid to hydrofluoric acid and boron trifluoride then shifted the equilibrium towards completion.

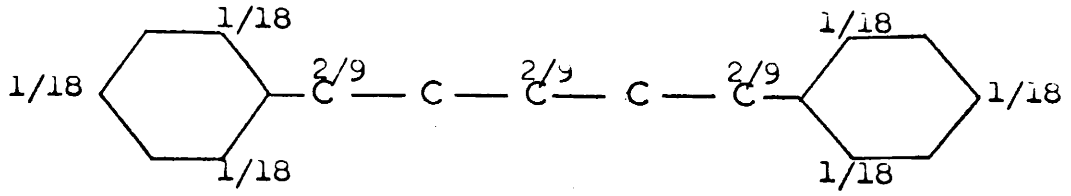


GRAPH 3.20 Reaction of (1-methyl,5-phenyl) PIT with methanol in nitromethane at 25° [⊙], with trifluoroacetic acid [⊡]

C: DISCUSSION

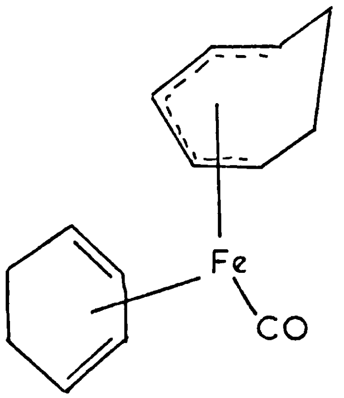
Reactions of open chain pentadienyl iron tricarbonyl complexes with nucleophiles appear to be considerably more complicated than those of their cyclic analogues in both kinetic and preparative aspects. Though the attack of the anion of acetyl acetone[40] and of activated arenes[42,43] on (cyclohexadienyl) iron tricarbonyl tetrafluoroborate is governed by overall second order kinetics, the open chain species do not all obey a simple rate law. Of the compounds examined in this work, only (1,5-dimethyl)- and (1,3,5-trimethyl)- pentadienyl iron tricarbonyl react with 1,3-dimethoxy benzene by a second order process under the conditions used. With (1-methyl, 5-phenyl)-, (1,4-dimethyl, 5-phenyl)- and (1-methyl)- P.I.T., the reactions follow a different rate equation, tending towards first order kinetics at high concentration of dimethoxybenzene. A third type of reaction was observed with (1,5-diphenyl) P.I.T. and 1,3-dmb which did not go to completion even with a large excess of arene. Finally, (1-methyl, 5-phenyl)- and (1,5-dimethyl)- P.I.T. were attacked by the more reactive 1,3,5-trimethoxybenzene in a first order process with a rate independent of the concentration of arene.

In discussing the reactions of these complexes, it is convenient to commence with an examination of the position of substitution of nucleophiles on the dienyl system. A Huckel molecular orbital (HMO) calculation of the electron density in the unbound pentadienyl system[48] indicates that the positive charge tends to reside at the 1,3 and 5 positions. A similar calculation performed on the (1,5-diphenyl) pentadienyl cation (which is an "alternate hydrocarbon")[49] also showed the charge at these positions, though some was also on the phenyl rings. This is shown in (3.7), the numbers indicating the fractional positive charge at each position.

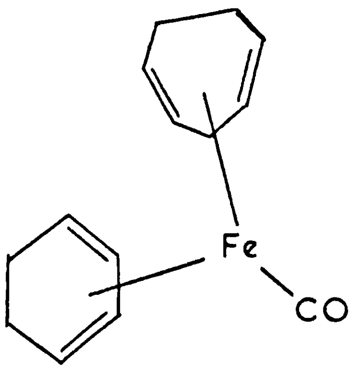


(3.7)

Using this simple model with all the associated errors and particularly neglecting the effect of stereochemistry and of the coordinated iron atom, one would expect that nucleophilic substitution would be more likely to occur at the 1,3 and 5 positions rather than at 2 or 4. In all cases reported, attack on the pentadienyl iron tricarbonyl system has only been observed at the 1 or 5 positions. (Examples illustrating this are discussed in Chapter 1). However, in certain circumstances, the 3 position does show some electrophilic character. Reduction of carbonyl (1,5-η-cycloheptadienylium)(η-cyclohexa-1,3-diene) iron (3.8) generated exclusively carbonyl (η-cyclohepta-1,4-diene) (η-cyclohexa-1,3-diene) iron (3.9).[50] An unusual attack on the 2 position has recently been reported by Lewis et al[51a] in the

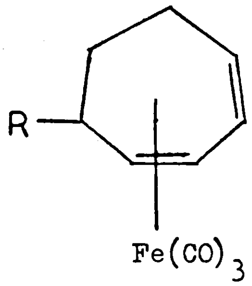


(3.8)



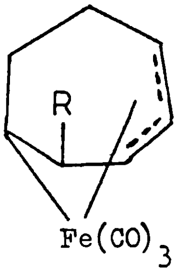
(3.9)

nucleophilic attack of the cation $[L(C_7H_9)Fe(CO_2)]^+$, where L is triphenylphosphine or triphenylarsine. Reduction of the tricarbonyl analogue (L = CO) resulted in attack at both the 1 and the 2 positions to generate a mixture of tricarbonyl (η -cyclohepta-1,3-diene) iron (3.10) and tricarbonyl (3,5-η-, 1-σ-cycloheptenyl) iron (3.11), the ratio of products depending on the conditions used. Attack of borohydride ion at the 1- and 2-positions of a dienyl system has also been shown to occur with (heptadienyl) iron tricarbonyl tetrafluoroborate, where the products were found to be a mixture of 1,3diene and (σ-,π-allyl) products.[51b] Thus, the application of simple HMO calculations to the free dienyl ligand does indicate the likely position of nucleophilic attack, but such conclusions should be treated with caution.



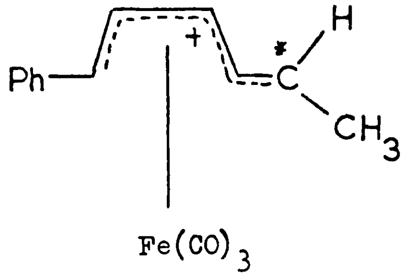
(3.10)

R=H

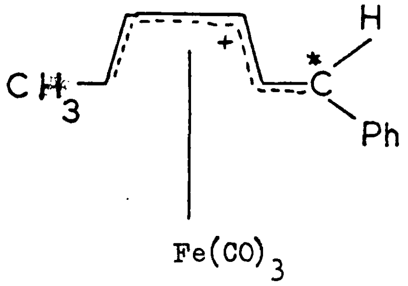


(3.11)

Returning to the open chain dienyl complexes, the position of attack in asymmetrically substituted complexes must be considered. Reaction of methanol with (1-methyl) P.I.T. generated one methyl ether formed by attack at the position adjacent to the methyl group.[17] In a simple picture of charge distribution, attack at the 5-position of the dienyl system would appear more likely, as C$_1$ would be stabilized by the inductive effect of the methyl group compared with C$_5$. This has been rationalized by postulating the involvement of a <u>trans</u> pentadienyl cation intermediate in the reaction, and it is the structure of this which controls the final product, and not the structure of the original cis species. This argument can be extended to another asymmetrically substituted P.I.T. complex used in this work -(1-methyl, 5-phenyl) P.I.T. The products from reaction with alcohols, and with 1,3-dmb all illustrated that attack had occurred at C_1 exclusively. The two trans ions which could be formed from this complex are shown as (3.12) and (3.13). From the structure of the



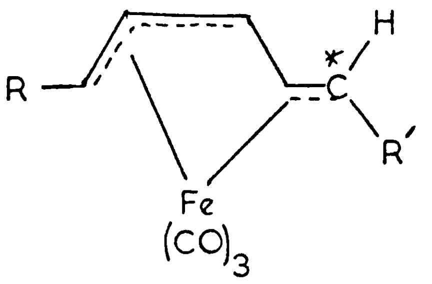
(3.12)



(3.13)

products, it is evident that (3.12) is the more likely reaction intermediate.

This appears consistent with the expected reactivity of each trans ion. Greater stability of a positive charge can be attained through delocalisation by a phenyl group than through the inductive effect of a methyl group.[52] The charge residing on the carbon marked with an asterisk in (3.13) would therefore be less than on the corresponding *C in (3.12). Hence, (3.12) would be more susceptible to nucleophilic attack than (3.13). Furthermore, if a π -allylic structure such as (3.14) is an important contributor to the bonding in the trans ions,[34] then the inductive effect of R = Me as in (3.13) would lead to destabilization from a decrease in bonding via backdonation from iron to the π -allyl system when compared with R = Ph, as in (3.12).



(3.14)

Turning to the position of substitution on the activated arenes, attack on 1,3-dimethoxybenzene was normally observed at the 4-position. Under forcing conditions, using a large excess of (1-methyl, 5-phenyl) P.I.T. further substitution occurred at the 6-position. This is consistent with the usual ortho, para directing properties of the methoxy group,[53] as positions 4- and 6- are ortho to one methoxy and para to the other. Substitution at the 2-position would not be expected to occur to any extent from steric considerations.

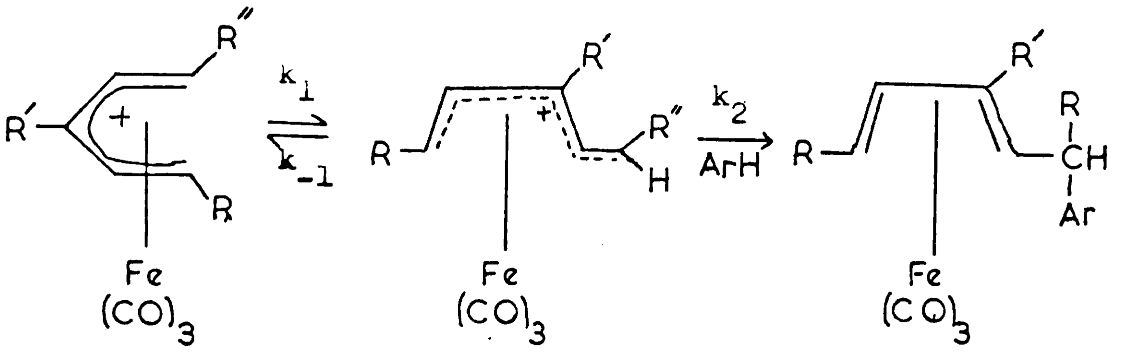
At this point, it is convenient to examine the kinetics of reaction with activated arenes. The results can be broadly summarized as follows:

1. The order of reaction is a function of
   (a) The position and nature of the substituents on the dienyl ligand.
   (b) The arene.
   (c) In some cases, the relative concentrations of dienyl complex and arene.

2. The rates of reaction of open chain complexes are faster than (cyclohexadienyl) iron tricarbonyl under similar conditions.

3. Generally, the rate of reaction increases with decreasing methyl substitution at the 1- and 3-positions.

One mechanism consistent with the above results and with the products formed in the reaction involves the assumption that the <u>trans</u> ion is a reactive intermediate. This is shown in Scheme 3.1, where ArH denotes



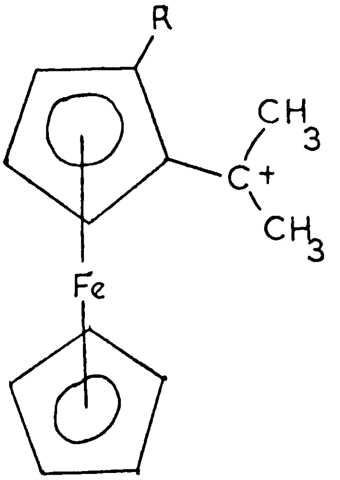
SCHEME 3.1

the activated arene. The observed order of reaction is dependent on the relative values of k_1, k_{-1} and $k_2[ArH]$. This mechanism is discussed below with reference to each dienyl complex studied.

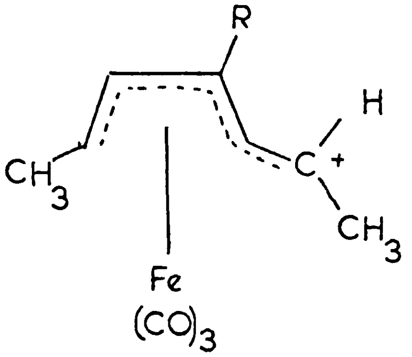
The reactions of (1,5-dimethyl)- and (1,3,5-trimethyl)- P.I.T. with 1,3-dimethoxybenzene both follow a second order rate law - first order in arene and first order in P.I.T. complex - up to at least sixty times excess of 1,3-dmb. The reaction of (cyclohexadienyl) iron tricarbonyl tetrafluoroborate with 1,3-dmb has been reported[43] to follow a similar rate law, with a rate constant of 1.5 x 10^{-6} $dm^3mol^{-1}sec^{-1}$.[54] The constants for (1,3,5-trimethyl)- and (1,5-dimethyl)- P.I.T. are somewhat larger by factors of 22 and over 700 respectively. Thus, it would appear that even when the kinetic forms are similar, the open chain dienyl complexes are more reactive than the cyclic analogue. This is cons istent with the involvement of the trans ion in the reaction mechanism, as such an ion can only be formed by open chain complexes but the cyclic complex can exist only in a cis form.

The rapidity of the rate determining step of the reaction with (1,3,5-trimethyl) P.I.T. is reflected in the relatively small value of the enthalpy of activation -44.0 ± 5.6 kJ mol^{-1} (-10.5 ± 1.3 kcal mol^{-1}). The entropy of activation, however, is very large at -189 ± 18 $JK^{-1}mol^{-1}$ (-45 ± 4 cgs entropy units), and is the controlling parameter. In other words, the transition state of the rate determining step is highly ordered when compared with the reactants but little enthalpy is required for its formation. This would be expected if the cis P.I.T. complex must first isomerise to the trans configuration before reaction with the arene can occur.

It is interesting to note that (1,3,5-trimethyl) P.I.T. is a less reactive electrophile than (1,5-dimethyl) P.I.T. by a factor of thirty. This is probably due to the inductive effect of the additional methyl group at the 3-position, which would tend to reduce the effective positive charge on the dienyl system. Analogies have been drawn between the reactivities of the P.I.T. trans ions and the ferrocenylalkylium ions (Chapter 2, section C), where it has been observed that 2-methyl substituents can destabilize the system, and so increase the electrophilic character of the complex. In the complex (3.15), pK_{R^+} values in aqueous sulphuric acid were found to be 0.01 where R = H, but −0.50 where R = CH_3.[36] [The analogous P.I.T. systems are shown in



(3.15)



(3.16)

(3.16)]. This difference may be attributed to a large steric interaction between the α-methyl and the CMe_2 substituents in the cyclic complex which outweigh the electronic effects. This steric repulsion would be expected to be smaller in the P.I.T. trans ion where the system is much less rigid, and can easily distort to accommodate the additional group.

Extending this argument further, removal of a methyl group from (1,5-dimethyl) P.I.T. should again increase the reactivity towards arenes. Indeed, under similar conditions, (1-methyl) P.I.T. does show enhanced electrophilic character towards 1,3-dmb when compared with (1,5-dimethyl) P.I.T. However, this reaction is complicated by exhibiting a kinetic form intermediate between first and second order depending on the relative concentration of the two reagents, tending to go towards first order in (1-methyl) P.I.T. at high concentration of arene. This can be interpreted in terms of the proposed mechanism as follows. At low concentrations of arene, the rate determining step is controlled by k_2[ArH] in Scheme 3.1. As [ArH] is increased, the overall rate becomes a function of the rate of formation of the <u>trans</u> ion (k_1), which is a first order process independent of the concentration of arene. The overall rate equation for all concentration of arene is thus:

$$\text{rate} = \frac{k_1k_2[\text{cation}][\text{ArH}]}{k_{-1}+k_2[\text{ArH}]}$$

when k_2[ArH] is small compared with k_{-1}, this becomes:

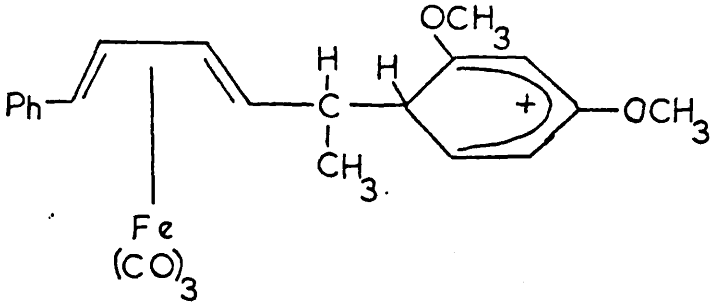
$$\text{rate} = \frac{k_1k_2}{k_{-1}}[\text{cation}][\text{ArH}]$$

when k_2[ArH] is very large, the equation becomes:

$$\text{rate} = k_1[\text{cation}]$$

On first consideration, it is somewhat surprising that kinetic equations of a similar form are also followed by the phenyl substituted complexes (1-methyl, 5-phenyl) P.I.T. and (1,4-dimethyl, 5-phenyl) P.I.T. in the reaction with 1,3-dmb. Furthermore, the overall rates are also of the same order of magnitude, though perhaps one would expect the two phenyl complexes to be similar on the ground that methyl substitution at the 4-position would not significantly stabilize the pentadienyl system.

That the rate determining step is a function of the concentration of arene is further illustrated in the reaction of (1-methyl, 5-phenyl) P.I.T. with deuterated 1,3-dimethoxybenzene. The deuterium isotope effect (k_H/K_D) is also a function of arene concentration, decreasing from 1.93 with a ten-fold excess to 1.68 with a fifty-fold excess. Thus, the nature of the arene exerts a diminishing effect as the rate of reaction increases towards the maximum, which is consistent with the proposed mechanism. Extrapolation back to zero arene concentration yields an estimated maximum ratio in the order of 2.5, which is indicative of a primary isotope effect.[55] The theoretical value, derived from infrared stretching frequency data, is 7.9 at 25°. Hence, the step controlled by $k_2[ArH]$ involves the breaking of a hydrogen-carbon bond, and so is probably the loss of a proton from the σ -complex (3.17) to form the final product.



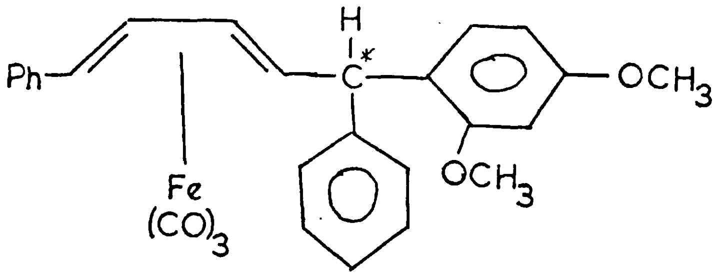
(3.17)

The calculated values of the rate constants for the reaction of (1-methyl, 5-phenyl) P.I.T. (Chapter 3, Section E) show several interesting aspects. Firstly, the magnitude of K, the equilibrium constant for the formation of the reactive intermediate from the <u>cis</u> ion, is of the order of 20. This means that approximately 5% of the complex in nitromethane solution is in the <u>trans</u> form. Thus on first mixing the reagents, a rapid reaction takes place between the arene and the <u>trans</u> isomer already present in solution. During this initial period, the concentration of the <u>trans</u> ion decreases to a steady state, and the overall rate can then be expressed in terms of simple second order kinetic equation. Hence, pseudo first order plots do not pass through the origin. As the nmr spectra of the cis and trans isomers are very similar, the concentration of trans ion present in solution would not be detected normally. In addition, the infrared carbonyl stretching bonds would be expected to occur at about the same frequency, so the trans ion would not be observed as a separate entity.

Secondly, the estimated value of k_2, the rate constant governing the reaction of the trans ion with the arene, is approximately $1 \times 10^{-1} dm^3 mol^{-1} sec^{-1}$. This is two orders of magnitude greater than the analogous reaction of (1,5-dimethyl) P.I.T. This difference is not only very large, but also in the opposite sense to that expected from the usual properties of phenyl compared with methyl substituents with regard to stabilization of positive charge. Thus, in a simple picture of charge distribution, the phenyl derivative would delocalize the positive charge on the system more effectively than the methyl derivative by induction. Furthermore, there is a need to explain why (1-methyl) P.I.T. should also be as reactive towards 1,3-dmb as (1-methyl, 5-phenyl) P.I.T. Again, it is the structure of the trans isomer which is the key factor, and one must return to the reason why nucleophilic attack on the ligand occurs at the positions found.

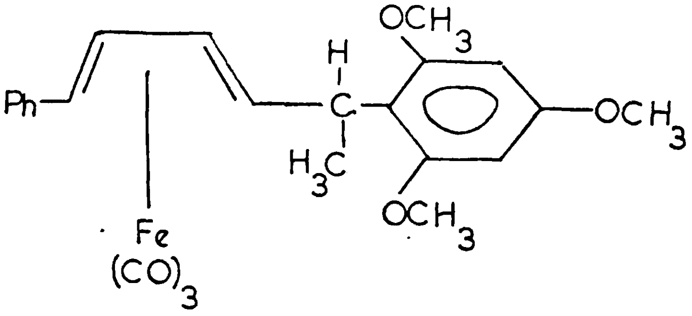
Referring back to (3.14) - a trans ion drawn as a π-allylic structure - it has been suggested that if R is a methyl group, then there would be a decrease in bonding via backdonation from the iron atom to the π-allylic system due to the inductive effect,[16] compared with the case when R is phenyl or hydrogen. This may then lead to an increase in bonding from the iron to C^* in (3.13), reducing the charge on this atom, and so having the effect of decreasing the electrophilic nature of the complex. Support for the postulated weakening of the iron π-allyl bond comes from the observation that non-conjugating alkyl substituents tend to weaken on olefin-metal bond and furthermore, conjugating systems (e.g. Ph) appear to stabilize such a bond in the case of iron.[56] In conclusion, although the above argument is tentative, it 's clear that the reactivity of the pentadienyl iron tricarbonyl system cannot be interpreted with reference to the cis isomer alone.

