DIRECTIVE EFFECTS

IN

SUBSTITUTED FERROCENES

THESIS

submitted to

THE UNIVERSITY OF GLASGOW

in fulfilment of the
requirements for the

DEGREE OF DOCTOR OF PHILOSOPHY

by

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July, 1962.

SUMMARY

This study describes some electrophilic substitutions of methylthio-, chloro-, and methoxy- ferrocene. The experiments were carried out in an attempt to determine the directive effects operative in these compounds.

The aminomethylation of methylthioferrocene afforded the three ($1,2$; $1,1'$ and $1,3$) isomeric dimethylaminomethyl-methylthioferrocenes, which were converted via their methiodides to the corresponding methyl- methylthioferrocenes. These compounds were then converted to the corresponding thiocyanates, eg. 1-thiocyanato-1'-methylferrocene, and thence to the corresponding disulphides, e.g. di-(1'-methylferrocenyl)disulphide. An independent synthesis of di-(1'-methylferrocenyl)disulphide from 1-carboxyferrocene-1'-sulphonic acid provided conclusive identification of this compound. The site reactivities, as determined from the weights of isomeric methyl- methylthioferrocenes isolated, indicate that the methylthio group is activating in nature.

Chloroferrocene was found to acetylate exclusively in the unsubstituted ring, thus demonstrating the deactivating effect of the chloro substituent.

A new route to ferrocenylboronic acid via ferrocenylboronyl dichloride, greatly simplified the preparation of methoxyferrocene. When methoxyferrocene was subjected to

Friedel-Crafts acetylation, a mixture of the three (1,2; 1,1' and 1,3) isomeric acetyl- methoxyferrocenes was isolated. These products were identified after reduction, as the corresponding ethyl- methoxyferrocenes. Site reactivities calculated from weights of isomeric ethyl-methoxyferrocenes, isolated from two different reduction methods ($LiAlH_4$-$AlCl_3$ and Clemmensen reductions), provided unsatisfactory results. Aminomethylation of methoxyferrocene yielded a mixture of the three isomeric dimethylaminomethyl-methoxyferrocenes, which were identified, after reduction of the mixture of methiodides, as the corresponding methyl-methoxyferrocenes. Site reactivities calculated from these reduction products showed the methoxy group to be activating in nature.

The displacement of ferrocene substituents by protons was observed in certain reactions. Methylthio- and methoxy- ferrocene on treatment with aluminium trichloride, afforded not only ferrocene, but mixtures of the isomeric di(methylthio)- and dimethoxy- ferrocenes. A similar treatment of chloroferrocene furnished only ferrocene.

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Professor P. L. Pauson for his continued guidance and helpful advice, to Dr. A. C. Syme and his staff in the microlaboratory, to Dr. P. Bladon for infrared spectra and vapour phase chromatograms, to Dr. J. C. D. Brand of the University of Glasgow for nuclear magnetic resonance spectra, to Mr. T. W. Boyle for technical assistance and also to the Cross Trust for the award of a research grant.

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INTRODUCTION

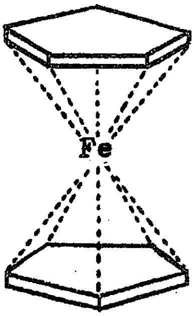
HISTORY

Since the discovery by Frankland[1] in 1849, of diethylzinc, the first true organometallic compound, the ensuing century has seen marked progress in this new branch of chemistry, and in recent years organometallic compounds have ceased to be exclusively the object of academic research. The importance of present day researches are best kept in perspective with the several major advances which made modern developments possible. These include the preparation of the first organomagnesium compound by Grignard[2] in 1900; the preparation of cyclopentadienylpotassium by Thiele[3], in 1901; the direct preparation of organolithium compounds by Ziegler and Colonius[4] in 1930, later utilised by Gilman for the preparation of aryl and alkyl derivatives of most of the elements of groups 4b and 5b of the periodic classification; the organosodium compounds by Gilman[5] in 1933 and Bockmühl[6] and Ehrhart in 1935[6], prepared for the first time from sodium and organic halides.

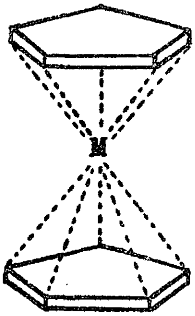
Despite the widely held belief that organic derivatives of the transition metals were inaccessible, a new field of organometallic chemistry was initiated by the discovery in 1951 of biscyclopentadienyliron or 'ferrocene'[7] by two independent groups[8,9] of workers. Since then, the chemistry of organic derivatives of the transition metals has expanded at an exceedingly rapid rate and a number of reviews[10-21] have been published.