It has already been shown that in reaction of (1-methyl, 5-phenyl) P.I.T. with nucleophiles, the phenyl group remains remote from the reaction centre. However, with the (1,5-diphenyl) derivative, a phenyl group is forced into this position. The reaction is then found to proceed to equilibrium rather than to completion. This can be understood with reference to the structure of the product, particularly at the reaction site, shown in (3.18). The carbon atom C^*, which was originally part of the pentadienyl system of the P.I.T. precursor, is bonded to three powerful charge-stabilizing groups - 2,4-dimethoxy phenyl, phenyl and (diene) iron tricarbonyl. This position is also somewhat crowded sterically by these bulky substituents.



(3.18)

Hence, this complex is less stable than the product from (1-methyl, 5-phenyl) P.I.T. and 1,3-dmb, and can disproportionate to a trans ion intermediate and 1,3-dmb more easily. This has the result of making the overall reaction reversible, with an equilibrium position dependent on the concentration of 1,3-dmb in solution. Similar effects are also observed with 1,3,5-trimethoxybenzene as the nucleophile even with (1,5-dimethyl) and (1-methyl, 5-phenyl) P.I.T. In this case, the steric effect is due to the two ortho methoxy groups, and the electronic effect from the trimethoxy substituted phenyl group. This can be seen from the structure of the product with (1-methyl, 5-phenyl) P.I.T. (3.19).

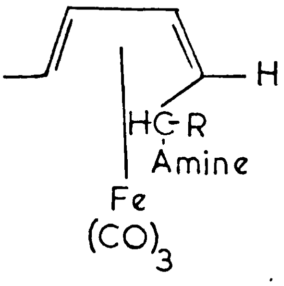


(3.19)

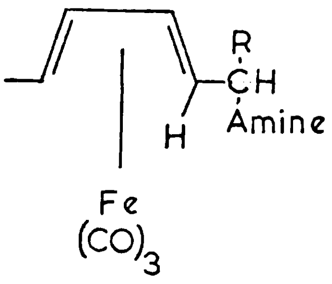
These latter two reactions are also interesting from a kinetic viewpoint, as the approach to equilibrium is controlled by a first order process in each case. Thus, while the position of equilibrium is a function of the concentration of arene, the rate of attainment is only dependent on the concentration of P.I.T. In other words, only k_1 and k_{-1} are involved in the rate equation. (It has been shown that the rate is a function of both the forward and reverse reactions in Section B(d). Hence, the rate of attack of 1,3,5-trimethoxybenzene is much faster than the rate of formation of the trans ion from the cis ion.

The rates found for these reactions are similar in magnitude, being 2.9 x 10^{-3} sec^{-1} for (1-methyl, 5phenyl) P.I.T. and 8.3 x 10^{-3} sec^{-1} for (1,5-dimethyl) P.I.T. Thus, the difference in behaviour of these complexes towards 1,3-dmb is due to the value of $k_2[ArH]$ and so the reactivity of the respective *trans* ions towards the arene rather than of the formation of these ions from the *cis* complexes.

It would appear from the above discussion that there is a maximum rate of reaction of the P.I.T. complexes with nucleophiles,which is the rate of formation of the *trans* ion. Thus, with methanol, the rate of disappearance of (1-methyl, 5-phenyl) P.I.T. is in the order of 2 x $10^{-3}sec^{-1}$, which is close to the value of k_1 at 2.57 x $10^{3}sec^{-1}$ determined indirectly from the kinetics of reaction of this complex with 1,3-dimethoxybenzene. However, with the very reactive nucleophile indole, the rate is extremely fast, 95% completion being achieved in two minutes. One explanation for this is that attack can occur both on the *cis* and *trans* ions with such a strong nucleophile. Direct reaction with the *cis* ion is analogous to reaction with the cyclic complex-(cyclohexadienyl) iron tricarbonyl which can only exist in the *cis* configuration.[40,42] Furthermore, this effect has been observed in the behaviour of amines towards (1-methyl) P.I.T.[18,19] and pentadienyl iron tricarbonyl tetrafluoroborate.[57] Thus, with strongly basic amines, only (3.20) was formed by direct reaction with the *cis* ion. Weakly basic amines gave (3.21) by attack of the *trans* ion in the way usually observed. The former product shows retention of geometric configuration at the reaction site, and the latter shows inversion.



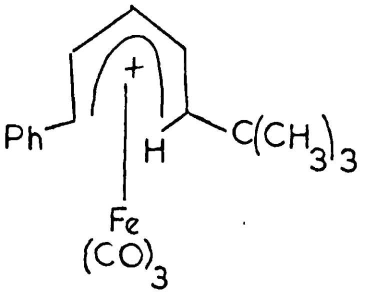
(3.20)



(3.21)

In summary, the effect of increasing the nucleophilicity of the attacking species is to change from a second order reaction with the trans ion, through to a first order reaction depending only on the rate of formation of the trans ion and finally to direct reaction with the cis ion.

Finally, mention should be made of some studies carried out after the completion of this work.[58] The complex (1-tertbutyl, 5-phenyl) P.I.T. (3.22) failed to react with 1,3-dimethoxybenzene under the usual conditions employed in this work. This is presumably due to the enhanced stability of the trans ion from the complex (3.23). The reaction centre has a tertiary butyl substituent, which would tend to stabilize the positive charge at this position to a greater degree than that of a centre with a methyl substituent in, for instance, (1-methyl, 5-phenyl) P.I.T. This site would also be sterically restricted for the attack of a large molecule such as 1,3-dimethoxybenzene.



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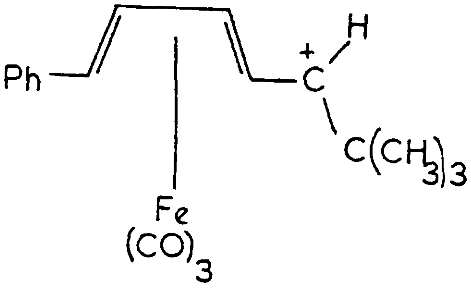


(3.23)

The reaction of (1-methyl, 5-phenyl) P.I.T. with 1,2,4-trimethoxybenzene was similar to that with 1,3-dimethoxybenzene both in terms of the form of the rate equation and in the magnitude of the rate constants. Thus, the behaviour of these arenes is consistent with the expected properties towards an electrophilic substitution reaction.

In conclusion, reactions of open chain pentadienyl iron tricarbonyl complexes with nucleophiles in general, and with arenes in particular, are complicated, but can be understood in terms of the involvement of a trans species.

D: EXPERIMENTAL

(i) Materials

Pentadienyl Iron Tricarbonyl Complexes

(1-Methyl)- and (1,5-dimethyl)- P.I.T. were prepared by the method of Mahler and Pettit.[16,17] The syntheses of (1-methyl, 5-phenyl)- and (1,3,5-trimethyl)- P.I.T. were from the corresponding alcohol complexes, exo (6-phenyl hexa-3,5-dien-2-ol) iron tricarbonyl and exo (4-methyl hepta-3,5-dien-2-ol) iron tricarbonyl using an adaption of the method used by Mahler and Pettit.[16] The latter preparation was performed by Mr. B. Cockerill. (1,4-Dimethyl, 5-phenyl) P.I.T. was prepared by Dr. P. Powell by a method based on that for (1-methyl, 5-phenyl) P.I.T. by substitution of 2-methyl cinnamaldehyde for cinnamaldehyde in the preparation of hexa-3,5-diene-2-one.[59] (1,5-Diphenyl) P.I.T. was made from (1,5-diphenyl-penta-2,4-dien-1-ol) iron tricarbonyl, which in turn was made by reaction of the uncoordinated diene with diiron enneacarbonyl in refluxing diethyl ether using a general method described by Dauben and Lorber.[60]

Purification of the P.I.T. complexes in each case was by dissolution in the minimum quantity of dry nitromethane followed by precipitation with dry diethyl ether under an atmosphere of nitrogen. This process was repeated three times, followed by filtration under nitrogen and washing with two aliquots of dry diethyl ether (50 cm^3). The complexes were dried in vacuo and stored in a vacuum desiccator over calcium chloride. Analytical data are shown in table 3.5.

TABLE 3.5

P.I.T. Complex		C	H	B	F
1-methyl	requires:	35.12	2.947	-	-
	found:	35.46	3.15	-	-
1,3,5-trimethyl	requires:	39.33	3.90	-	22.63
	found:	39.39	4.04	-	22.54
1-methyl, 5-phenyl	requires:	46.92	3.42	2.82	-
	found:	46.76	3.26	2.78	-
1,4-dimethyl,5-phenyl	requires:	48.29	3.80	2.72	-
	found:	48.41	3.75	2.58	-
1,5-diphenyl	requires:	53.87	3.39	-	-
	found:	54.31	3.47	-	-

1,3-dimethoxybenzene

1,3-dimethoxybenzene (Ralph Emanuel) was refluxed over sodium metal for 2 hours, followed by distillation under reduced pressure through a 25 cm Vigreux fractionating column. B.Pt 85°/6.5 mm Hg.

d_3 1,3-dimethoxybenzene

d_3 1,3-dimethoxybenzene was prepared from purified 1,3-dimethoxy benzene in an exchange reaction with a deuterium oxide solution of deuterium sulphate. 1,3-dimethoxybenzene (14 g, 0.1 mol) was added to a solution of deuterium sulphate (10 g, 0.1 mol) in deuterium oxide (10 g, 0.5 mol). The suspension was stirred for four days, after which the acid layer was removed. An nmr spectrum of the organic layer indicated that 80% deuteration had occurred at the 2,4 and 6 positions on the 1,3-dimethoxybenzene ring. A further aliquot of D_2O/D_2SO_4 was added and the process repeated for four days, by which time 94.5% deuteration was observed. This was repeated again to give a product with 97% deuteration. The organic layer was dissolved in methylene chloride (50 cm^3) and washed with a saturated solution of sodium hydrogen carbonate (20 cm^3), followed by water (20 cm^3). The solution was then dried over calcium chloride, followed by distillation from sodium metal under reduced pressure (b.pt 89°/5.5 mm Hg). The purity of this compound was checked by two methods. Nmr analysis indicated 97.2% dueteration, and mass spectroscopy indicated the presence of 93% d_3, 2% d_2 and 4% d_1 species.

1,3,5-trimethoxybenzene

1,3,5-trimethoxybenzene (Ralph Emanuel) was dissolved in diethyl ether, and the solution shaken with aqueous sodium hydrogen carbonate solution. The ether extract was separated, and the aqueous solution extracted with further quantities of diethyl ether. After drying with magnesium sulphate, the ether was distilled off leaving a white residue. The residue was crystallized from the minimum quantity of hot petroleum ether (40-60°). (melting point 55°) [literature value,[61] 54-55°].

Indole

Indole (Ralph/Emanuel) was purified by two recrystallizations from benzene.[62] (melting point 52°) [literature value,[61] 52.5°].

Methanol

Methanol (AR) was dried by the "magnesium/iodine" method,[63] followed by fractional distillation through a 500 cm Vigreux column.

(ii) Kinetic Procedure

Two methods were employed for observing the kinetics of reactions discussed in this chapter. The choice of method for a particular system was governed by the rate of reaction. Method A was adopted for reactions where the half-life was shorter than thirty minutes, and method B where the half-life was significantly longer. These are described below:

Method A.

Fresh solutions of the P.I.T. complex and of the arene were prepared in dry nitromethane prior to each kinetic run. Particular attention was paid to ensure that all glassware was dry. An aliquot (4 cm^3) of each reactant was pipetted into a separate reaction vessel. This vessel, shown in Figure 3.2, was fitted with a "Subaseal" septum cap, and the side arm was closed by means of a "Rotaflow" tap. The contents of each vessel were frozen quickly in liquid nitrogen, and the side arm was connected to a vacuum pump to remove air. The tap was then closed and the contents allowed to warm up to room temperature. The solution was frozen again, and the apparatus evacuated. This process was repeated three times in all to ensure that the reactants were completely degassed. Finally, the vessels were transferred to a constant temperature bath, and dry nitrogen admitted.

After the solutions had attained thermal equilibrium, they were mixed, and the clock started. Mixing was achieved under an atmosphere of nitrogen by use of an all-glass syringe with a capacity of 5 cm^3, which was fitted with a 180 mm long stainless steel needle. The syringe was flushed with dry nitrogen, then inserted through the septum of the vessel containing the arene solution. The entire contents were drawn into the syringe by placing the tip of the needle into a small indentation at the base of the vessel. This solution was then injected into the vessel containing the P.I.T. complex, and the contents thoroughly mixed by rapidly withdrawing part of the solution into the syringe, and returning it into the remaining liquid. A portion of this solution (4 cm^3) was used to rinse out the first vessel which had contained the arene. This mixing procedure was usually completed within 90 seconds. A portion of the reaction mixture was transferred to the constant temperature infra-red cell, shown in Figure 3.1. The reference solution was the arene in nitromethane at the same concentration as that used in the reaction. The infra-red spectrum was repeatedly scanned across the region 2200-1900 cm^{-1} using a Perkin Elmer 337 double beam spectrometer. The concentration of P.I.T. complex remaining in solution was determined directly from the intensity of the 2105 cm^{-1} carbonyl band, using a calibration curve. All the P.I.T. complexes used in this work were found to obey Beer's Law.

The constant temperature cell was constructed from a Beckman-RIIC FH01 cell fitted with calcium fluoride windows. This was placed in a stainless steel jacket through which water was pumped from a constant temperature water bath. The temperature of this was set such that the cell remained at $25^o \pm .1^o$, this being determined by a thermistor which could be inserted into the cell windows. The whole jacket was insulated by a 20 mm thick layer of plastic foam. In order to prevent excessive heating of the cell contents by radiation absorbed by the cell windows, a calcium fluoride filter was attached to the front of the unit. The cell was filled through stainless steel tubes (22 gauge) which had luer fittings and could be attached directly to the syringe containing the reaction solution.

Method B.

This is a modification of method A, which was found to have the disadvantage that oxygen could leak into the cell over an extended time period. Thus, for prolonged experiments, the reacting solution was stored under an atmosphere of dry nitrogen, and samples were removed for the determination of the concentration of unreacted P.I.T. complex by infra-red analysis.

An aliquot (10 cm^3) of each freshly prepared solution was pipetted into a reaction vessel. The reactants were mixed prior to degassing by the freeze-thaw method as the rates were slow. Nitrogen was introduced to the apparatus, and the solution allowed to attain thermal equilibrium in a constant temperature water-bath. Samples were removed at intervals by syringe, and quickly placed in an infra-red cell fitted with calcium fluoride windows. The infra-red analysis was the same as that described in method A.

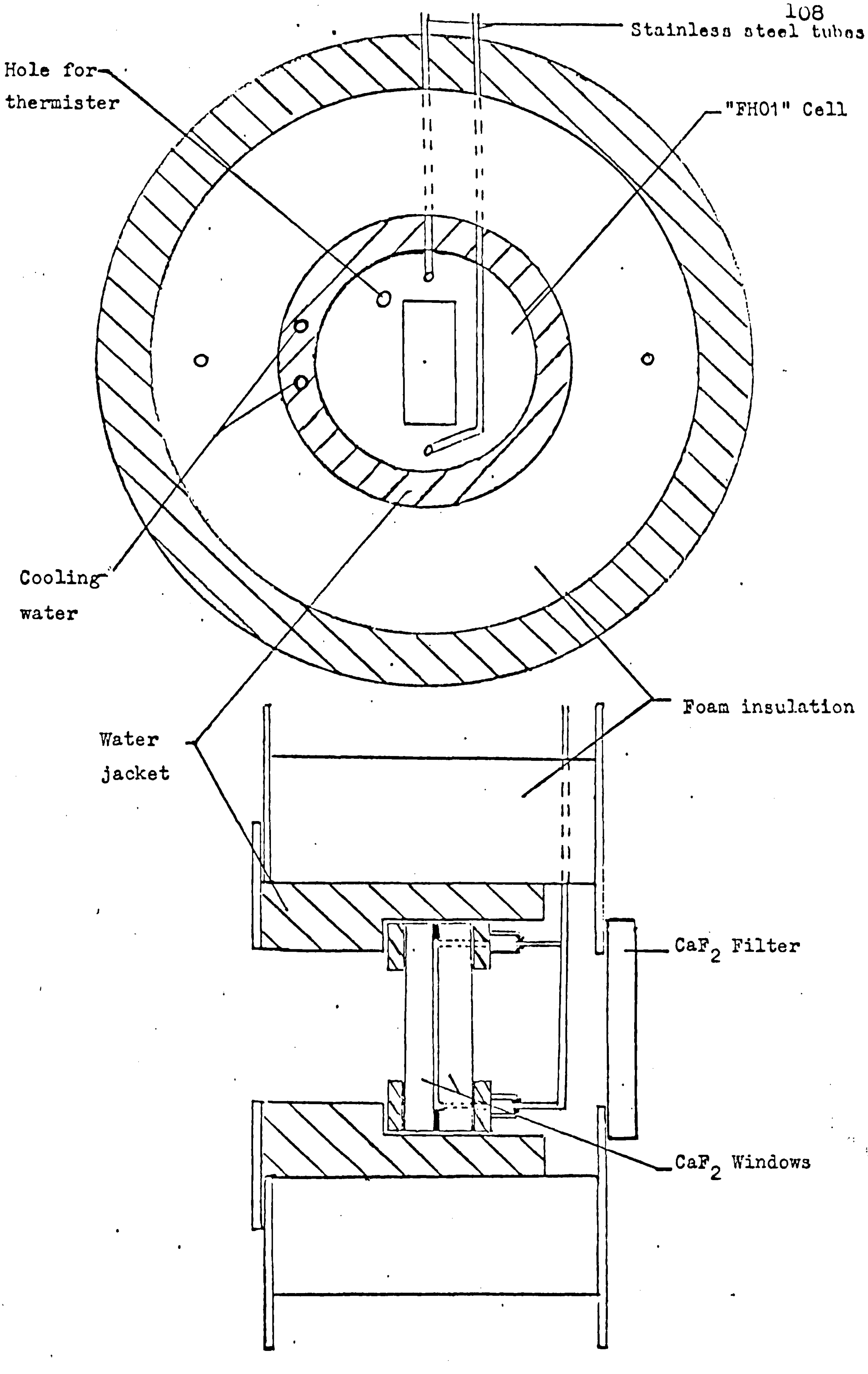


FIG 3.1 Constant temperature infra-red cell

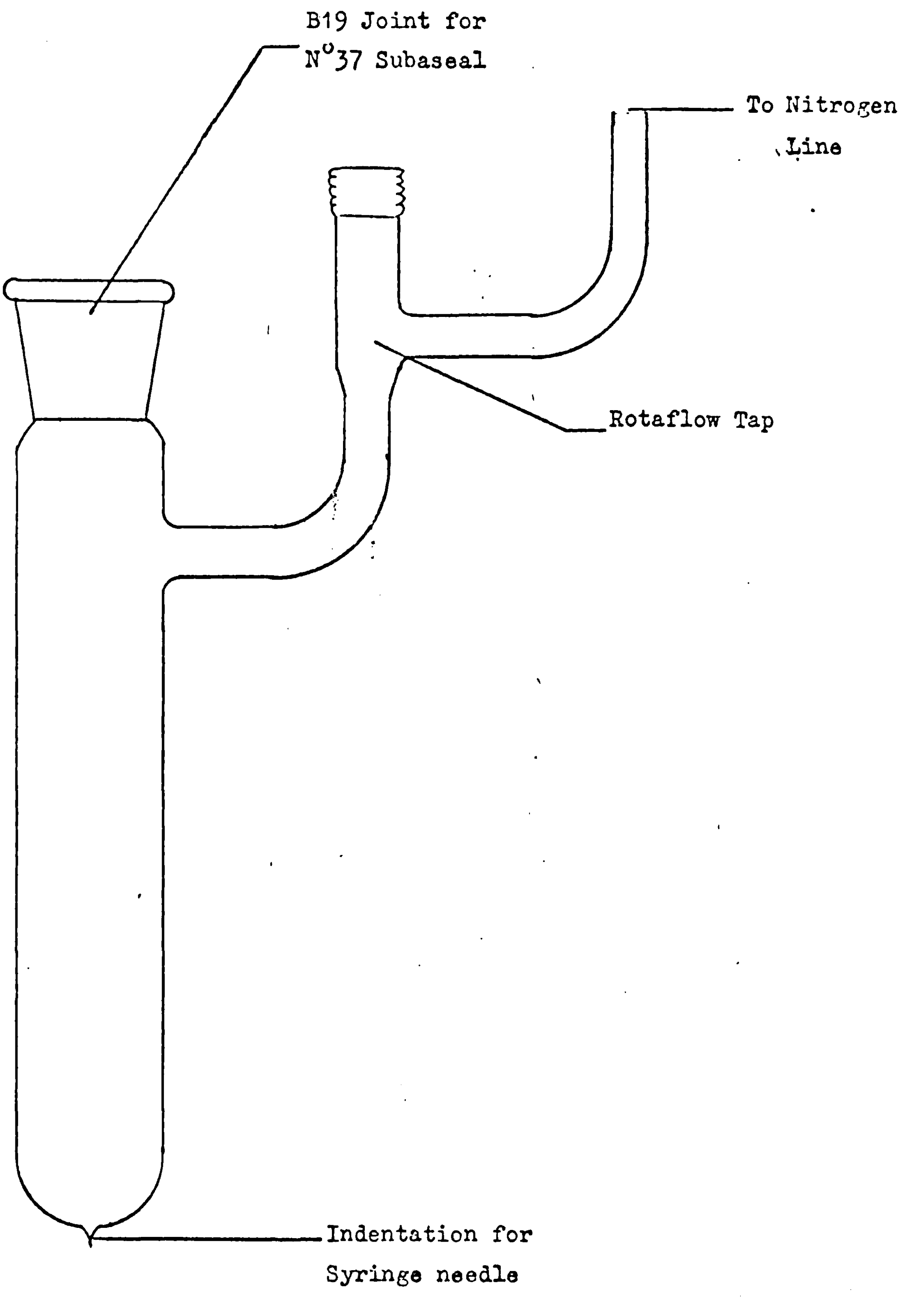


FIG 3.2 Reaction Vessel

(iii) Preparation of products from reaction of P.I.T. complexes with nucleophiles.