STRUCTURE

The now well known 'sandwich' structure[22,23] of ferrocene (I), originally suggested by its diamagnetic nature, non-polar character[22] and its possession of a single C-H stretching frequency in the infrared region,[22] was further substantiated by detailed X-ray crystallographic data demonstrating its centrosymmetric nature,[23-27] with the two rings placed in parallel planes about the central iron atom. Ferrocene crystallises in the monoclinic space group $P2_1/c$ with two molecules in the unit cell,[23,27] and hence the metal atom lies at a centre of symmetry both within the unit cell, and within the molecule.[22,23] This leads to ferrocene having the pentagonal antiprismatic or 'staggered' conformation (I), while the analogous ruthenocene[28,29] (II, M = Ru) and



I



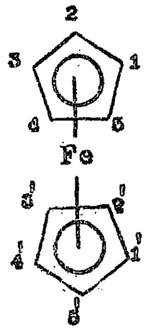
II

osmocene[30] (II, M = Os) have the pentagonal prismatic or opposed conformation of the rings in their orthorhombic crystals. One suggested reason for this difference from ferrocene, is the larger size of the ruthenium and osmium atoms, which thus causes a reduction in the repulsion between the hydrogen atoms of the different rings.

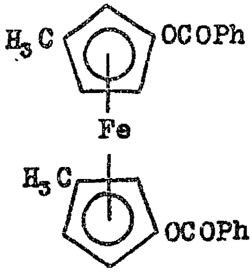
Both physical and chemical evidence indicate that the rings are freely rotating[31] in solution and in the vapour state, and considerable oscillation is even thought to occur in the crystal state, with the 'staggered' conformation being preferred.[27]

NOMENCLATURE

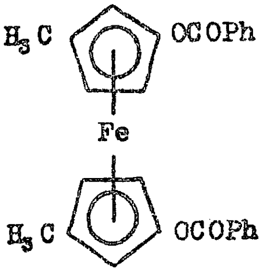
The procedure for numbering ferrocene derivatives is usually quite straightforward. As can be seen from diagram (III), the carbon atoms of one ring are numbered 1 to 5, while those of the other ring are numbered 1' to 5', in the same direction. In a monosubstituted ferrocene therefore, carbon atoms 2 and 5, and 3 and 4 become equivalent, although this is not necessarily true when both rings bear a substituent,



III



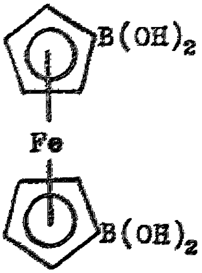
IV



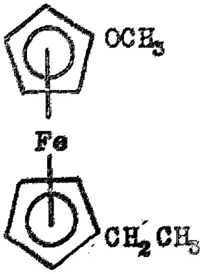
V

even when both substituents are identical. It will be seen that (IV) and (V) are stereoisomers, and as such can be separated,[32] thus stressing the importance of numbering in the same direction.

The nomenclature at all times is kept analogous to that of the benzene series, except where word order prevents this, e.g. (IV) is named 1,1'-ferrocenylenediboronic acid, whereas (VII) becomes 1-methoxy-1'-ethylferrocene.



VI



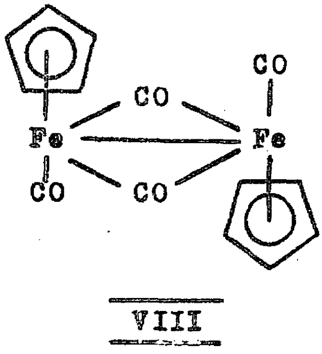
VII

PREPARATIONS OF FERROCENE

Since the discovery of ferrocene, many methods for the preparation of it, its derivatives and other biscyclopentadienylmetal compounds have been devised, but these may be generally thought of as falling into two main groups, viz. those involving cyclopentadiene itself, and the others involving cyclopentadienide ions.

1 (a). In the original preparation of ferrocene,[9] the method employed entailed heating the metal itself with cyclopentadiene. This method has not been extended to other metals except magnesium[33] because of the poor yields, but this has been partially overcome by using the metal oxide[34,35] and hydrogen.[32] Iron oxalate[41] has also been used as a source of iron oxide.

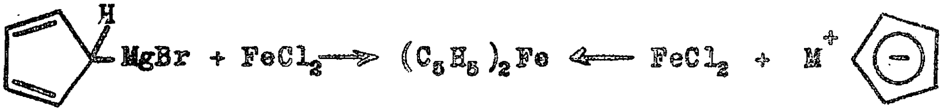
(b). Cyclopentadiene also reacts readily with iron carbonyls at 200°, to give reasonable yields of ferrocene.[36,37] This reaction has been shown to progress via the tetracarbonyl (VIII),



VIII

which is formed exclusively at 135° by the same reaction.[36,37]

2 (a). The most widely used preparative technique involves the use of the cyclopentadienide anion, $C_5H_5^-$, as the Grignard reagent,[8] or as an alkali metal salt with anhydrous ferrous chloride.