[2-(2,4-dimethoxyphenyl), trans,trans-hepta-3,5-diene] iron tricarbonyl.

(1,5-Dimethyl)pentadienyl iron tricarbonyl tetrafluoroborate (2.0 g, 6.2 mmol) was added to a solution of 1,3-dimethoxybenzene (0.40 g, 2.9 mmol) in dichloromethane (30 cm^3). The solution was degassed by the freeze-thaw method, followed by stirring for 17 hours in the absence of light. The solution was filtered, and evaporated to leave a black residue which was extracted with pentane (2 x 30 cm^3). The clear yellow extract was evaporated to yield a yellow oil which was then heated at 90° for 2 hours under vacuum. The residue was recrystallized from pentane (5 cm^3) in a solid carbon dioxide/acetone bath to give a yellow solid m.p. 88°. The yield was 0.17 g (16%).

Analysis $C_{18}H_{20}O_5Fe$ requires 58.08%C, 5.417% H
found 58.49%C, 5.60%H.

[2-(2,4-dimethoxyphenyl), 6-phenyl, trans,trans-hexa-3,5-diene] iron tricarbonyl.

(1-methyl, 5-phenyl)pentadienyl iron tricarbonyl tetrafluoroborate (1.0 g, 2.6 mmol) was added to a solution of 1,3-dimethoxybenzene (0.40 g, 2.9 mmol) in dichloromethane (50 cm^3). The suspension was stirred overnight, and the excess P.I.T. complex filtered off. The solvent was evaporated to give a residue which was extracted with pentane (2 x 30 cm^3). The clear yellow solution was evaporated to remove the pentane, followed by heating at 90° for 3 hours under vacuum to remove excess 1,3-dimethoxybenzene. The yellow residue was recrystallized from 60 - 80 petroleum ether to give yellow crystals m.p. 95°:

The yield was 0.126 g (11%)

Analysis	$C_{23}H_{22}O_5Fe$	requires	63.60%C, 5.12%H
		found	64.56%C, 5.18%H.

[1-(2,4-dimethylphenyl), 1,5-diphenyl, trans,trans-penta-2,4-diene] iron tricarbonyl.

(1,5-diphenyl)pentadienyl iron tricarbonyl tetrafluoroborate (1.0 g, 2.2 mmol) was added to a solution of 1,3-dimethoxybenzene (0.3 g, 2.2 mmol) in dichloromethane (25 cm^3). Potassium hydrogen carbonate (anhydrous) (1 g) was added to the suspension, and the solution was degassed by the freeze-thaw method. The suspension was stirred for 6 days under nitrogen, before being filtered. The filtrate was evaporated to yield a solid which was washed with cold pentane (20 cm^3), followed by a recrystallization from hot 60 – 80 petroleum ether (20 cm^3) containing sufficient benzene to dissolve the residue (several cm^3). A yellow solid crystallized out of solution at room temperature m.p. 160° (dec). The yield was 0.60 g (55%).

Analysis	$C_{28}H_{24}O_5Fe$	requires	67.75%C, 4.87%H
		found	67.55%C, 5.11%H.

[2-(alkoxy), 6-phenyl, trans,trans-hexa-3,5-diene] iron tricarbonyl.

(1-methyl, 5-phenyl) pentadienyl iron tricarbonyl tetrafluoroborate (0.50 g, 1.3 mmol) was suspended in the corresponding dry alcohol (10 cm^3) until all the solid dissolved. The time taken for dissolution varied from 2 minutes with methanol to approximately 15 hours with propan-2-ol. The alcohol solution was diluted with water (20 cm^3) and extracted with diethyl ether (3 x 25 cm^3). The extract was washed with saturated aqueous sodium hydrogen carbonate (10 cm^3) and dried with anhydrous potassium carbonate. Evaporation of diethyl ether gave a solid in each case, which was recrystallized from hot pentane (10 cm^3). Yields and analytical data are shown in table 3.6.

TABLE 3.6

Alcohol used	Yield	m.p.		Analysis C%	Analysis H%
Methanol	0.20 g, 46%	76°	requires:	58.56	4.92
			found:	58.70	5.02
Ethanol	0.25 g, 56%	58°	requires:	59.67	5.30
			found:	59.83	5.36
Isopropanol	0.15 g, 32%	44°	requires:	60.69	5.66
			found:	61.01	5.62

E: APPENDIX

Estimation of the rate constants in the reaction of (1-methyl, 5-phenyl). Pentadienyl iron tricarbonyl tetrafluoroborate with 1,3-dimethoxybenzene.

For two reversible consecutive reactions:

$$A_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} A_3$$

It has been shown[46] that the concentration of A_1 at time t is given by:

$$A_1 = A_1^{o} \left\{ \frac{k_{21}k_{32}}{\lambda_2 \lambda_3} + k_{12} \frac{\lambda_2 - k_{23} - k_{32}}{\lambda_2 (\lambda_2 - \lambda_3)} e^{-\lambda_2 t} + \frac{k_{12}(k_{23} + k_{32} - \lambda_3)}{\lambda_3 (\lambda_2 - \lambda_3)} e^{-\lambda_3 t} \right]$$

Where A_1^{o} is the concentration of A_1 at $t = 0$.

and $\lambda_2 = \frac{1}{2} (p + q)$

$\lambda_3 = \frac{1}{2} (p - q)$

where $p = (k_{12} + k_{21} + k_{23} + k_{33})$

and $q = [p^2 - 4 (k_{12}k_{23} + k_{21}k_{32} + k_{12}k_{32})]^{\frac{1}{2}}$

In the case required, $k_{32} = 0$, and k_{23} also includes the concentration of 1,3-dmb. The above equation then simplies to:

$$A_1 = \frac{A_1^{o} k_{12}}{\lambda_2 - \lambda_3} \left\{ \frac{(\lambda_2 - k_{23})}{\lambda_2} e^{-\lambda_2 t} + \frac{(k_{23} - \lambda_3)}{\lambda_3} e^{-\lambda_3 t} \right\} \quad (4)$$

where $\lambda_2 = \frac{1}{2}(p + q)$; (5)

$\lambda_3 = \frac{1}{2} (p - q)$ (6)

and $p = (k_{12} + k_{21} + k_{23})$ (7)

$q = [p^2 - 4(k_{12}k_{23})]^{\frac{1}{2}}$ (8)

The rate of reaction is governed by two exponential terms λ_2 and λ_3. The first term mainly determines the initial slope of the curve, and the second term the latter part of the curve. The result of this is that a semi logarithmic plot of concentration against time consists of two straight lines. The actual curve is given by the sum of these lines. Thus, the gradient of the latter part of the curve is very close to λ_3.

Estimates of k_{23} and k_{21} were made using the experimental values of λ_3, k_1 and the ratio k_2/k_{-1}. From equations (5) and (6),

$$\lambda_2 \lambda_3 = 1/4(p + q)(p - q) = 1/4 (p^2 - q^2)$$

$$\text{and } \lambda_2 + \lambda_3 = \tfrac{1}{2}(p + q) + \tfrac{1}{2}(p - q) = p$$

substituting for p and q from (5) and (6)

$$\lambda_2 \lambda_3 = (k_{12}k_{23}) \tag{9}$$

$$\lambda_2 + \lambda_3 = k_{12} + k_{21} + k_{23} \tag{10}$$

eliminating λ_2 from (10),

$$\frac{(k_{12}k_{23})}{\lambda_3} + \lambda_3 = k_{12} + k_{21} + k_{23}$$

If $k_{21}/k_{23} = x$, then $k_{21} = xk_{23}$

$$\therefore \quad \frac{(k_{12}k_{23})}{\lambda_3} + \lambda_3 = k_{12} + xk_{23} + k_{23} = k_{12} + k_{23}(x+1)$$

$$\therefore \quad k_{23}(x+1) - \frac{k_{12}k_{23}}{\lambda_3} = -k_{12} + \lambda_3$$

$$\therefore \quad k_{23}\left\{(x+1) - \frac{k_2}{\lambda_3}\right\} = -k_{12} + \lambda_3$$

$$\therefore \quad k_{23} = -k_{12} + \lambda_3 / \left\{(x+1) - \frac{k_{12}}{\lambda_3}\right\} \tag{11}$$

From the steady state method, k_1 and k_{-1} are equivalent to k_{12} and k_{21} respectively. However, k_2 in a second order rate constant and k_{23} is a pseudo first order rate constant which includes the concentration of dimethoxybenzene. Hence, k_2 must be multiplied by this concentration in order to be in the units of $\sec^{-1}$ as with the other rate constants i.e.

$$k_2[C] = k_{23}$$

$$\therefore \quad k_{21}/k_{23} = k_{-1}/k_2[C] = x$$

$$\therefore \quad k_2/k_{-1} = 1/x[C] = 2.47 \text{ dm}^3\text{mol}^{-1}.$$

The following constants were determined from the reaction of a fifty-fold excess of 1,3-dmb with (1-methyl, 5-phenyl) P.I.T.:

$$k_1 = 2.57 \times 10^{-3} \text{ sec}^{-1} \qquad \lambda_2 = 1.39 \times 10^{-3}\text{sec}^{-1}$$

$$x = 0.808$$

These values were used to calculate:

$$k_{23} = 3.0 \times 10^{-2}\text{sec}^{-1} \qquad k_2 = 6.0 \times 10^{-2}\text{dm}^3\text{mol}^{-1}\text{sec}^{-1}$$

$$k_{-1} = 2.4 \times 10^{-2} \text{ sec}^{-1} \qquad k_{-1}/k_1 = K = 9$$

The constant K is the ratio of rate constants for the formation and decomposition of the intermediate B from A, and so is an equilibrium constant for the formation of B which lies on the side of A. This was expected as only A was observed spectroscopically.

When the process was repeated with other values of λ_3 from different concentrations of 1,3-dmb, the values of K were scattered. Reaction with 0.25 and 0.6M 1,3-dmb gave K as 20 and 16 respectively but with 0.1 and 0.4M 1,3-dmb K was very large. This was because $(x + 1)$ and k_{12}/λ_3 in (11) were very similar in magnitude, so a small error in either quantity produced a very large error in k_{23} and so in K.

A further method to calculate K was attempted using a technique by Fersh t and Jencks.[47] This is also based on the non steady state equations for a series equilibrium reaction. The concentration of the intermediate is given by:

$$B = \frac{A_1^{\circ} k_{12}}{\lambda_2 - \lambda_3} \left(e^{-\lambda_3 t} - e^{-\lambda_2 t}\right) \qquad (12)$$

The experimental value of λ_3 was determined as before from the gradient of a semilogarithmic plot of concentration of reactant ~~agent~~ against time. Extrapolation of this line back to zero time gave an intercept on the y axis which was used to calculate the preexponential term in equation 12. As k_{12} and λ_3 were known in the present case, λ_2 was found. The intercept varied between kinetic runs, mainly because of the precise time of mixing was not known. However, the intercept was generally equivalent to 95% ± 2 of A_1° for the reaction of 0.1M 1,3-dmb with 1-methyl, 5-phenyl P.I.T. This meant that the concentration of B at $t = 0$ was 5 ± 2% of A_1°. The error in B was large but was used in order to estimate the magnitude of the rate constants:

$$\text{at } t = 0 \quad B = \frac{A_1^{\circ} k_{12}}{\lambda_2 - \lambda_3}$$

$$\therefore \quad \lambda_2 = \frac{A_1^{\circ}}{B} k_{12} + \lambda_3$$

But $\lambda_2 + \lambda_3 = k_{12} + k_{21} + k_{23}$ (10)

Eliminating λ_2; $\frac{A_1{}^{o}k_{12}}{B} + 2\lambda_3 = k_{12} + k_{21} + k_{23}$

$$= k_{12} + k_{23}\,(1 + x)$$

$$\therefore \quad k_{23} = \frac{k_1\left(\frac{A_1{}^{o}}{B} - 1\right) + 2\lambda_2}{(1 + x)}$$

k_{23} was then used to calculate k_2, k_{-1} and k as before. The errors were estimated by repeating the calculation using intercept values of 93% and 97% $A_1{}^{o}$, and the results are summarized in table 3.7.

TABLE 3.7

Calculated Rate constants for the reaction of 1,3-dimethoxybenzene (0.1M) with (1-methyl, 5-phenyl) P.I.T. (0.01M)

Intercept $\% A_1{}^{o}$	k_{23} sec^{-1}	k_2 $dm^3mol^{-1}sec^{-1}$	k_{-1} sec^{-1}	K –
93	1.7×10^{-2}	1.7×10^{-1}	6.8×10^{-3}	11
95	9.9×10^{-3}	9.9×10^{-2}	4.0×10^{-3}	16
97	7.0×10^{-3}	7.0×10^{-2}	2.8×10^{-3}	26

The order of magnitude of K using the second method was the same as for the first at about 10 → 20, and k_2 was approximately $10^{-1}dm^3 mol^{-1}sec^{-1}$.

CHAPTER 4

Spectroscopic Properties of (diene)- and (dienyl)-iron tricarbonyl complexes

A Nuclear Magnetic Resonance Spectroscopy

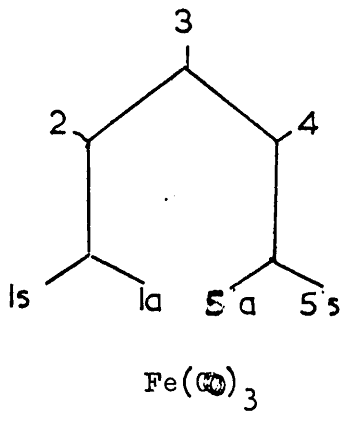
Nuclear magnetic resonanance techniques have been used extensively in studies of the structures of organic ligands in organometallic compounds. Recently, the information derived from proton nmr spectroscopy has been supplemented increasingly by carbon-13 nmr spectroscopy. Possibly one of the major contributions to the rapid growth of this latter technique has been the development of Fourier transform nmr which has enabled rapid recording of the spectrum of a complex molecule containing natural abundance levels of ^{13}C.

The work on nmr spectroscopic properties of the iron tricarbonyl complexes described in this chapter is divided into three sections. The first two sections refer to proton nmr data of (dienyl)- and (diene)-iron tricarbonyl complexes respectively. The third section is concerned with ^{13}C nmr spectra of these compounds.

(i) Proton nmr spectra of pentadienyl iron tricarbonyl complexes.

Proton nmr spectra of the tetrafluoroborate salts of pentadienyl, (1-methyl) pentadienyl and (1,5-dimethyl) pentadienyl iron tricarbonyl were first reported by Mahler and Pettit.[16,17] The results were consistent with a structure in which the pentadienyl ligand was composed of a cissoid arrangement of all five sp^2 carbon atoms. Methyl substituents at 1- and 5-positions were shown from the chemical shift data to be exclusively in a syn configuration. This was confirmed by Lillya,[28] who prepared a complex containing a 1-methyl substituent in an anti position which was shifted to ~~Low~~ high field compared with a syn-1-methyl group.

The data for the P.I.T. complexes, shown in table 4.1, tend to confirm the original structure proposed for this system. The numbering of each proton in this table is based on the scheme in (4.1) below. The letters in the table (s,d,t,dd,dt,m) indicate the multiplicity of each resonance and refer respectively to singlet, doublet of doublets, doublet of triplets and unresolved multiplet. Assignment was confirmed in several cases by ~~subsiding~~ double resonance experiments. Peak integrals are not shown, but are all consistent with the assigned labels.



(4.1)

Substitution of the pentadienyl system with phenyl or methyl groups appears to have little effect on the magnitude of the vicinal proton coupling constants. Long range spin couplings are not normally observed in these complexes. It can be seen that trans couplings are generally much larger than cis couplings in the dienyl system. Thus, for a range of substituents, the trans $J_{2,3}$ and $J_{4,5a}$ fall in the range 12–13 Hz and the cis $J_{1a,2}$ and $J_{4,5a}$ fall within 6–8 Hz. It is interesting to note that the cis coupling constants are in the same range as those found in the sterically similar cis coupling across an olefinic bond in cyclopentane systems (5.1 – 7.0 Hz).[64] For comparison, the cis olefinic couplings in cyclohexene systems are generally larger (8.8 – 10.5 Hz), representing an increased proximity of the coupled protons.

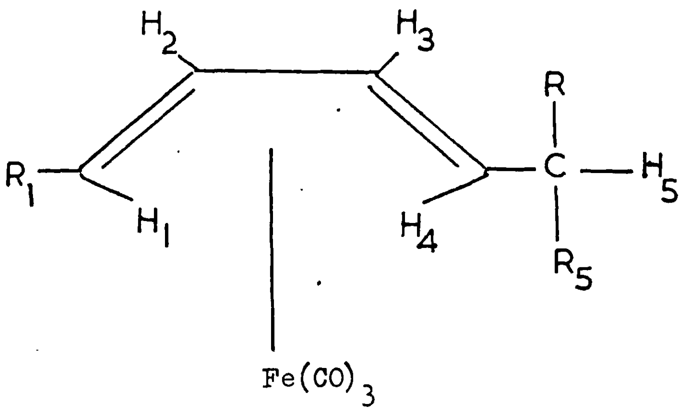
In complexes where 1a = 1s = H, the magnitude of the cis coupling $J_{1s,2}$ is larger than the other cis couplings at 10 Hz, and is within the range typical of alkyl substituted ethene derivatives.[65] However, in the case where 1a = methyl, 1s = H, $J_{1s,2}$ is reduced to 7 Hz, perhaps indicating that the spin-coupled atoms are no longer coplanar. This could be due to steric over-crowding, the methyl group being forced away from the metal, out of the plane containing the dienyl system. Such a distortion would tend to introduce a dihedral angle between positions 1s and 2, and so reduce the effective spin-coupling. This effect has been observed in (diene)iron tricarbonyl complexes containing amine substituents from X-ray crystallographic data.[9]

The nmr spectra of solutions of exo- and endo- (6-phenyl hexa-3,5-dien-2-ol) iron tricarbonyl in sulphur dioxide solutions containing fluorosulphuric acid are shown in spectrum 4.1 and spectrum 4.2 respectively. The former spectrum is identical with one of a sample of cis, syn,syn (1-methyl, 5-phenyl pentadienyl) iron tricarbonyl tetrafluoroborate, and does not change significantly with temperature over the range -80° to +30°. However, spectrum 4.2 does change with temperature, decomposing to form a black heterogeneous mixture above -20° with a loss of signal resolution owing to the formation of paramagentic species. This spectrum is consistent with cis(anti-1-methyl, syn-5-phenyl) P.I.T. as shown by the unusual shielding of the 1-methyl (1.57δ) characteristic of anti rather than syn substitution. The syn-1-methyl protons in cis (syn-1-methyl, syn-5-phenyl) P.I.T. resonate at 1.92 . This effect can also be seen with the proton on C_1, an anti proton resonating at 3.89 ppm and a syn proton at 4.61 ppm, and is in accord with the observation that anti substituents generally lie to ~~low~~ high field of syn substituents.[27,28]

Turning to the effect of substitution of the P.I.T. system on the protons bonded directly to the dienyl carbon atoms, as the degree of methyl substitution increases, the resonances at all five positions tend to move to ~~low~~ high field. As expected, this is more marked at C_1 than at C_3. Phenyl substituents also tend to cause a similar behaviour, but the magnitude of this shift is much greater. In the (1,5-diphenyl) complex, protons are deshielded by 1-2 ppm relative to the 1,5-dimethyl complex. This is possibly caused by an increase in electron density on the dienyl system due to these substituents.

(ii) Proton nmr spectra of (diene) iron tricarbonyl complexes.

The proton nmr spectrum of (butadiene) iron tricarbonyl has been discussed in Chapter 1, particularly with regard to the unusual chemical shifts. The four terminal protons have resonances of 1.68δ (syn) and 0.22δ (anti), but the two "centre" protons are much more deshielded at 5.85δ. This pattern is maintained in substituted derivatives, as shown in tables 4.2 and 4.3. The numbering of each proton is based on the scheme in (4.2) below, and in consistent with the numbering scheme of the dienyl complexes. Assignments were confirmed (particularly for H_2 and H_3) by double resonance experiments. The data for (6-phenyl hexa-3,5-dien-2-ol)- and (hepta-3,5-dien-2-ol)- iron tricarbonyl are literature values,[23] and refer to the *exo* isomer in each case.



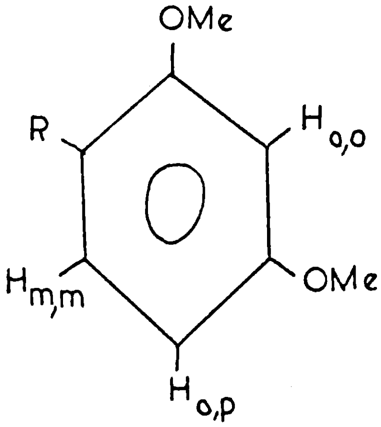
(4.2)

The *trans*,*trans* structure of the diene unit is shown by the vicinal proton coupling constants, which do not appear to be significantly modified by the nature of any substituent present. Thus, the *cis* $J_{2,3}$ couplings are all in the range 5-6 Hz, while the *trans* $J_{1,2}$ couplings are larger at 9 Hz. The other *trans* coupling $J_{3,4}$ is generally smaller than $J_{1,2}$, possibly indicating that H_3 and H_4 are not co-planar with C_3 and C_4. This could arise from steric interactions of the terminal $-CR(R_5)(H_5)$ group with the iron tricarbonyl group.[9]

The shifts of the protons bonded directly to the carbon skeleton of the di ene system are somewhat shielded relative to those in the dienyl system. This is reasonable as the latter system carries a formal positive charge, though from the shift data it would appear that it is extensively delocalised throughout the system.

The proton shifts in these complexes are relatively insensitive to changes in the substituents at C_1 or C_4. For a series of complexes with R_1 = Ph, R_5 = Me and R = OH, OMe, OEt, O*i*Pr, the only significant changes in the nmr spectra are due to the resonances of the protons in the substituent R. Even in the case when R = 2,4-dimethoxy phenyl, R_5 is deshielded by only 0.1 ppm relative to the methoxy derivative (R = OMe). Small shifts also occur at H_1 when the nature of R_1 is changed - H_1 becoming more shielded when R_1 = Me than when R_1 = Ph. This feature is useful in determining the structure of substituents on the system, as the protons bonded to carbon atoms of the <u>trans,trans</u> diene can readily be recognised in the spectrum by reference to the chemical shifts of the corresponding alcohol complex.

The position of substitution on the 1,3-dimethoxybenzene ring in the reaction of 1,3-dimethoxybenzene with P.I.T. complexes can be seen from the nmr spectra of the (diene) iron tricarbonyl products. The chemical shift data of these products are shown in table 4.2 and table 4.3. The latter table shows the shifts due to the protons in the 1,3-dimethoxybenzene residue and 1,3-dimethoxybenzene itself for comparison. The labelling of the protons is shown in (4.3.).



(4.3)

This assignment is based on several observations. Firstly, the methoxy groups in the arene residue of the reaction products resonate at different frequencies. Thus, substitution must have occurred at the ortho, para position, which is the only position which would lead to a loss of symmetry in the molecule. Secondly, if the integrals of each arene hydrogen peak are compared with those of 1,3-dimethoxybenzene, it is clear that the ratios are different for the protons at low field (7.2 ppm) indicating that the reaction products have lost one proton at the ortho, para position, and thus the position of substitution is ortho to one methoxy group and para to the other.

(iii) Carbon-13 nmr spectra of (diene)- and (dienyl)- iron tricarbonyl complexes.

The use of carbon-13 nmr spectroscopy in the study of organometallic complexes has increased very rapidly over the last decade with the advent of commercial routine Fourier transform instruments. Recently, the ^{13}C spectraldata of metal carbonyl compounds have been reviewed[66] with reference to the carbonyl carbon resonance frequencies. Using this technique, it has been found that the (diene) iron tricarbonyl system is fluxional.[67] All three carbonyl groups in(butadiene)iron tricarbonyl resonate at the same frequency at room temperature, but split to give two signals in the ratio 1:2 at 180°K, consistent with the structure of this compound based on a square pyramid geometry.[68] Similar phenomena are exhibited by (cyclohexa-1,3-diene) iron tricarbonyl and in (cycloheptatriene) iron tricarbonyl.

The ^{13}C nmr experiments described in this work were designed to measure the resonance frequencies of the carbon atoms in the diene (or dienyl) system rather than those of the carbonyl carbons. These cannot easily be measured simultaneously using a Fourier transform nmr technique owing to the very different spin-lattice relaxation times (T_1).[66] The relaxation times of the diene carbons are much less than one second which enables rapid pulsingof the RF signal so that spectra can be recorded in approximately 1 hour. However, the carbonyl carbons have relaxation times in the order of 100 seconds, which would mean that large time intervals would be required between successive pulses in order to prevent saturation and hence loss of sensitivity. Indeed, in all the spectra determined in this work, the absorption of the carbonyl carbons were never observed.

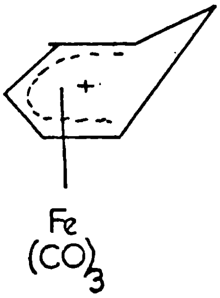
The ^{13}C resonance frequencies of each complex were determined by use of broad band proton decoupling. There were two reasons for this. Firstly, the ^{13}C-H spin-spin couplings were destroyed, so that each carbon atom gave rise to a single absorption frequency, which simplified the spectrum. Secondly, the signal intensities were enhanced by the Nuclear Overhauser Effect,[69] so that the time required for each experiment could be substantially reduced. The disadvantages in using this method were that the ^{13}C-H spin-spin couplings had to be measured by additional experiments without proton decoupling, and that the intensities of the signals were not proportional to the number of carbon atoms resonating at a particular frequency.

The ^{13}C nmr spectra of the (dienyl) iron tricarbonyl complexes were recorded as their tetrafluoroborate salts in CD_3NO_2 at a concentration of approximately 0.5 mmol in 0.5 cm^3 of solvent. The deuterated solvent was employed so that the spectrometer could be locked to the deuterium resonance frequency. Preliminary experiments showed that the use of an external lock signal from a capillary of D_2O in the sample were unsatisfactory as this gave rise to large spinning side-bonds. For similar reasons, the nmr spectra of (diene) iron tricarbonyl complexes were determined in deuterated chloroform solution. The solutions also contained approximately 1% TMS, which was used as an internal standard, and all shifts were recorded as parts per million relative to internal TMS.

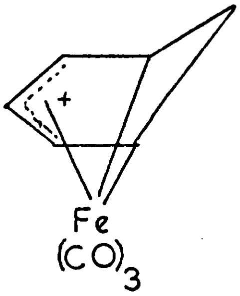
The ^{13}C nmr shifts of substituted P.I.T. complexes are shown in table 4.4. Assignments were verified for (1-methyl)- and (1,5-dimethyl)-P.I.T. using heteronuclear double resonance. The broad band proton decoupled spectrum of (1,5-dimethyl) P.I.T., shown in spectrum 4.3, indicates that four distinct carbon atoms are present. The multiplet at 63.5 ppm is due to the carbon atoms in the solvent, CD_3NO_2. Spectrum 4.3 is of the same complex, but with only the protons at 3.4δ on the TMS proton scale fully decoupled. This has the effect of producing only one singlet in the carbon spectrum at 89.62 ppm. Thus, this carbon must be directly bonded to the proton at 3.4δ, which has been established as H_{1a} in table 4.1, and so the carbon is at the 1-position. Similarly, in spectrum 4.4, irradiation of H_2 at 3.92 δ causes the carbon at C_2 to appear as a singlet at 105.22 ppm. Assignment of the carbon nmr spectrum in (1-methyl) P.I.T. was more complicated as each of six carbons in the dienyl ligand resonate at different frequencies. The fully decoupled spectrum is shown in spectrum 4.6, and the partially decoupled spectra in spectra 4.7 - 4.11, with irradiation at 1.85, 2.25, 3.5, 6.1 and 6.95 δ respectively. This gives sufficient information to interpret the position of each carbon atom of the organic ligand in the spectrum.

Vicinal ^{13}C-H coupling constants were determined in three dienyl complexes: (1-methyl)-, (1,5-dimethyl)- and (1-methyl, 5-phenyl)-P.I.T. The values obtained are shown in table 4.5. The methyl group coupling (C_{Me}-H) are all typical values of sp^3 hybridized carbons. For comparison, the analogous couplings in ethanol are 125.0 Hz.[70] The ^{13}C-H coupling constants for carbons in the dienyl system are in the range 158 - 181 Hz and are in accord with sp^2 rather than sp^3 hybridization. Similar values have been reported for the cyclic system in (cyclohexadienyl) iron tricarbonyl and its methyl derivatives.[71] It has been suggested that structure (4.4), in which the carbon atoms of the dienyl system are sp^2 hybridized, serves as a better description of the bonding of the cyclic cations than does structure (4.5), for which a wider range of coupling constant values would be expected.[71]

However, it can be seen that the data for the acyclic cations listed in table 4.5 indicate that the proton–carbon coupling constants for C_2, C_3 and C_4 are generally larger than those for C_1 and C_5. This would tend to suggest that the bonding is best described as mainly of a dienyl structure but with a small contribution from a 1,5 σ ; 3,4,5-π-enyl bonding pattern analogous to that present in (4.5).



(4.4)

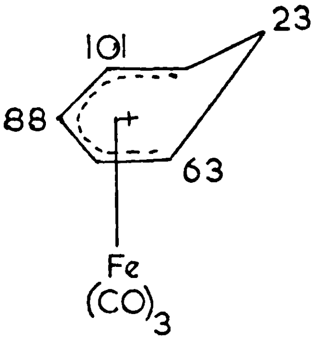


(4.5)

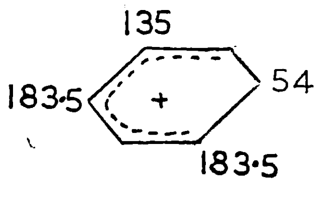
Examination of the chemical shifts of the carbon atoms in the dienyl system of the acyclic pentadienyl cations (table 4.4) reveals several trends. Firstly, carbons at methyl substituted positions tend to be deshielded by approximately 10 Hz relative to carbons at proton substituted positions. This effect appears to be a general feature in the ^{13}C nmr spectra of olefins. Thus, in general, methyl substitution of an olefin causes a 10 Hz shift to low field. This has been used in a series of empirical rules for the calculation of the carbon-13 spectra of olefins.[72] Thus, it seems unlikely that these shifts in the dienyl spectra provide sufficient information regarding any effect of methyl substituents on the distribution of charge density within the complexes.

Phenyl substitution at C_1 appears to have a shielding effect on C_2, the shift being in the order of 15 ppm. This suggests that there is some degree of conjugation of the phenyl group with the dienyl system, which would tend to shield C_2. However, shifts of similar magnitude have been reported for 1-phenyl ethene,[73] where C_2 is shielded by 10.1 Hz relative to ethene. Hence, it is not clear that the observed shift at C_2 in the 1-phenyl pentadienyl complexes can be directly related to any changes in the electronic structure.

The shifts of the dienyl carbons in the methyl substituted acyclic P.I.T. complexes fall in a pattern where carbons 1,3,5 resonate upfield of carbons 2 and 4. A similar pattern has also been observed in the cyclic complexes (cyclohexadienyl) iron tricarbonyl and (1,3,5-trimethylcyclohexadienyl) iron tricarbonyl.[71] The values determined for (cyclohexadienyl) iron tricarbonyl are shown in (4.6), the shifts having been converted to the TMS scale from the CS_2 scale (using $C^{13}S_2$ = 192.8 ppm downfield of TMS). For comparison, the shifts in protonated



(4.6)



(4.7)

benzene in the strongly acid medium - HF/SbF_5 in SO_2ClF are shown in (4.7).[74] Thus, it appears that the stabilizing effect of iron tricarbonyl on the pentadienyl system is essentially the same in both the cyclic and acyclic systems. Any large differences in the charge distribution of the two systems would be expected to have a profound effect on the ^{13}C spectra, as in (4.7), where the system can be regarded as a pentadienyl cation with no external stabilization.

The ^{13}C nmr shifts of the ψ exo and ψ endo isomers of (6-phenylhexa-3,5-dien-2-ol) iron tricarbonyl are shown in table 4.6. The "shift difference" column refers to the difference in resonance frequencies of each carbon for the two isomers. A positive sign indicates that the carbon in the ψ exo complex is shifted to high field relative to the ψ endo complex. The largest difference between the two spectra is at C_2, the asymmetric carbon. The shifts at the other positions are consistent with the conformational analysis of Clinton and Lillya,[23] who suggested that the most stable configuration was with the methyl group in the least crowded position in each isomer. Furthermore, the asymmetry of the terminal group would be expected to be most significant in interactions with C_4.[25] This is reflected in the relatively large shift of 1.88 Hz at this position.

The spectra of the above complexes are typical of the substituted (diene) iron tricarbonyl system. The reported shifts in (hexa-3,5-~~diacetal~~ dien-1-ol) iron tricarbonyl[75] are very similar, except for C_5, which in this case does not bear a phenyl substituent. In (butadiene) iron tricarbonyl, C_2 and C_3 resonate at 85.8 ppm and C_1 and C_4 at 41.1 ppm relative to TMS.[7] Thus, if the diene complexes are compared with the dienyl compounds of iron tricarbonyl, the shifts in the latter cases are generally at lower field by 10 – 30 ppm. This deshielding effect may well be caused by the reduction in electron density in the π system of the dienyl compounds. However, the ^{13}C chemical shift is approximated by the sum of three terms; the diamagnetic contribution, the paramagnetic contribution, and the contribution from neighbouring nuclei.[69,76] Although the paramagnetic shielding term is a function of the electron density of the system, and is often considered to be the dominant factor[76] controlling the chemical shifts in organic compounds, the other terms must be borne in mind especially when the resonant carbon is in the vicinity of a metal atom.

The magnitude of the "neighbouring group effect" of the metal atom in organometallic complexes appears to be uncertain. In a recent study of substituted (arene) chromium tricarbonyl complexes, it was suggested that the steric and anisotropic effects were similar for both the coordinated and the free ligands.[77] In addition, the shielding of the ring carbons in 1,3,5-trimethylbenzene on coordination in complexes of the type (arene) $M(CO)_3$ [where M = Cr, Mo, W] has been said[78] to arise from the formation of a negative charge on the arene ligand. However, Brill et al[79] postulated that the magnetic anisotropy of a heavy atom near a resonant carbon nucleus is the dominating influence on the nmr spectrum, with the local electron density at the carbon superimposed as fine structure. This would explain why a general feature in the ^{13}C spectra of organometallic complexes appears to be that olefinic ligands π-bonded directly to the metal usually fall in a small shift range. This is generally in the order of 70 - 110 ppm, falling in between the shifts of alkanes and alkenes. Thus, in the complex $[(\eta - C_2H_4)PtCl_3]^- K^+$, the ethene residue resonates at 75.1 ppm, and in $[(CO)_2(\eta - C_5H_5)FeCN]$, the cyclopentadienyl residue resonates at 85.9 ppm. In the arene complex $(\eta - C_6H_6)Cr(CO)_3$, the ring carbons resonate at 93.7 ppm.

B. Infra-red Spectroscopy

In this work, infra-red spectroscopy was used mainly as an analytical tool for the determination of the concentration of dienyl complex in solution. This used the strong carbonyl bond at 2105 cm^{-1}, which was in a region free from overlap of other absorption bnads. The dienyl complexes also gave a further characteristic carbonyl absorption at 2060 cm^{-1} which generally appeared as a broad band, though it could be resolved in dilute solution to two absorptions. No significant variation in these frequency bands were observed between the substituted complexes used in this study,the spectra generally being determined in nitromethane solution. The cyclic derivatives also have absorptions in the same frequency range; (cyclohexadienyl) iron tricarbonyl tetrafluoroborate having carbonyl bands at 2120 and 2072 cm^{-1}.[81]

The (diene) iron tricarbonyl complexes have been investigated by infra-red spectroscopy. It was found that in a series of para substituted (1-phenyl butadiene) iron tricarbonyl complexes, the carbonyl stretching frequencies all were linearly related to the Hammett σ_p factor of the substituent.[82] The carbonyl bands in these complexes appear at 2050 and 1990 cm^{-1}, the latter being a broad absorption which can be resolved into two bonds. Again, in the complexes studied in this work, no significant variation in carbonyl frequencies was observed. However, the contrast between the diene and dienyl complexes is clear. Dienyl carbonyl absorptions are higher by approximately 50 cm^{-1}, reflecting a reduction of back donation of electrons into the antibonding orbitals of the carbonyl groups. Thus, some of the positive charge on the dienyl system is "felt" by the carbonyl groups.

C. Mossbauer Spectroscopy

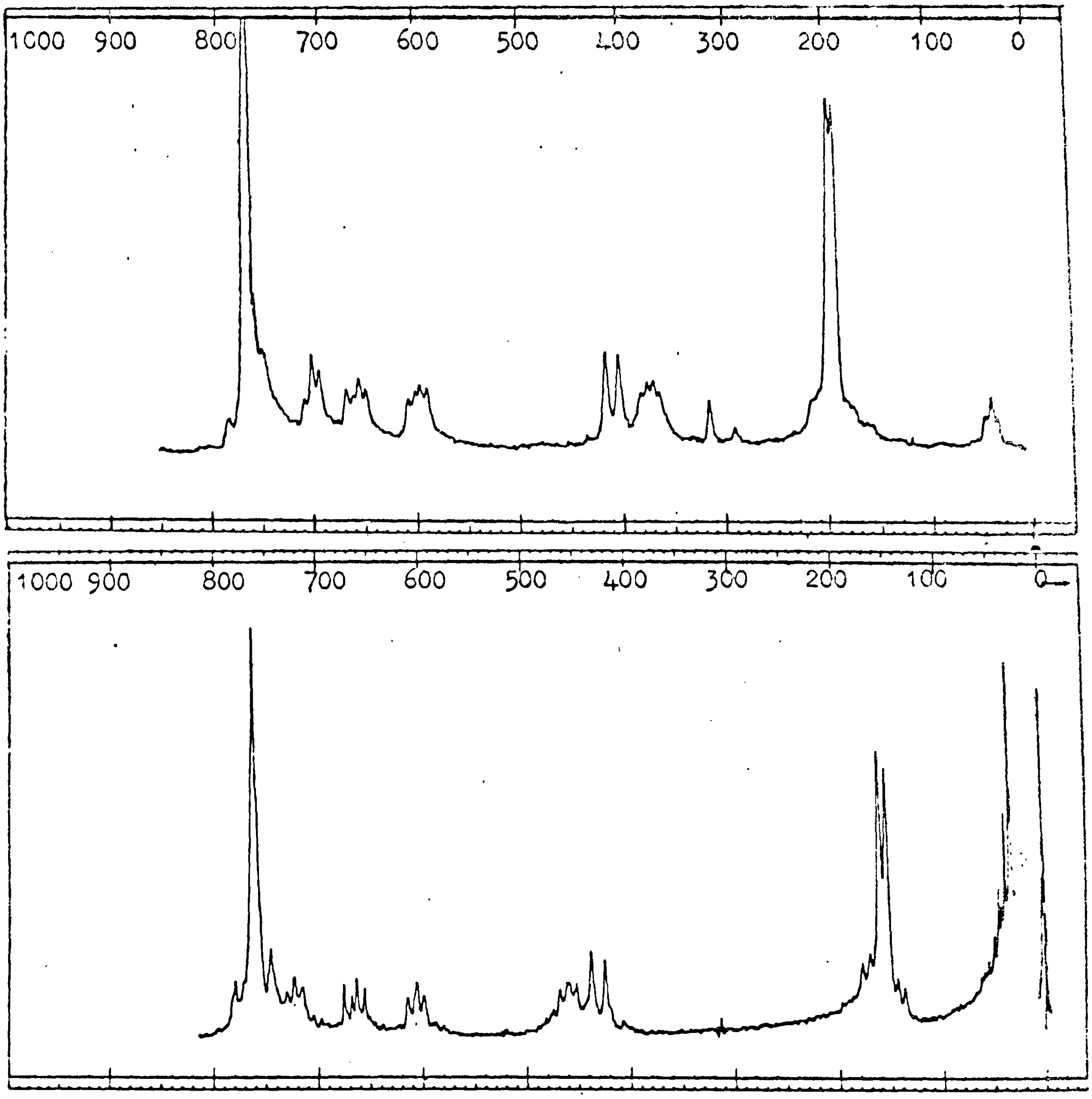
The ^{57}Fe Mossbauer parameters for two diene and eight dienyl complexes of iron tricarbonyl are shown in table 4.7. The Mossbauer spectra of these compounds consist of two absorption lines of equal intensity. The centre of gravity of the two lines (δ) and the quadrupole splitting are given in millimetres per second, and are relative to a standard iron absorber. The data refer to measurements carried out at 195°K.