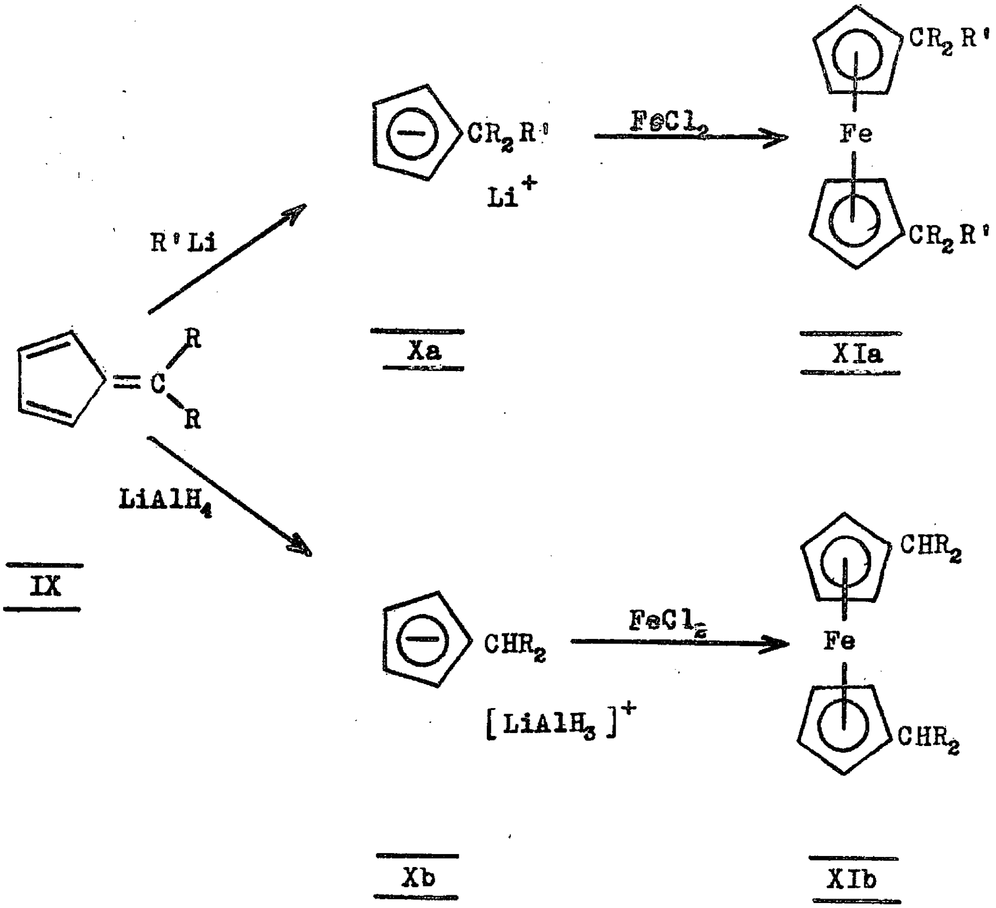


The alkali metal salts of cyclopentadiene have been prepared by treating the hydrocarbon with an alkali metal,[43-46] sodamide or sodium acetylide[47] in liquid ammonia, with sodium tert. butoxide in tert. butanol,[39] with sodium ethoxide in ethanol,[42] with sodium in tetrahydrofuran or ethylene glycol dimethyl ether,[39,40,48-50] and also with alkyl- and aryl- lithium compounds in ligroin or ether.[51]

(b). One method which has been found particularly convenient, is the reaction of the anhydrous halide with cyclopentadiene, in an amine such as diethylamine,[38] pyridine or piperidine, which acts both as solvent and halogen acceptor.[39,40] The reaction may be represented as

$$FeCl_2 + 2C_5H_6 + 2\text{ amine} \longrightarrow C_5H_5FeC_5H_5 + 2\text{ amine.HCl}$$

A wide variety of substituted ferrocenes can be prepared by the above methods i.e. from substituted cyclopentadienes.[51,52] Another most useful preparatory method, involves the conversion of fulvenes[53,55] to their corresponding cyclopentadienyl salts, (the reduction being effected with R'Li or LiAlH$_4$) and treating these with anhydrous ferrous chloride to give the desired ferrocenes (XIa) and (XIb).



Many other syntheses incorporating fulvenes have been described[54-60] in the literature, and lately Watts[61] has further expanded this field.