Before examining the data in any detail, it is useful to consider the origin of the Mossbauer effect in iron.[83] The radio-isotope ^{57}Co contained in the source decays to give ^{57}Fe in an excited nuclear state. This subsequently decays with a half life of 10^{-7}sec. to yield a γ ray at 14.4 keV. If the ^{57}Fe nuclei in the sample are in the same environment as those in the source, resonant absorption of the γ radiation will occur. In order to determine any displacement in the resonant frequency of the sample nuclei, the sample is given a velocity relative to the source, so that the incident radiation is subjected to the Doppler effect. Thus, shifts in the resonant frequency are measured in units of velocity - in this case mm.sec^{-1}. The isomer shift arises because the electron density at the nucleus interacts with the positive nuclear charge, and so the relative energies of the ground and excited nuclear states can be affected by the electronic environment of the atom. As only electron density in the s orbitals has a finite value at the nucleus, electrons in other orbitals can affect the isomer shift only by screening the s electrons from the nuclear charge. For ^{57}Fe, a positive shift indicates that the sample has less s electron density at the nucleus than the source. The quadrupole splitting is a measure of the asymmetry of the s electron distribution at the nucleus, symmetrical fields giving a splitting of zero.

The shifts (δ) of all the complexes studied fall within a narrow range of +0.11 to -0.10 mm.sec^{-1}. However, it can be seen that the dienyl complex VI has a shift which is slightly more positive than the corresponding dienol complex I by 0.06 mm sec^{-1}. Similarly, the dienyl complex IX is shifted by +0.08 mm.sec^{-1} relative to the corresponding dienol II. This phenomenon has also been noted by Collins and Pettit,[84] in a study of similar complexes. They conclu ded that the shift differences were too small to support the suggestion that the dienyl complexes should be regarded as Fe^{2+} systems.

The shift differences between the diene- and dienyl-complexes are much smaller than would be at first expected. However, this has been rationalized by postulating two opposing effects.[84] The charged dienyl ligand would be expected to cause a decrease in overall electron density on the iron atom when compared with a neutral diene ligand. This would tend to reduce the s electron density at the nucleus, and result in a positive isomer shift. This is accompanied by an increase in the back donation of d electrons from the metal to the ligand, which would be stronger in the dienyl than in the diene system. This latter process would lower the 3d electron density and decrease the shielding of the 4s electron density, so causing a negative isomer shift. The combination of these two effects, which tend to nullify each other, result in a very small net change in effective s electron density at the nucleus and so small shifts.

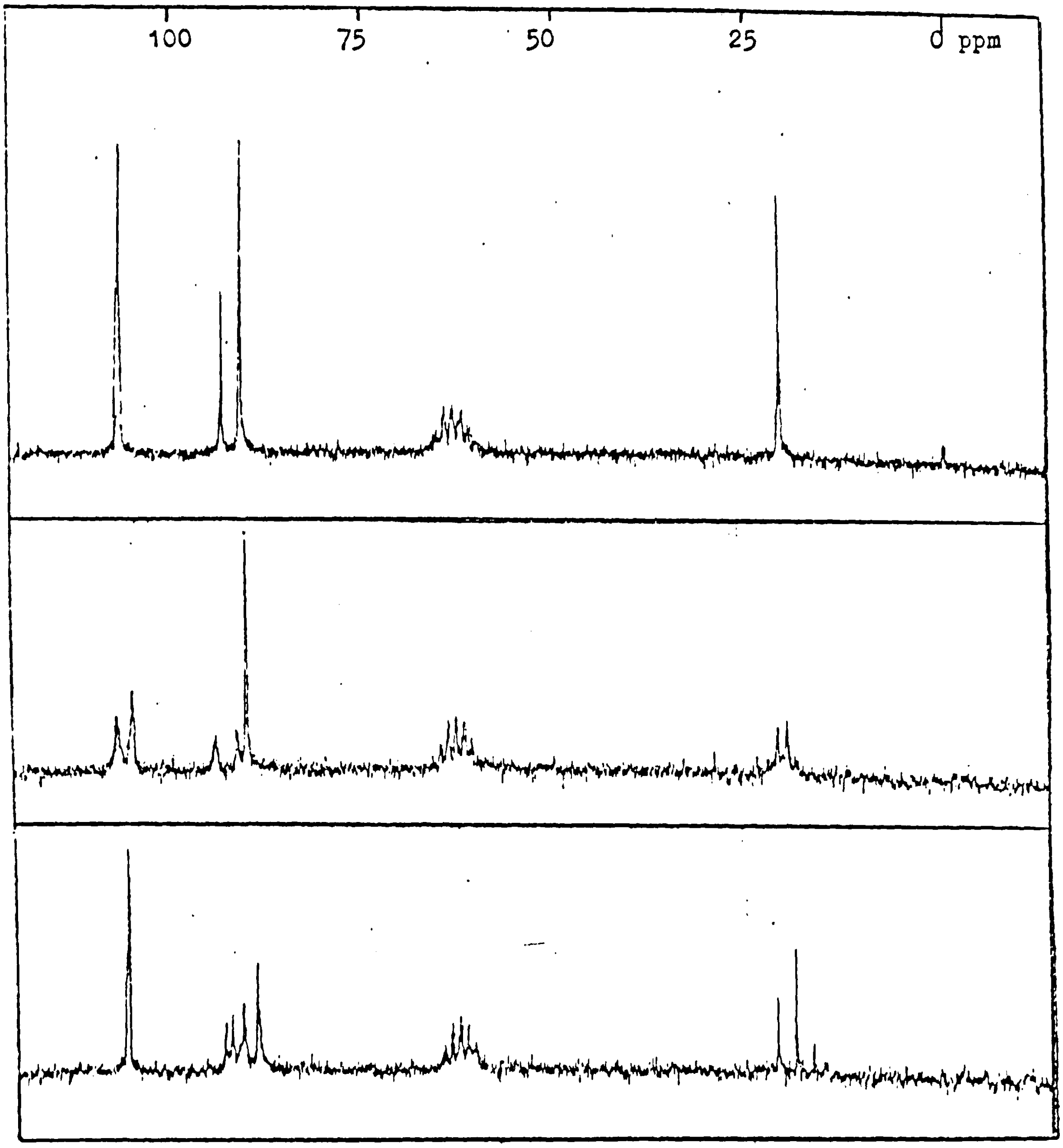
The quadrupole splitting cover a wider range than the isomer shifts. The splittings for diene complexes appear to be somewhat smaller than those of the dienyl complexes. This means that the electric field at the iron nucleus is more asymmetrical in the latter systems. However, it is not clear why there is some variation in the values obtained from the substituted dienyl systems. Similar variations have been reported in the quadrupole splittings of cyclic dienyl systems,[85] where the splitting was found to decrease with increasing ring size. Thus, small change in the structure of the dienyl complexes cause relatively large changes in the quadrupole splittings.



100 MHz Spectra of the Diastereoisomers of (6-phenyl hexadien-2-ol) iron tricarbonyl in FSO_3H / SO_2 at -60° 1000Hz scan

SPECTRUM 4.1 ψExo isomer

SPECTRUM 4.2 ψEndo isomer



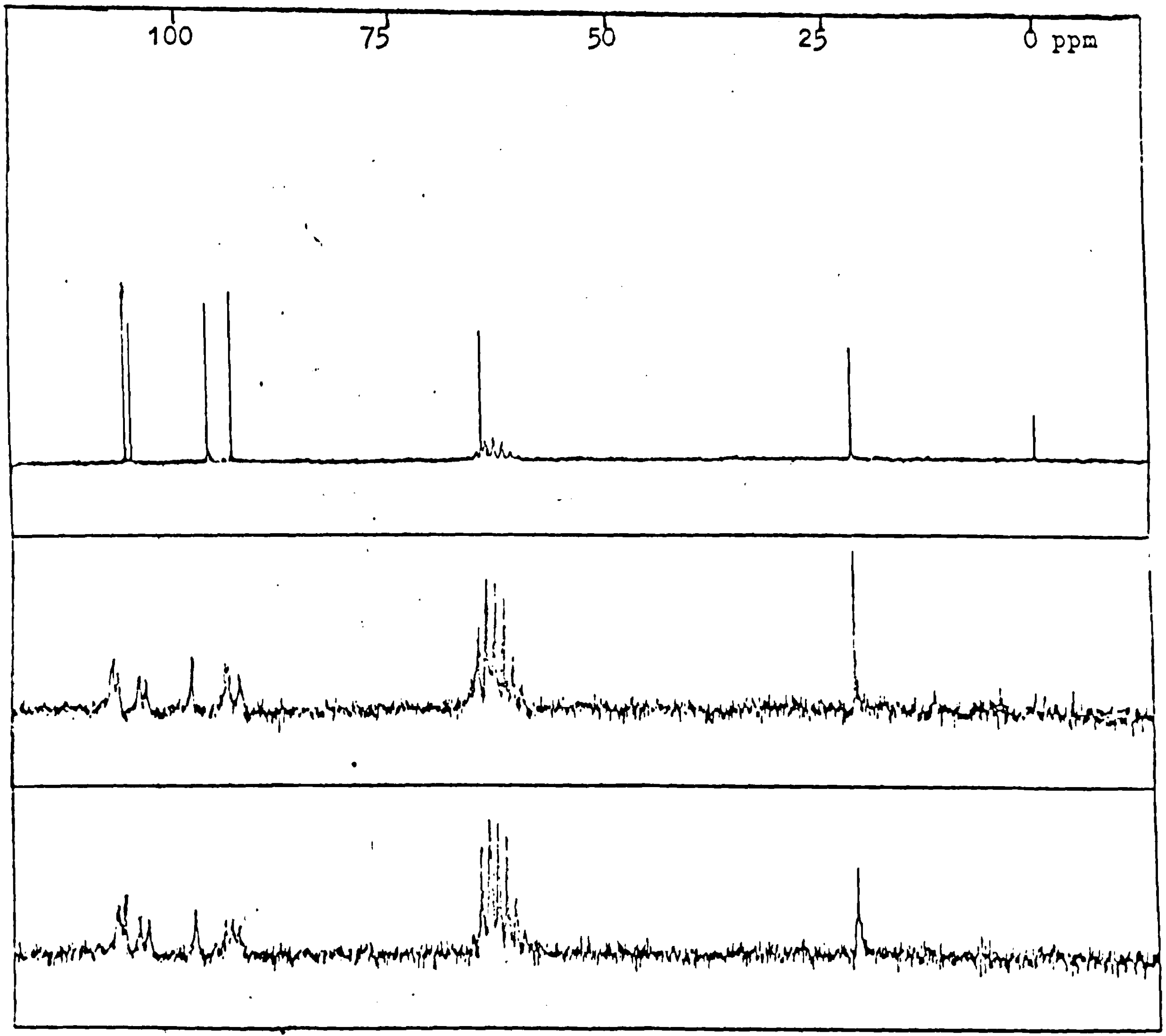
22.63 MHz ^{13}C Spectrum of (1,5-dimethyl) P.I.T. in CD_3NO_2 3000Hz scan

ppm relative to internal TMS

SPECTRUM 4.3 Protons broad band decoupled

SPECTRUM 4.4 Irradiation at 3.4 δ on proton spectrum

SPECTRUM 4.5 Irradiation at 5.92 δ on proton spectrum



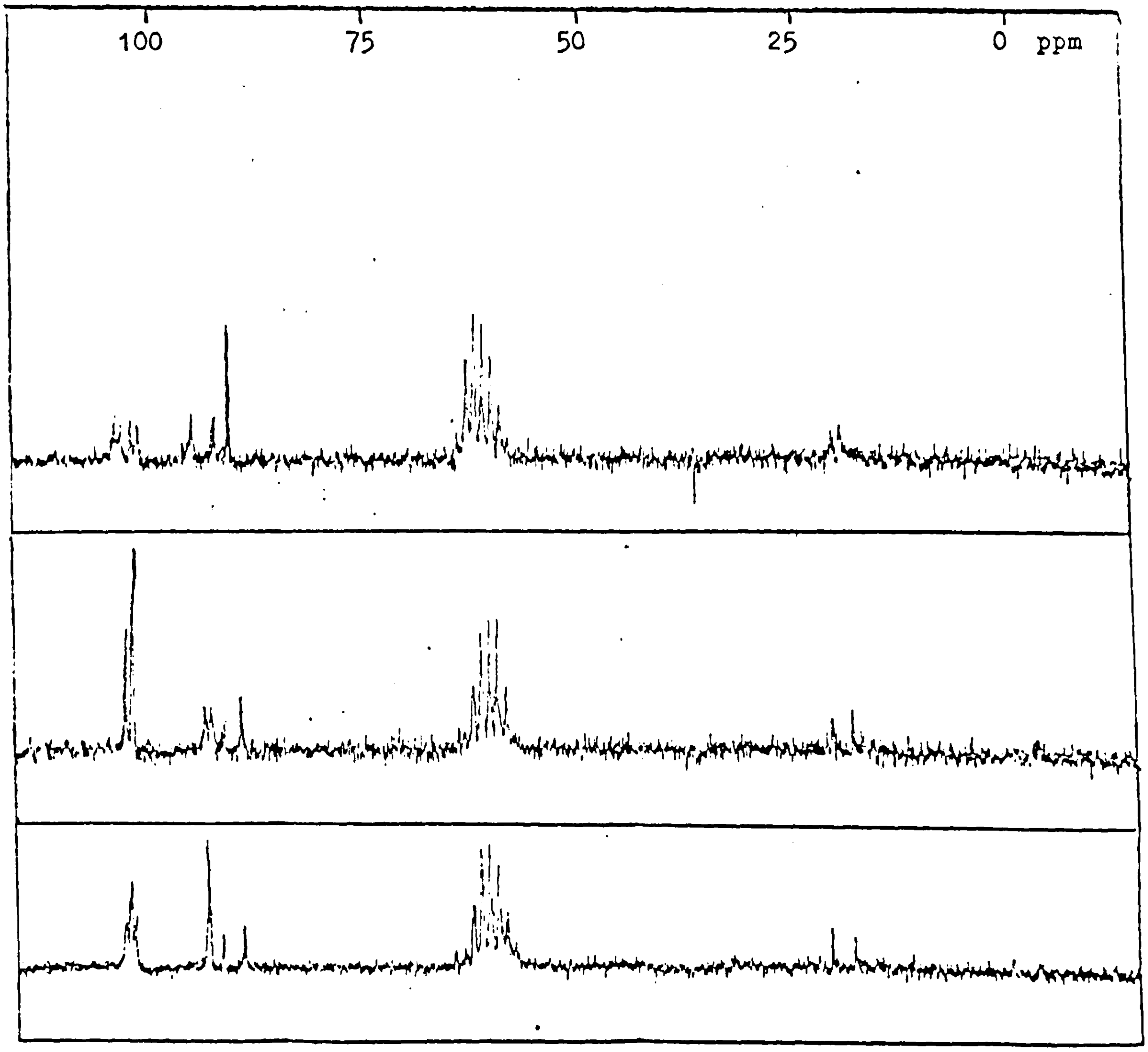
22.63 MHz ^{13}C Spectrum of (1-methyl) PIT in CD_3NO_2 3000Hz scan

ppm relative to internal TMS

SPECTRUM 4.6 Protons broad band decoupled

SPECTRUM 4.7 Irradiation at 1.85 δ on proton spectrum

SPECTRUM 4.8 Irradiation at 2.25 δ on proton spectrum



22.63 MHz ^{13}C Spectrum of (1-methyl) PIT in CD_3NO_2 3000Hz scan

ppm relative to internal TMS

SPECTRUM 4.9 Irradiation at 3.5 δ on proton spectrum

SPECTRUM 4.10 Irradiation at 6.1 δ on proton spectrum

SPECTRUM 4.11 Irradiation at 6.95 δ on proton spectrum

	Proton nmr shifts relative to TMS (δ)							Coupling constants (Hz)							
	1_a	1_s	2	3	4	5_s	5_a	$1_a,1_s$	$1_a,2$	$1_s,2$	2,3	3,4	$4,5_s$	$4,5_a$	$5_a,5_s$
Pentadienyl[(1,2)]	1.17 dd	3.75 dd	6.26 M	7.22 t	6.26 M	3.75 dd	1.17 dd	3.5	13	9.8	6.8	6.8	9.8	13	3.5
1-methyl	3.35 dt	1.82 Me d	5.96 dd	6.94 t	6.22 dd	3.61 dd	2.28 dd	7	12	-	7	7	10	12.5	3.5
1,5-dimethyl	3.40 dt	1.84 Me d	5.92 dd	6.86 t	5.92 dd	1.84 Me d	3.40 dt	6	12	-	7	7	-	12	6
1,3,5-trimethyl	3.36 dt	1.86 Me d	6.09 d	2.82 Me s	6.09 d	1.86 Me d	3.36 dt	6	12.5	-	-	-	-	12.5	6
1-s-methyl 5-phenyl	3.89 dt	1.92 Me d	6.02 dd	7.02 t	6.64 dd	7.58 Ph M	4.28 d	6	12.5	-	6	7	-	12.5	7
1-a-methyl[(2,3)] 5-phenyl	1.57 Me d	4.61 M	6.06 dd	7.23 t	6.26 dd	7.64 Ph M	4.31 d	6	-	7.5	7	7	-	12.5	7
1,4-dimethyl 5-phenyl	4.15 M	1.92 Me d	5.95 dd	6.91 d	2.63 Me s	7.58 Ph M	3.38 s	7	13	-	7	-	-	-	-
1,5-diphenyl[(1)]	5.10 d	7.78 Ph M	7.37 dd	7.89 t	7.37 dd	7.78 Ph M	5.10 d	-	13	-	8	8	-	13	-
1-^{t}butyl,5-phenyl	4.05 d	1.28 Me s	6.06 dd	7.06 t	6.74 dd	7.56 Ph M	4.38 d	-	13	-	7.5	7.5	-	7.5	-

TABLE 4.1 Proton nmr shifts and coupling constants of substituted P.I.T. complexes.
All data refer to solutions in CD_3NO_2 at 100 MHz, except where otherwise stated.
(1) 60 MHz; (2) in liquid SO_2; (3) at -60°.

Substituents			Proton nmr shifts relative to TMS (δ)								Coupling constants (H_z)					
R_1	R_5	R	R_1	1	2	3	4	5	R_5	R	R_1,1	1,2	2,3	3,4	4,5	5,R_5
Ph	Me	OH*	7.30 Ph M	2.17 d	5.78 dd	5.39 dd	1.27 M	3.68 M	1.4 d	1.85 s	–	9	6	7	8	7.5
Ph	Me	OMe	7.29 Ph s	2.06 d	5.71 dd	5.32 dd	1.2 M	3.12 M	1.35 d	3.29 s	–	9	5	8	7	6.5
Ph	Me	O t	7.24 s	2.4 d	5.73 dd	5.35 dd	1.3 M	3.26 M	1.36 d	3.57(CH_2) 1.25(CH_3)	–	9	5	8	6.5	7
Ph	Me	O^{i}Pr*	7.25 s	2.16 d	5.77 dd	5.33 dd	1.3 M	3.3 M	1.39 d	3.80(CH) 1.20(CH_3)	–	9	5	9	7.5	8
Me	Me	OH*	1.46 M	1.4 M	5.2 M	5.2[illegible] M	0.92 M	3.57 M	1.29 d	1.80 s	6			8	8	7
Me	Me	DMP*	1.38 M	1.4 d	5.98 dd	5.24 dd	1.4 M	3.0 M	1.42 d	I	5	9	5	8		6
Ph	Me	DMP	7.34 M	2.08 d	5.75 dd	5.52 dd	1.5 M	3.10 M	1.48 d	See 4.3 table II	–	9	5	8	7	7
Ph	Ph	DMP	7.3 M	2.16 d	5.72 dd	5.50 dd	1.96 dd	4.33 d	7.3 M	III	–	9	5	8	11	–

TABLE 4.2 Proton nmr shifts and coupling constants of substituted (diene) iron tricarbonyl complexes. All data refer to solutions in $CDCl_3$ at 100 MHz, except where indicated by an asterisk. DMP = (2,4-dimethoxyphenyl).

Proton nmr shifts relative to TMS (δ)				
Compound	$H_{o,o}$	$H_{m,m}$	$H_{o,p}$	Methoxy
1,3-dimethoxybenzene	6.6	6.6	7.2	3.82
I	6.5	6.5	7.12	3.87, 3.91
II	6.42	6.42	7.3	3.87, 3.93
III	6.5	6.5	7.3	3.83

TABLE 4.3 Proton nmr shifts of 1,3-dimethoxybenzene and of (diene) iron tricarbonyl complexes containing a 1,3-dimethoxybenzene residue (continued from Table 4.2)

I = [2-(2,4-dimethoxyphenyl), *trans*,*trans*-hepta-3,5-diene] iron tricarbonyl.

II = [2-(2,4-dimethylphenyl) 6-phenyl, *trans*,*trans*-hepta-3,5-diene] iron tricarbonyl.

III = [2-(2,4-dimethylphenyl), 1,5-diphenyl, *trans*,*trans*-penta-2,4-diene] iron tricarbonyl.

Substituents	^{13}C nmr shifts relative to TMS						
	1	2	3	4	5	Methyl	Phenyl
1-Methyl	93.49	105.32	96.35	106.03	64.21	21.32	-
1,5-dimethyl	89.62	105.22	92.22	105.22	89.62	21.12	-
1,3,5-trimethyl	87.22	105.22	110.87	105.22	87.22	23.20 (1,5) 20.99 (3)	-
1-methyl,5-phenyl	90.69	104.99	91.79	90.36	97.90	21.41	135.27, 132.41 130.05, 128.90
1,4-dimethyl, 5-phenyl	89.82	103.27	90.92	121.40	93.39	21.51 (1) 22.03 (4)	135.31, 131.08 130.70, 130.37
1,5-diphenyl	97.81	91.44	91.70	91.44	97.81	-	135,50, 132.84 131.28, 129.27
$1-^{t}$butyl, 5-phenyl	99.82[a]	114.19	89.88[b]	89.03[b]	98.13[a]	30.68 (Me_3) 37.39 ($-C\equiv$)	135.24, 132.58 131.15, 129.13

TABLE 4.4 Carbon -13 nmr shifts of substituted P.I.T. complexes. All data refer to solutions in CD_3NO_2 at 22.63 MHz.

[a,b - These assignments could be reversed].

Substituents	Vicinal C^{13} - H coupling constants (H_z)					
	$C_1 - H_{1a}$	$C_2 - H_2$	$C_3 - H_3$	$C_4 - H_4$	$C_5 - H_{5a}$	C_{Me}-H
1-methyl	164.7*	173.6	180.9	175.0	166.2	123.6
1,5-dimethyl	161.8	171.3	178.7	171.3	161.8	129.4
1-methyl,5-phenyl	158.0	179.4	179.7	158.4	165.5	128.8

TABLE 4.5 Carbon-13 nmr coupling constants of substituted P.I.T. complexes.

All data refer to solutions in CD_3NO_2 at 22.63 MHz.

[* Average value of couplings of $C_1 - H_{1a}$ and C_1-H_{1s}).

Carbon	exo	endo	Shift difference
1 Me	26.02	26.06	+0.04
2	65.83	69.60	+3.37
3	70.84	69.86	-0.98
4	82.47	80.59	-1.88
5	80.59	79.35	-1.24
6	61.74	61.29	-0.45
6 Ph C_1	139.34	139.53	-
$C_{2,6}$	128.68 [a]	128.68[b]	-
$C_{3,5}$	126.73[a]	126.67[b]	-
C_4	126.21	126.21	-

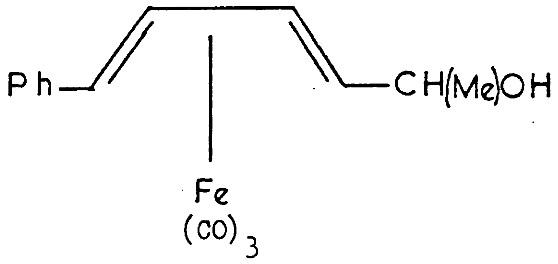


TABLE 4.6 Carbon -13 nmr shifts of the isomers of (6-phenyl, hexa-3,5-dien-2-ol) iron tricarbonyl in $CDCl_3$ solution at 22.63 MHz relative to TMS.

[a,b - These assignments could be reversed].

Complex	δ mm.sec^{-1}	Q.S. mm.sec^{-1}
I *exo* (6-phenyl hexa-3,5-dien-2-ol)-$Fe(CO)_3$	-0.10	1.58
II *exo* (2,2-dimethyl, 7-phenyl hepta-4,6-dien-2-ol)-$Fe(CO)_3$	+0.02	1.58
III [(1-methyl pentadienyl)-$Fe(CO)_3]^+BF_4^-$	+0.09	1.62
IV [(1,5-dimethyl pentadienyl)-$Fe(CO)_3]^+BF_4^-$	-0.04	1.66
V [(1,3,5-trimethyl pentadienyl)-$Fe(CO)_3]^+BF_4^-$	+0.11	1.66
VI [(1-methyl,5-phenyl pentadienyl)-$Fe(CO)_3]^+BF_4^-$	-0.04	1.66
VII [(1,4-dimethyl, 5-phenyl pentadienyl)-$Fe(CO)_3]^+BF_4^-$	+0.10	1.73
VIII [(1,5-diphenyl pentadienyl)-$Fe(CO)_3]^+BF_4^-$	+0.11	1.64
IX [(1-phenyl,5-*tert*-butyl pentadienyl)-$Fe(CO)_3]^+$ BF_4^-	+0.10	1.67

TABLE 4.7 Mossbauer parameters for (diene)- and (dienyl)- iron tricarbonyl complexes at 195°K.

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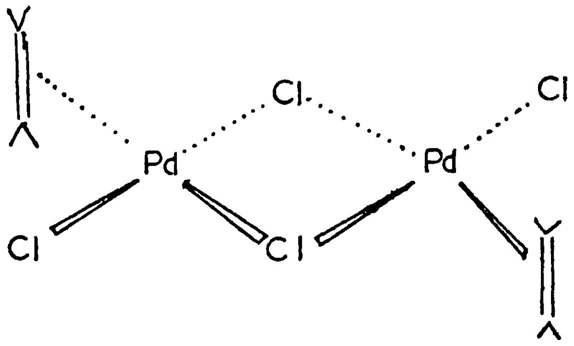
PART II

CHAPTER 5

(4-substituted but-2-enyl)palladium II complexes

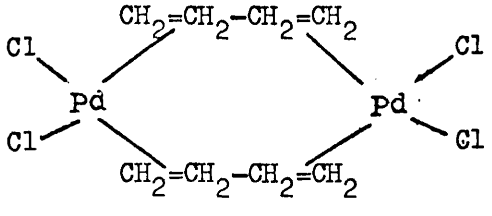
A: INTRODUCTION

The first palladium–olefin complex to be described was synthesized in 1938 by Kharasch,[1] from the reaction of ethene with bisbenzonitrile palladium II chloride. This unstable complex was shown by X-ray crystallography[2] to have the structure (5.1), with the olefin groups ~~anti~~ trans. to each other, perpendicular to the plane formed by the palladium and chlorine atoms.



(5.1)

When the reaction was repeated using butadiene in place of ethene ,[3] a dimeric complex was isolated. The first structure proposed was (5.2), with the butadiene acting as a bridging ligand between the two metal atoms. Shaw, however, on the basis of infra-red and n m r data, showed that this was incorrect,[4] and concluded that the compound was a chloro-bridged dimer, the



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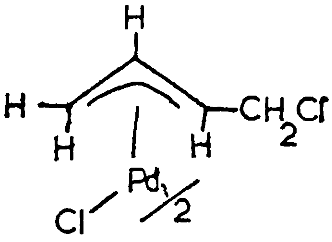
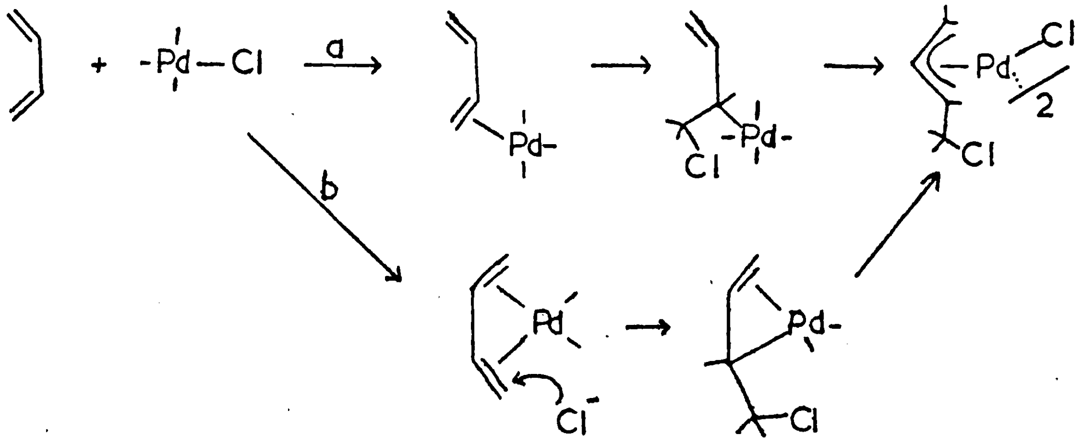


(5.3)

butadiene becoming a π-allylic ligand with a chloro group at the 4-position (5.3). The complex - di-μ-chloro (but-2-enyl) dipalladium II - was solvolysed readily by methanol to give a new complex with the chloro group replaced by methoxy.

If a ligand exchange reaction was carried out at -40° between butadiene and (n-pentane-$PdCl_2)_2$, a π-complex was isolated[5] with the butadiene π-bonded to the metal by only one double bond, which is analogous to the ethene complex (5.1). The evidence for this was provided by the infra red spectrum which contained two bands, one at 1660 cm^{-1} suggesting an uncoordinated double bond, and one at 1500 cm^{-1} suggesting a double bond which was π-bonded to the metal. Furthermore, when the complex was allowed to warm up to room temperature, it was quantitatively converted to (5.3), which was the product isolated when the reaction was carried out at room temperature. This suggests[6] that formation of the π-allyl complex could be via an intermediate in which an olefin was π-bonded to palladium which could rearrange by the intramolecular addition of chloride from the Pd-Cl bond. [Scheme 5.1a]. Another possible mechanism [Scheme 5.1b] involves the formation of a π-olefin complex, followed by attack of a free chloride ion to yield a σ, π- intermediate which rearranges to give the π allylic complex.



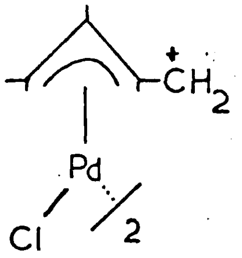
SCHEME 5.1

The kinetics of the reaction between isoprene and lithium tetrachloropalladate were recently studied,[7] and it was shown that the rate was independent of the concentration of hydrogen ions, but was retarded by chloride ions. This was consistent with a two term rate equation:

$$k_{obs} = \frac{k_1}{[Cl^-]^2} + \frac{k_2}{[Cl^-]} \quad [\text{isoprene}]$$

This indicated the formation of two π-olefin intermediates, and it was suggested that one was a mono olefin complex as in [Scheme 5.1a] and the other a cisoid diolefin complex as in [Scheme 5.1b], which were both attacked by methanol from outside the coordination sphere, followed by loss of a proton to give the same 4-methoxyπ- allyl complex.

Robinson and Shaw[8] prepared a series of 4-methoxy substituted complexes analogous to (5.3) by the reaction of the diene with sodium tetrachloropalladate in methanol. These complexes were easily converted to the ethoxy derivatives by warming in a solution of 10^{-2}M ethanolic hydrogen chloride. The ease of solvolysis increased with increasing methyl substitution at C_4, as would be expected if the reaction proceeded via a carbonium ion intermediate. It was suggested that this was (5.4), which could be stabilized by the adjacent π-allyl group, as in the ferrocenyl carbonium ion,[9] which is stabilized by overlap with the π-orbitals of the ferrocene ring, and possibly direct participation of the metal (5.5).



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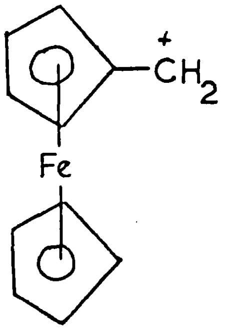
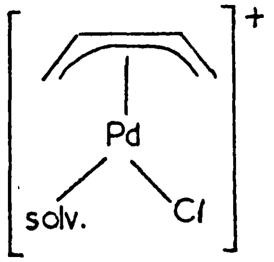


(5.5)

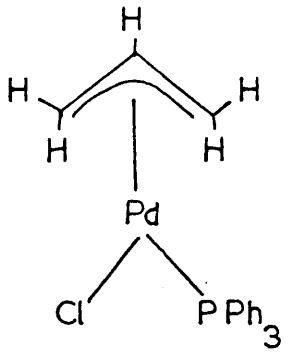


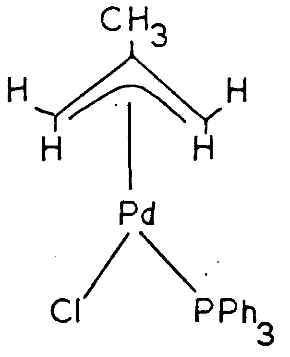
(5.6)

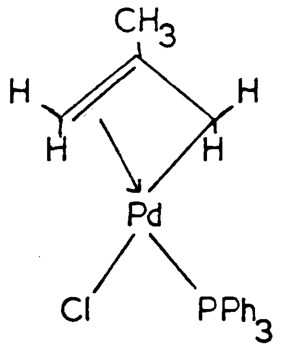
Lukas and Kramer[10] observed a cationic(butadiene)palladium chloride complex which was formed by the abstraction of chloride from (5.3) with antimony pentafluoride at low temperatures. The structure was assigned by n.m.r. spectroscopy as (5.6) rather than (5.4). It was also found that the same complex could be produced by abstraction of hydride from 1-methyl π-allyl palladium chloride. The ease of abstraction of hydride and chloride ions was found to increase with increasing alkyl substitution at the 4-position, which is consistent with the solvolysis experiments of Robinson and Shaw.[8]

In 1967, Rowe and White[11] extended the series of 4-substituted π-allyl palladium complexes by carrying out the reaction between the diene and palladium chloride in acetic acid as a solvent in the presence of sodium or lithium acetate. The 4-acetoxy complexes were similar to the methoxy complexes of Robinson and Shaw. The bridging chloro groups could be replaced by acetato groups with silver acetate to give di-μ-acetato (4-acetoxy but-2-enyl) dipalladium II. The two different acetate groups have very different carbonyl stretching frequencies in the infra red - with the acetoxy carbonyl abosrption frequency at 1735 - 40 cm^{-1} and the bridging acetato group at a much lower frequency 1420 - 25 cm^{-1}.

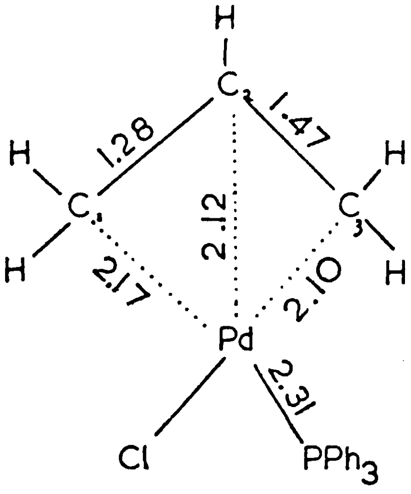
Palladium π- allyl complexes with bridging carboxylato ligands have also been obtained from unsubstituted π-allyl palladium chloride by treatment with silver carboxylates.[12] The trifluoro compound was made from the corresponding acetate on reaction with trifluoroacetic acid, and the bridging chloro complex can be reformed by the action of dry hydrogen chloride. The bridging chloro ligand can also be replaced by acetylacetonato and cyclopentadienyl in 4-methoxy[8]- and 4-acetoxy-[11] π- allyl compounds by treatment with the appropriate thallium I compound. Bridge splitting reactions which do not destroy the π-allylic structure have also been reported for the simple π-allyl ligands including π-allyl-(5.7) and 2-methyl π-allyl- (5.8) palladium chloride,[13,14] using a group V ligand, particularly triphenyl phosphine.


(5.7)

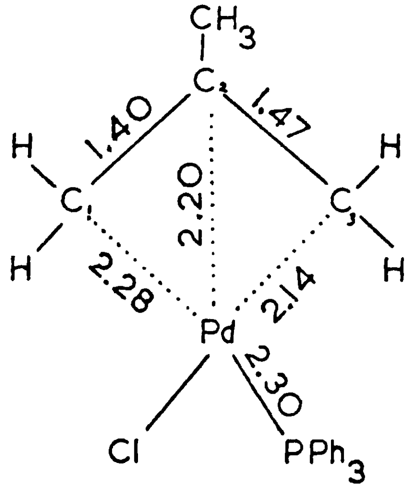

(5.8)


(5.9)

The n m r spectra of these complexes have been studied extensively,[13,14,15] particularly with (5.8), which has a much simpler spectrum than (5.7). The data indicate that the triphenyl phosphine ligand exerts a *trans* effect on the π-allyl ligand, tending to shield the *trans* protons but having little effect on the *cis* protons. This led to the suggestion that the bonding could be represented as (5.9),[13] with enhanced double bond character in the C–C bond of the allyl group <u>trans</u> to the phosphine. X-ray structure determinations of (5.7)[16] and (5.8)[17] gave the following results, shown in (5.10) and (5.11) respectively. In each case, the allyl group is not bonded

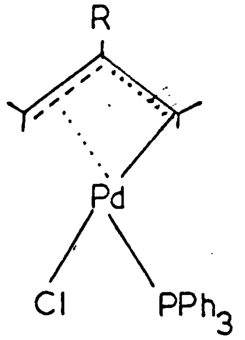


(5.10)



(5.11)

symetrically, the Pd–C_1 bond <u>trans</u> to the phosphine being longer than the <u>cis</u> Pd–C_3 bond. The carbon–carbon bond lengths are also different, particularly in (5.10) where there appears to be more double bond character in the $C_1 - C_2$ bond than in the $C_2 - C_3$ bond. This is in agreement with Shaw's original structure (5.9). However, Cotton[18] ruled out this $\sigma - \pi$ structure on the grounds that the X-ray data do not show as much distortion as would be expected from (5.8). Also, he suggested that such bonding would be geometrically impossible because if the ligand is placed so as to form a π-bond with the metal, the other end of the ligand would be too far away to form a σ-bond and vice versa. Powell and Shaw[14] then proposed a modified structure (5.12) to counter these objections. In this structure, the bonding is represented as a hybrid between the extremes of (5.8) and (5.9), with some double bond character in the $C_2 - C_3$ bond rather than a formal double bond.



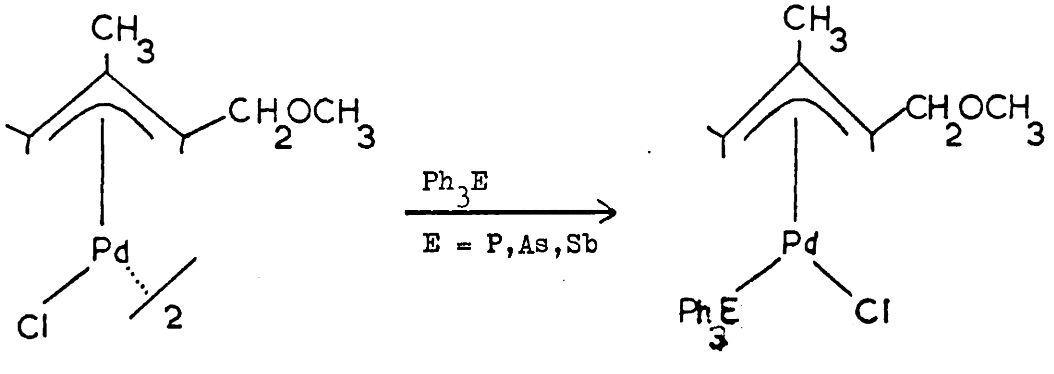
(5.12)

The purpose of the present work was to investigate the influence of ligands on the solvolysis of 4-substituted π-allyl palladium complexes in order to throw some light on the mechanism of these reactions.

B: Preparation and Properties of complexes containing group V ligands

(i) 4-Methoxy derivatives

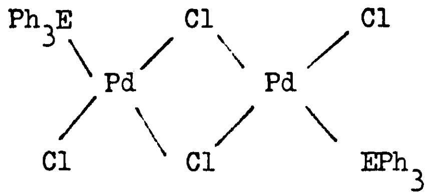
Other than the original preparation by Robinson and Shaw,[8] little work has been done on 4-methoxy-π-enyl complexes of palladium. The exchange reaction using ethanolic hydrogen chloride to convert a methoxy to an ethoxy derivative as mentioned in the preceding section was of interest as the proposed intermediate was a cationic complex which resembled the ferrocinium ions. Attempts were made to prepare derivatives with ligands other than bridging chloro groups in order to establish whether any change in the reaction occurred. Ligands containing group V elements - triphenyl phosphine, triphenyl arsine and triphenyl stibine - were all found to split the chloro bridge of (5.13) to give (5.14). Most of the work was carried out using the 2-methyl but-2-enyl complex as a model because of the simplified n m r spectrum and because of the ready availability of isoprene used in the synthesis.



(5.13) (5.14)

The reaction was found to be almost quantitative if an equimolar amount of the appropriate ligand was added to the π-enyl complex in solution. These complexes are all air stable solids which vary in colour from yellow for the chloro-bridged dimer and triphenyl stibine complex to the almost white triphenyl phosphine derivative.

When exchange reactions were attempted in dilute ($\sim 10^{-2}$ M) ethanolic hydrogen chloride, a brown precipitate containing all the palladium always appeared. This was found to be a dimeric complex in each case (5.15), identical to samples prepared by the method of Hartley.[19] Isoprene was detected in solution by gas chromatography.



E = P,As,Sb

(5.15)

(ii) 4-Acetoxy derivatives.

The chloro-bridged (2-methyl, 4-acetoxy but-2-enyl) complex, first reported by Rowe and White[11] was also found to be cleaved by group V ligands to give complexes analogous to (5.14). They had very similar properties, but were even more unstable towards acids than the methoxy derivatives. On addition of acid, (5.15) was precipitated almost immediately, whereas the precipitation took several hours for the methoxy derivatives. When the acid used was methanolic hydrogen chloride (10^{-2} M), the solution, after precipitation of (5.15), contained isoprene and methyl acetate. The latter was formed by the esterification of acetic acid by the acidic methanol solution under the conditions used.

(iii) 4-Chloro derivatives

When the reaction of triphenyl phosphine was repeated with di-μ-chloro (2-methyl, 4-chloro but-2-enyl) dipalladium II, the 4-chloro derivative of (5.13), the expected product (5.14) was not obtained. Isoprene was detected in solution, and a precipitate was formed. This was shown to be (5.15). This indicates that the triphenyl phosphine group destabilizes the 4-chloro complex even more than the 4-acetoxy or 4-methoxy complexes.

Pyridine and 2,4,6-trimethyl pyridine react with the complex when added in excess to give a precipitate of L_2PdCl_2 and liberate isoprene. By comparison with the reported infra-red spectrum of trans Py_2PdCl_2,[20] the products were both found to have the expected trans configuration. Also the Raman spectrum of each complex was recorded and showed no coincident lines with the infra-red spectrum, showing the complexes to be centrosymmetric,[21] and so in the trans configuration. The frequencies are listed in Table 5.1.

Table 5.1

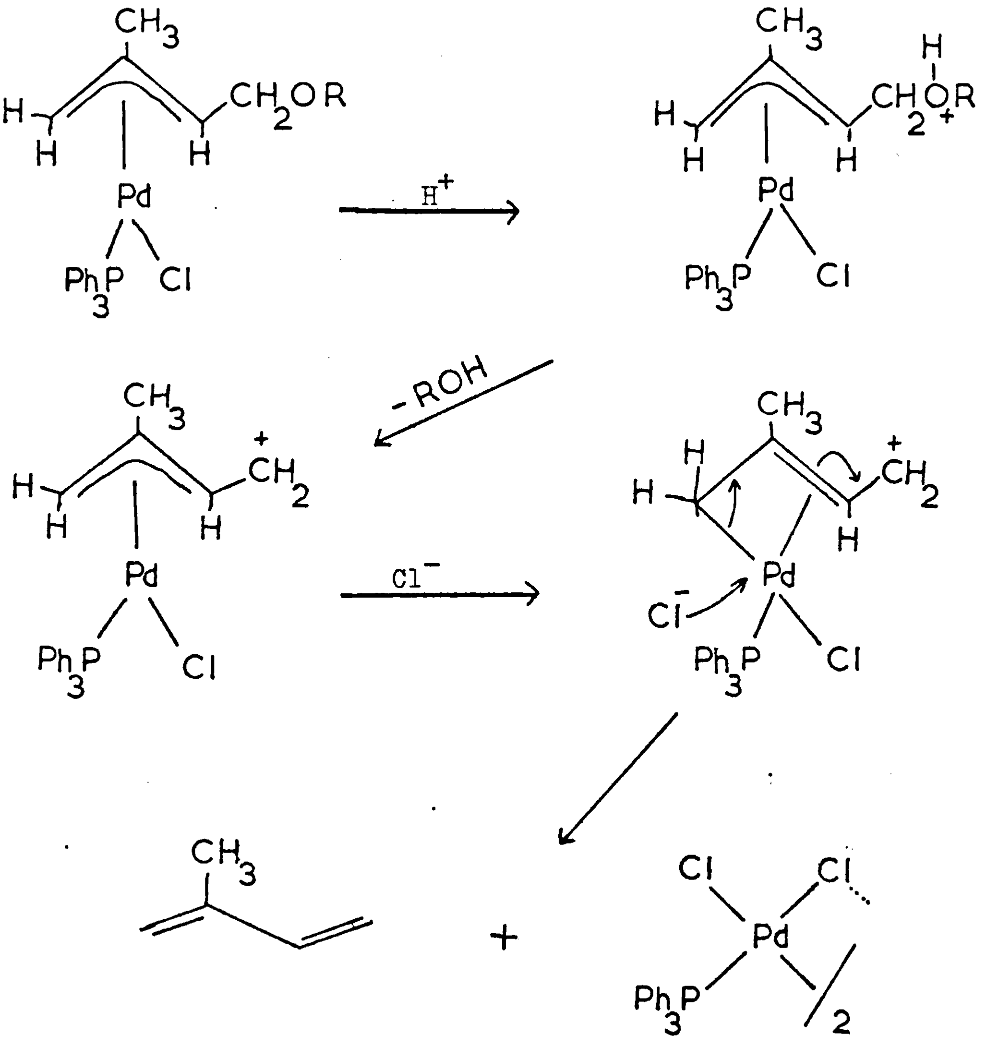
Far i.r. and Raman spectra of(Pyridine)$_2$PdCl$_2$ and (2,4,6-trimethyl pyridine)$_2$ PdCl$_2$

(Pyridine)$_2$PdCl$_2$		2,4,6-trimethyl pyridine)$_2$PdCl$_2$	
i.r.	Raman (cm^{-1})	i.r.	Raman (cm^{-1})
353 s	300 s	377 s	287 s
275 m	198 m	362 m	235 m
266 m	125 m	327 m	137 m
237 m		311 m	
		258 m	

(iv) Discussion

In the complexes described above, the addition of a group V ligand appears to destabilize the complex towards acid. As the 4-methoxy complexes were more stable than the 4-acetoxy complexes under acidic conditions, the decomposition probably requires protonation of the alkyl oxygen to give methanol and acetic acid respectively. As the acetoxy alkyl oxygen will be easier to protonate owing to the presence of a carbonyl group, the acetoxy complex will decompose more readily, as is observed. In the 4-chloro derivative, chloride ion is a sufficiently good leaving group to cause decomposition without any addition of acid. In summary, the ease of decomposition of these complexes in acid solution is a function of the ease of departure of the leaving group at the 4-position.

Loss of this group would give rise to a carbonium ion such as (5.6) or (5.4), which would then decompose to give isoprene and (5.15). The major effect of the group V ligand is probably at this step, as it has already been noted that phosphines tend to stabilize σ,π-enyl rather than π-enyl structures by increasing the double bond character in the carbon-carbon bond <u>trans</u> to the ligand.[14,16] The proposed mechanism is outlined in Scheme 5.2.

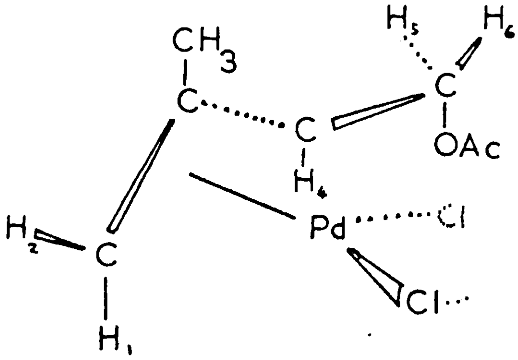

CH3
H
H
H
CH2OR
Pd
Ph3P
Cl
H+
CH3
H
CH2OR
2+
Pd
Ph3P
Cl
-ROH
CH3
+
CH2
Pd
Ph3P
Cl
Cl−
CH3
+
CH2
Pd
Cl−
Ph3P
Cl
CH3
+
Cl
Cl
Pd
Ph3P
2

SCHEME 5.2

C: Spectroscopic Properties

(i) Proton n m r

The 60 MHz spectra of both the chloro-bridged acetoxy[11] and the methoxy[8] derivatives have been reported. In the former case, protons 4,5 and 6 in (5.16) were reported as multiplets. However, the 100 MHz spectra (spectrum 5.1, 5.2) show that they are of a typical ABX system, with H_4 as X and H_5H_6 as A and B. The non equivalence of H_5 and H_6 is because the π-allyl group is unsymmetrically bonded - the palladium is on one side of the group.



(5.16)

The exact coupling constants could not be determined from the spectra, as there is not sufficient information in this type of system.[22]

The methoxy derivative shows H_4, H_5, H_6 as one singlet in both the 60 and 100 MHz spectra, though at 220 MHz (spectrum 5.3), the line is a multiplet. Further expansion (spectrum 5.4) shows this more clearly. This is now an ABC system with each proton having almost identical chemical shifts.

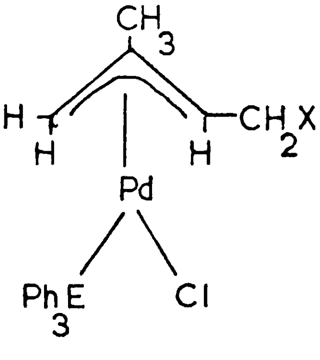
The spectra of the chloro-bridged and derivatives with group V ligands are shown in Table 5.2. These were all determined at 100 MHz in $CDCl_3$ solution, and are relative to TMS.

TABLE 5.2

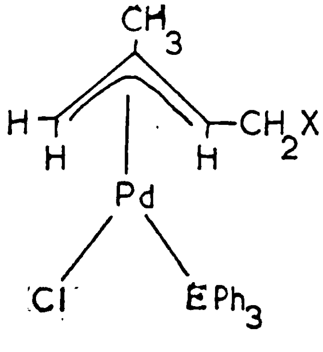
NMR shifts for (4-methoxy- and 4-acetoxy - π-allyl)palladium complexes

Complex				(δ)				
	1	2	3	4	5,6	OMe	$O\overset{O}{C}Me$	ϕ
Methoxy chloro	2.85	3.81	2.22	3.62	3.62	3.40	-	
" Ph_3P	2.60	2.71	1.96	4.16	4.16	3.46	-	7.4
" Ph_3As	2.74	3.34	2.01	4.10	4.10	3.41	-	7.5
" Ph_3Sb	2.78	3.76	2.04	3.93	3.93	3.33	-	7.35
Acetoxy chloro	2.82	3.79	2.11	3.53	4.26	-	2.02	-
" Ph_3P	2.71	2.83	2.05	4.14	4.80	-	1.98	7.4
" Ph_3As	2.70	3.27	2.10	4.13	4.76	-	2.07	7.3
" Ph_3Sb	2.71	3.76	2.09	4.17	4.72	-	2.04	7.5

With the unsymmetrical monomeric complexes containing group V ligands there are two possible geometric isomers (5.17) and (5.18).



(5.17)



(5.18)

Previous work has found[23] that phosphine ligands tend to be bonded trans to the most substituted end of the π-allyl group as in (5.17).

Also, the protons trans to the phosphine tend to be deshielded, and protons cis slightly shielded, as would be expected if there is significant double bond character in the part of the π-allyl system which is trans to the phosphine - i.e. there is more contribution from (5.12) in the complex.

The data in Table 5.2 were used to calculate the change in shift on adding a phosphine or other ligand to the chloro complex. The change, $\Delta\delta$, is shown in Table 5.3 for the methoxy derivatives and in Table 5.4 for the acetoxy derivatives. Significant changes in the chemical shifts occurred for H_1, H_2, H_4, H_5, H_6, though little change was noted in the methyl groups. A negative sign for $\Delta\delta$ indicates an increase in the shielding of a particular proton going from the chloro-bridged to the substituted complex.

TABLE 5.3

$\Delta\delta$ values for 4-methoxy derivatives

	Ph_3P	Ph_3As	Ph_3Sb
H_1	-0.15	-0.11	-0.07
H_2	-1.10	-0.47	-0.05
$H_{4,5}$	+0.54	+0.48	+0.30

TABLE 5.4

$\Delta\delta$ values for 4-acetoxy derivatives

	Ph_3P	Ph_3As	Ph_3Sb
H_1	-0.11	-0.12	-0.11
H_2	-0.96	-0.52	-0.03
H_4	+0.61	+0.60	+0.65
H_5	+0.54	+0.50	+0.46

This data is consistent with (5.17) for the following reasons:-

1. H_4 and H_5 are deshielded and H_1, H_2 slightly shielded on complex formation. This would be expected if there is contribution from (5.9) to the bonding in the complex.

2. On going up the series Sb, As, P, $\Delta\delta$ for each proton behaves differently. $\Delta\delta$ for H_2 is almost zero when the ligand in Ph_3Sb, but rapidly increases to a shielding of 1.10 ppm for Ph_3P in the 4-methoxy complexes. A parallel effect also occurs in the 4-acetoxy complex, the change being from -0.03 to -0.96 ppm. However, with H_4, H_5, the deshielding is large at 0.30 ppm for Ph_3Sb and increases to 0.54 ppm with Ph_3P.

This indicates that the protons on C_1 are more sensitive to the electronic character of the ligand than those on C_3 and C_4. This would also be so in (5.17), where C_1 is σ-bonded direct to the metal and C_3 is π-bonded - or even free in the extreme case.

(ii) Variable Temperature n.m.r.

The change in n.m.r spectra with temperature has been reported for many phosphine and arsine derivatives of π- allyl palladium chloride.[6, 15] These normally show an increase in splitting at low temperatures from the arresting of $\sigma \longrightarrow \pi$ type transitions in the molecule which cause exchange of protons and so line broadening. In the triphenyl phosphine derivative of the acetoxy complex, the reverse was found to occur. This is shown in Spectra (5.5) and (5.6), where the proton spectrum at room temperature simplifies on cooling. The protons 1 and 2 at 2.71 and 2.83 ppm respectively became one signal at 2.85 ppm on cooling to -40°C.

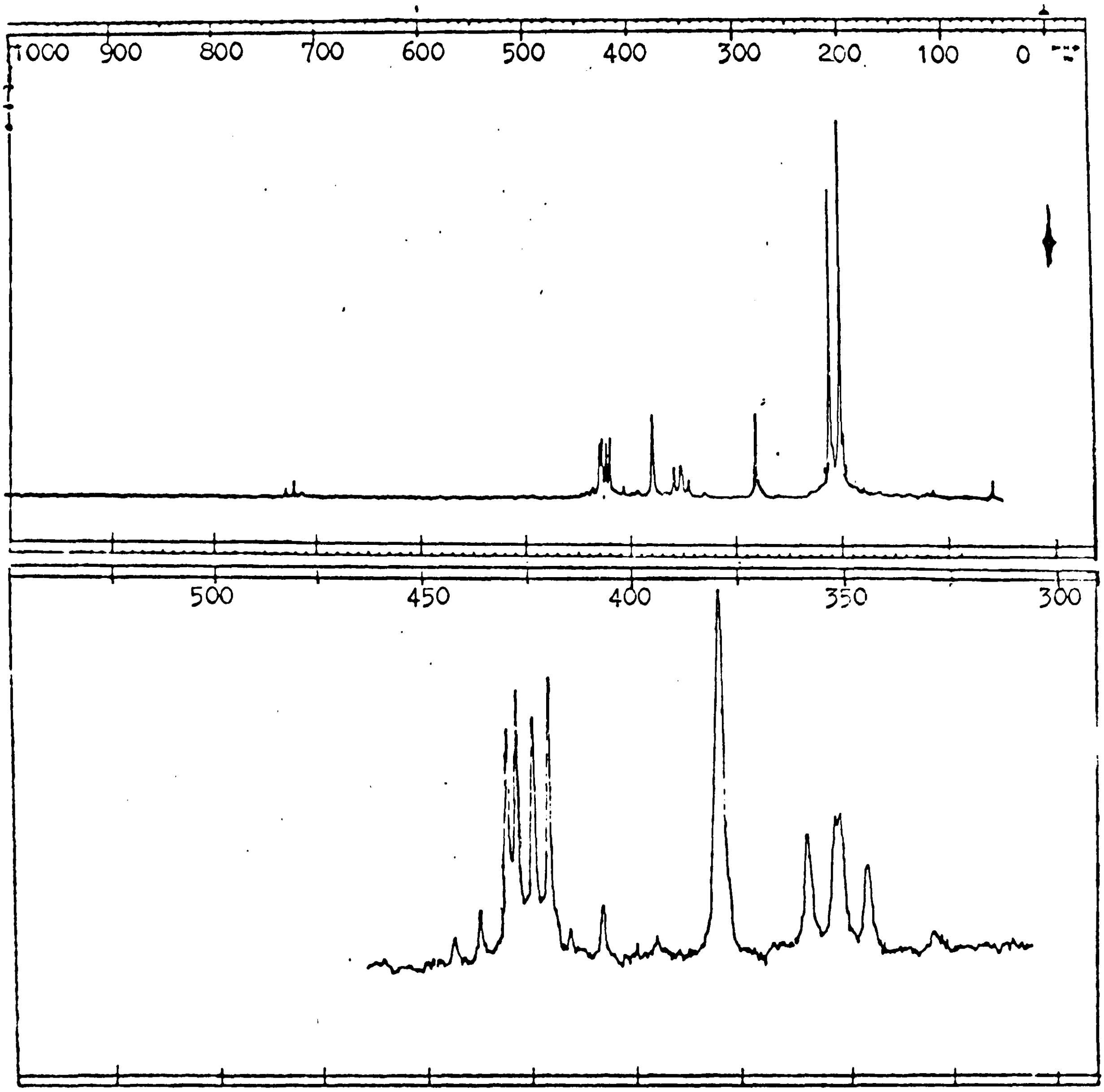
No further change was found to occur down to $-60^{\circ}C$. There is also a slight drift in the shifts of the methyl groups on cooling. This could be explained if the spectrum at room temperature is of a $\sigma - \pi$ complex which on cooling, changes into a π-allyl complex in which protons 1 and 2 have coincident shifts, though it would be expected that this change would have a more dramatic effect on the rest of the spectrum.

The spectrum of the triphenyl arsine derivatives was also found to vary with temperature. At room temperature, it consists of 4 broad peaks corresponding to protons 1,2,4,5 and two narrow peaks from the two methyl groups (Spectrum 5.7). On cooling below $0^{\circ}C$ (Spectrum 5.8), the broad lines gradually sharpen, and become similar to that of the triphenyl stibine and chloro-bridged complexes.

The n m r spectrum of triphenyl arsine palladium chloride is also reported[24] to be broad at room temperature, and was interpreted as a change from a π-allyl complex at low temperatures to a σ- complex, as well as loss of ligand, causing line broadening of the π-allylic protons.

At higher temperatures, the expanded spectra (5.9) and (5.10) show that H_3 is beginning to become a triplet at $70^{\circ}C$, but decomposition took place at higher temperatures, giving isoprene, identified by its n m r spectrum. This is consistent with a $\pi — \sigma$ exchange reaction which tends to favour the π form at low temperature and the σ form at higher temperatures.

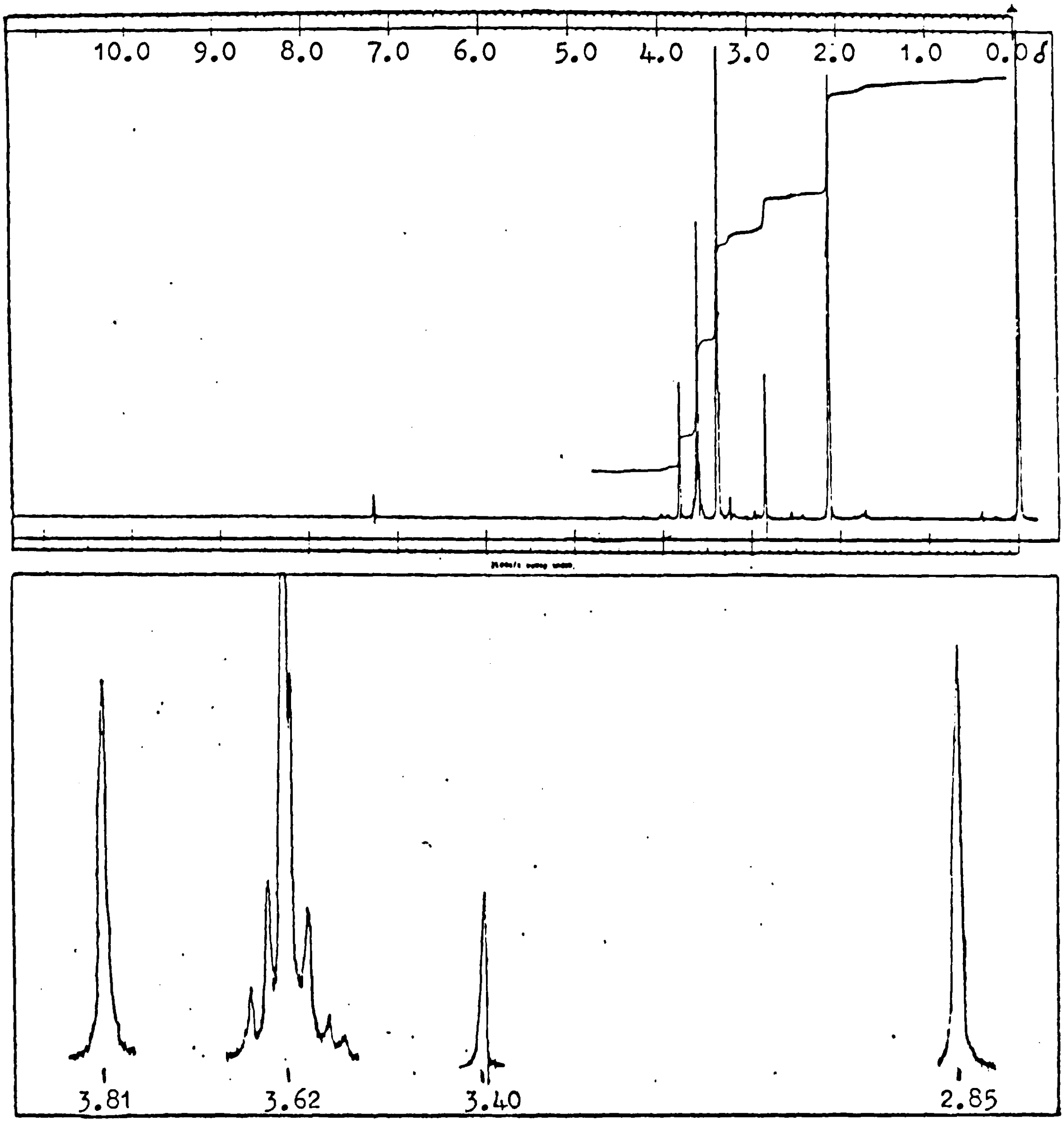
The triphenyl stibine and chloro-bridged complexes were found to have temperature-independent n m r. spectra between -60 and $+70^{\circ}C$, though decomposition occurred above $100^{\circ}C$. Hence, the lability of the π-allyl group increases as one goes up group V.



100 MHz Spectrum of di-μ-chlorobis(2-methyl4-acetoxy but-2-enyl) dipalladiumII in CDCl$_3$

SPECTRUM 5.1 1000Hz scan at 25°

SPECTRUM 5.2 250Hz scan at 25°

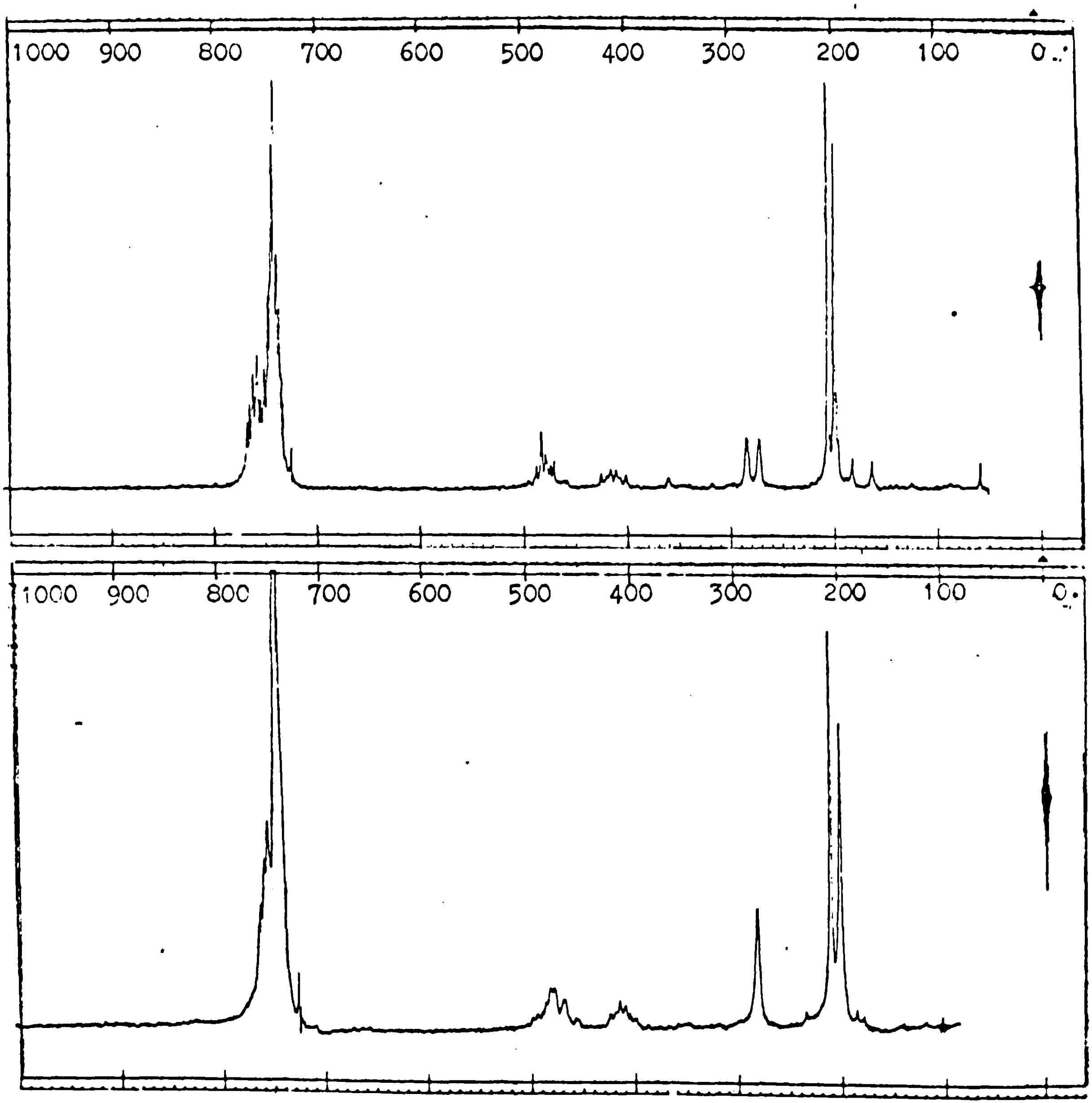


220 MHz Spectrum of di-μ-chlorobis(2-methyl4-methoxy but-2-enyl)

palladiumII in CDCl$_3$

SPECTRUM 5.3 2500Hz scan at 19°

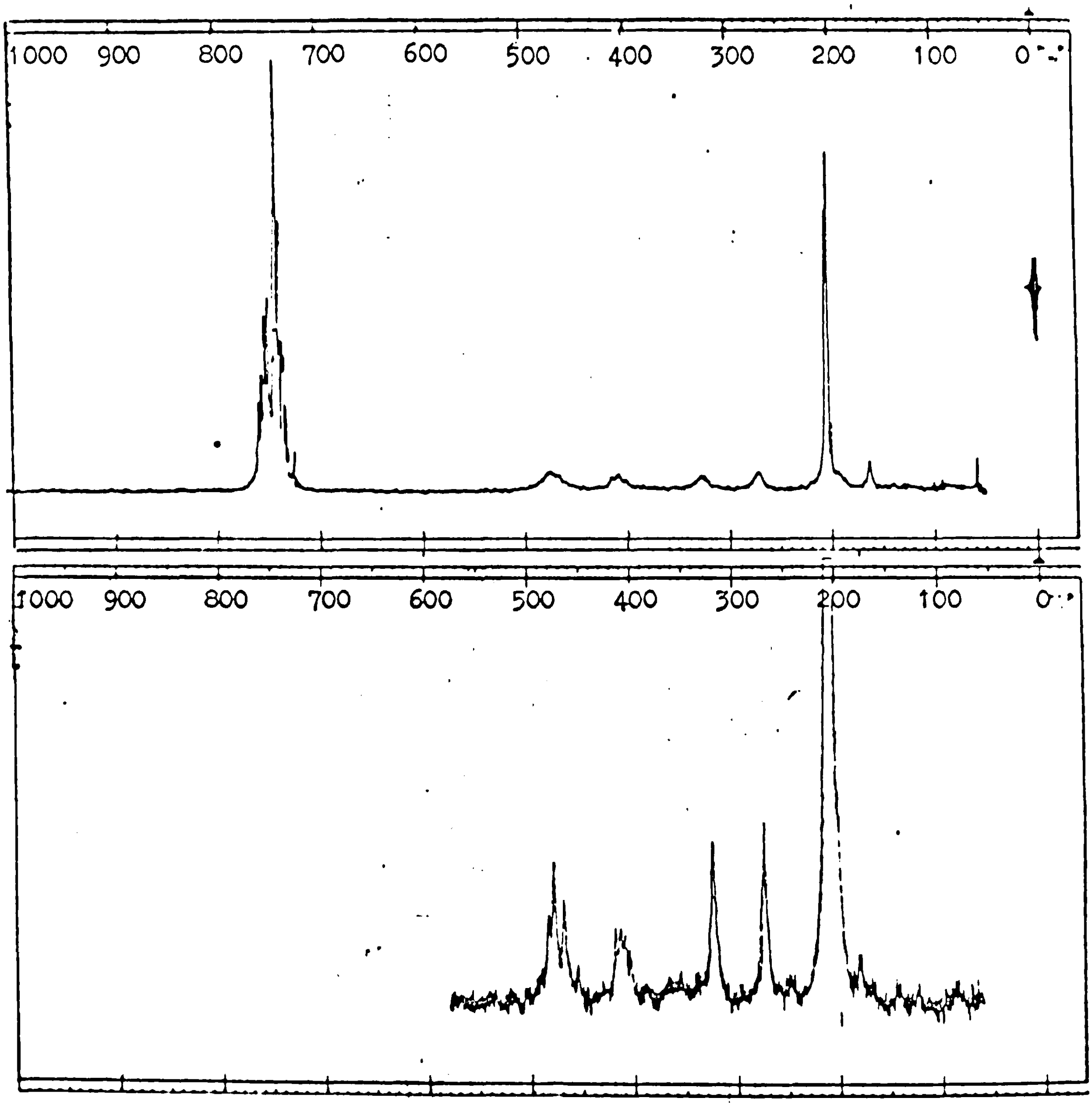
SPECTRUM 5.4 250Hz scan at 19°



100 MHz Spectrum of chloro(triphenylphosphine)(2-methyl4-acetoxy but-2-enyl)palladiumII in $CDCl_3$

SPECTRUM 5.5 1000Hz scan at +40°.

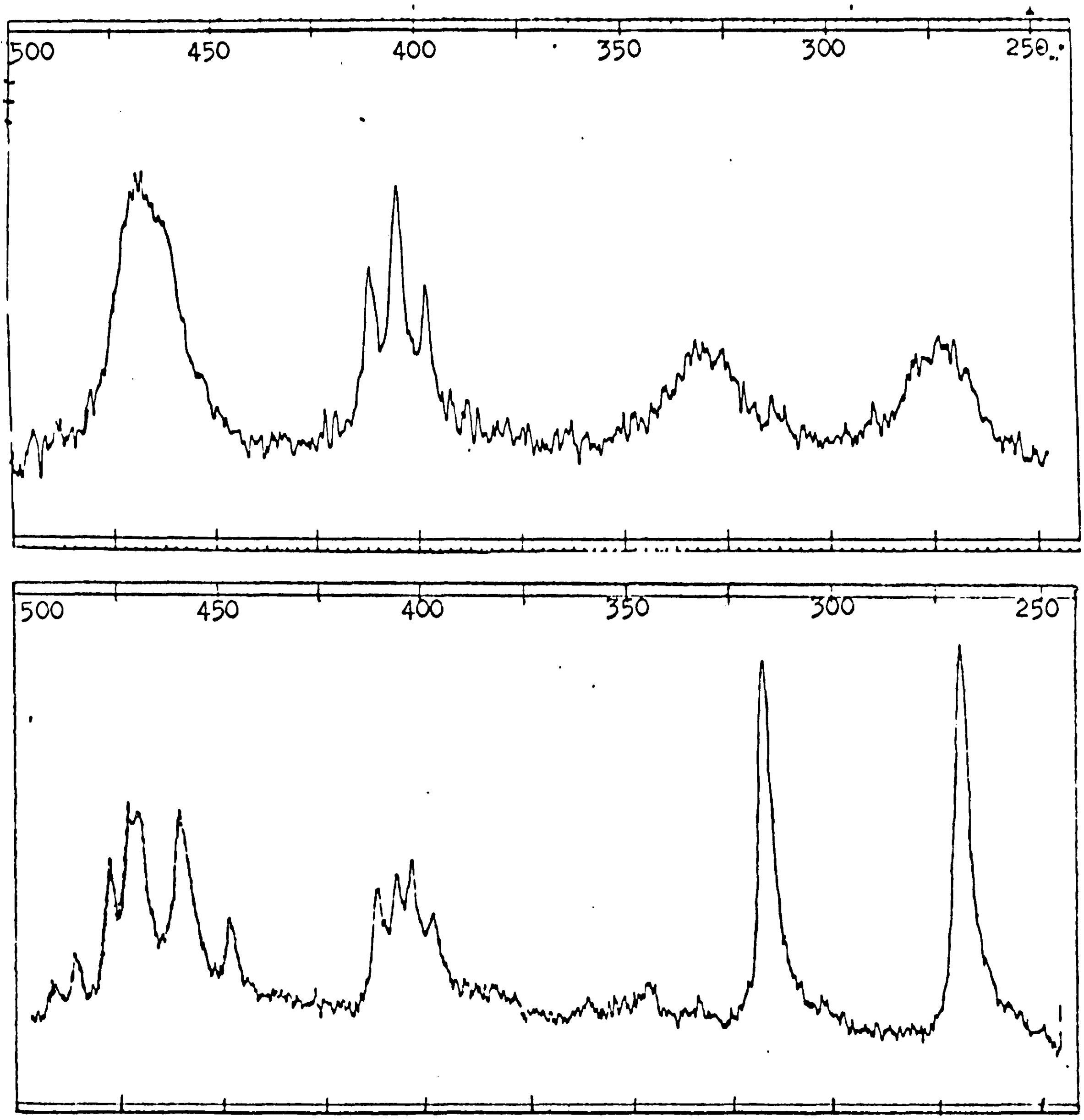
SPECTRUM 5.6 1000Hz scan at -60°



100 MHz Spectrum of chloro(triphenylarsine)(2-methyl4-acetoxy but-2-enyl) palladiumII in $CDCl_3$

SPECTRUM 5.7 1000Hz scan at +40°

SPECTRUM 5.8 1000Hz scan at 0°



100 MHz Spectrum of chloro(triphenylarsine)(2-methyl4-acetoxy but-2-enyl) palladiumII in $CDCl_3$

SPECTRUM 5.9 250Hz scan at +60°

SPECTRUM 5.10 250Hz scan at -40°

D: Experimental

Preparation of substituted π- allyl complexes containing group V ligands.

The ligand dissolved in a minimum of warm benzene was added with stirring to an equimolar solution of the chloro-bridged complex in the minimum of benzene. After standing for 1 hr at 10°C, 40–60° petroleum ether was added to precipitate the complex. The precipitate was washed with petroleum ether, then with diethyl ether and dried in vacuo.

The sample was purified by dissolving in benzene and precipitating with 40–60° petroleum ether. Analytical data for the 4-methoxy complexes are shown in Table 5.5, and for the 4-acetoxy complexes in Table 5.6.

TABLE 5.5

Analytical Data for 4-methoxy complexes

Ligand	Colour	m.p.	yield %		C%	H%	other
Ph_3P	white	133–135° dec.	85	required:	57.16	5.16	Cl 7.03
				found:	57.81	5.30	6.86
Ph_3As	yellow	136° dec.	80	required:	52.68	4.75	
				found:	52.69	4.69	
Ph_3Sb	yellow	113°	77	required:	48.52	4.38	
				found:	48.68	4.56	

TABLE 5.6

Analytical Data for 4-Acetoxy Complexes

Ligand	Colour	m.p.	yield %		C%	H%	other
Ph_3P	white	116-119° dec.	68	required:	56.42	4.93	P 5.82
				found:	56.40	4.85	5.68
Ph_3As	yellow	124-126° dec.	67	required:	52.20	4.56	As 13.03
				found:	52.06	4.69	13.24
Ph_3Sb	yellow	137°	41	required:	48.27	4.22	Sb 19.57
				found:	48.13	4.32	19.33

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Journal of Organometallic Chemistry, 77 (1974) C37—C39

Preliminary communication

ELECTROPHILIC SUBSTITUTION OF 1,3-DIMETHOXYBENZENE BY PENTADIENYLTRICARBONYLIRON CATIONS

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(Received July 1st, 1974)

Summary

Kinetics of reactions of several open-chain pentadienyltricarbonyliron cations with 1,3-dimethoxybenzene have been studied; the reactions are faster than those of the cyclohexadienyltricarbonyliron cation and a mechanism is proposed.

Kane-Maguire and coworkers have recently shown that the cyclohexadienyltricarbonyliron cation acts as an electrophile towards activated aromatic systems including indole, pyrrole [1] and 1,3-dimethoxybenzene [2]. These reactions show second order kinetics (rate = k_2 [cation] [ArH]) over an appreciable range of concentration of the aromatic compound [3].

We have studied kinetically the attack of several open-chain pentadienyltricarbonyliron cations (I) on 1,3-dimethoxybenzene, and have found not only that the reactions are considerably faster than those of their cyclic analogues, but also that some show different kinetic characteristics. Only compounds Ib and Ic* obey second order kinetics (up to at least sixty times excess of dimethoxybenzene, with the rate of reaction of Ic almost 700 times faster than that of the cyclic Ia. With compounds Id, Ie and If the reactions follow a different rate equation (rate = $k_1 k_2$ [cation] [ArH] /(k_{-1} + k_2 [ArH])) tending towards first order kinetics at high concentration of dimethoxybenzene. This implies the formation of a reactive intermediate, which can either react further to yield the products or can reform the starting material. We suggest that this reaction intermediate is the *trans*-pentadienyltricarbonyliron cation II, postulated by Clinton and Lillya [4] on the basis of the stereochemistry and kinetics of hydrolysis of the dinitrobenzoates of dienoltricarbonyliron complexes. Sorensen and Jablonski [5] obtained evidence for such a *trans* iron from ^{1}H NMR studies at low temperatures.

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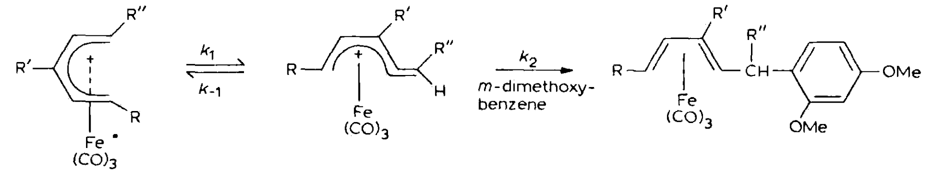
*See Table 1 for substituents.

The mechanism of Scheme 1 is consistent not only with the observed kinetic form, but also with the fact that the cations with open-chain ligands, and which can form *trans* cations, are more reactive towards nucleophiles than those with cyclic ligands, which can exist only in the *cis* form. The difference in the kinetics between compounds Ib, Ic and Id, Ie, If implies that k_1 and k_{-1} do not influence the rate-determining step in the former cases either because k_1 and k_{-1} are much greater, or that k_2 is smaller, than in the latter cases.



(I) (II) (III)

SCHEME 1

The rate constants were measured by following the rate of disappearance of the dienylcarbonyl band at ca. 2110 cm^{-1} in the IR. Linear pseudo-first order plots were obtained up to at least 75% reaction. Some representative results are listed in Table 1.

TABLE 1

RATES OF REACTION OF SUBSTITUTED PENTADIENYLTRICARBONYLIRON(II) TETRAFLUOROBORATES (0.01 *M*) WITH 1,3-DIMETHOXYBENZENE (DMB) IN NITROMETHANE AT 25 ± 0.1°C.

Compound	Substituents	k_2 (l mol^{-1} sec^{-1})	k_{obs} (sec^{-1}) 0.1 *M* DMB	k_{obs} (sec^{-1}) 0.5 *M* DMB
Ia	cyclohexadienyl [a]	1.5×10^{-6}	—	—
Ib	1,3,5-trimethyl	3.3×10^{-5}	—	—
Ic	1,5-dimethyl	1.0×10^{-3}	—	—
Id	5-methyl	—	4.0×10^{-4}	1.3×10^{-3}
Ie	1-phenyl-5-methyl	—	5.1×10^{-4}	1.4×10^{-3}
If	1-phenyl-2,5-dimethyl	—	5.6×10^{-4}	1.4×10^{-3}

[a] At 20.8°C [3].

Only one product, in which the aromatic ring is substituted in the 4-position, was observed in each reaction. Nucleophilic attack on the cations occurs at a terminal carbon atom. For the unsymmetrically substituted cations Id, Ie, If, this is the carbon which bears a methyl substituent. The rate of reaction increase along the series Ib, Ic, Id with decreasing methyl substitution at the 1 and 3 positions. Compounds Ie and If react at very similar rates, indicating that a methyl substituent at the 2-position has little effect, as might be predicted from a simple picture of the charge distribution in the pentadienyl system.

Further evidence for the intermediacy of *trans* cations in our reactions comes from the ^{1}H NMR spectra of the products III, which are consistent with the *trans,trans* structure shown. This arises via geometrical inversion at C(5) during nucleophilic attack [6]. Direct attack on the *cis* cation leads to a *cis, trans* configuration in the product [7].

Acknowledgements

We are grateful to Dr. L.A.P. Kane-Maguire for permission to quote unpublished results. We thank the S.R.C. for a research studentship (to K.A.H.).

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