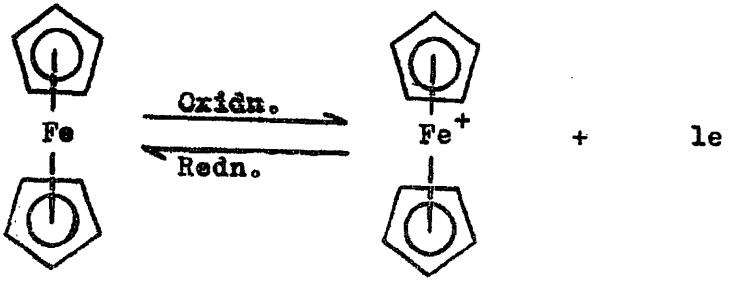
PROPERTIES

Physical

Ferrocene is an air stable orange crystalline solid, m.p. 173°, soluble in all organic solvents, and insoluble in and unattacked by water, acids and alkalis, in the absence of oxidising agents. It sublimes readily at 100°, and from vapour pressure measurements up to 400°, Kaplan *et al.*,[62] estimate the boiling point at 249° at normal pressure.

Extensive studies of the dichroism[63] in ferrocene crystals, the thermodynamic properties,[62,64-67] the infrared,[32] Raman[65-67] and nuclear magnetic resonance[68-70] spectra gave results which agreed with the X-ray analyses results, confirming the 'sandwich' structure already mentioned.

Oxidation of ferrocene to the blue water soluble ferricinium cation (XII), is easily achieved in acid media, and the cation can be precipitated from aqueous or alcoholic solutions by various anions, e.g., tri-iodide,[71] reineckate[23] etc. The oxidation-reduction system is reversible, and reduction of the ferricinium cation to ferrocene can be accomplished with such mild reducing agents as titanous chloride and stannous chloride.



XII

The oxidation-reduction potentials of ferrocene[72] and a number of derivatives[73-75] have been measured polarographically and some of these values have been further substantiated by chronopotentiometric oxidation measurements.[76,77] The oxidation potential of ferrocene is close to that for the ferrocyanide-ferricyanide system.

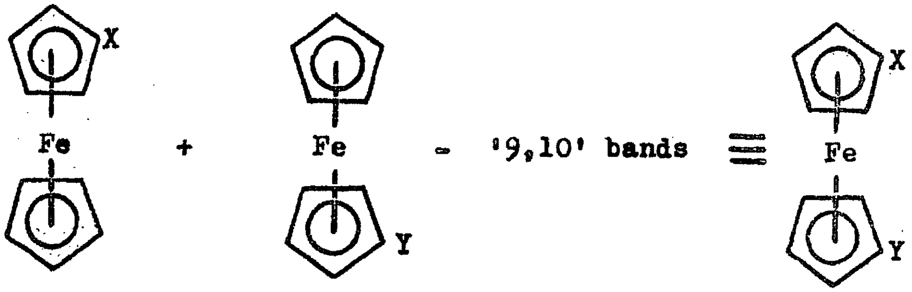
$$[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-}$$

Substituents attached to the ring have a marked influence on the oxidation potential, electron donating groups lowering the oxidation potential, and electron withdrawing groups having the opposite effect.

The infrared spectrum of ferrocene[22] is surprising in its simplicity, having only five main bands. One at 3075 cm.$^{-1}$, a region typical for aromatic C-H bonds, arises from the C-H stretching vibration; two at 811 and 1002 cm.$^{-1}$ are due to C-H bending vibrations;[65,66] and the others at 1108 and 1411 cm.$^{-1}$ are due respectively to an antisymmetrical ring breathing and an antisymmetrical C-C stretching vibration. The last four bands are reported to be present in all mono-substituted ferrocene derivatives, although their intensities are reduced, and those at 1108 and 1002 cm.$^{-1}$ disappear completely when both rings are substituted. These observations have given rise to a rule generally known as Rosenblum's[78] '9,10' rule:-

'When there is at least one free cyclopentadienyl ring, the infrared spectrum will possess bands at 9μ and 10μ'.

No exceptions to this rule have been reported, but Rinehart[79] has indicated with good reason, that peaks in these positions do not necessarily mean an unsubstituted ring. Another generalisation derived by Rosenblum,[78] is the additivity of spectra of singly substituted compounds, represented diagrammatically as shown. Thus the infrared spectrum of (C) will consist of the spectrum of (B) superimposed on the spectrum of (A), with the bands at 9μ and 10μ absent. Further corroboration of these results has been presented by Boichard.[80]



(A) (B) (C)

Aromaticity

The essential electrical neutrality of the cyclopentadienyl rings, was demonstrated by measurements of the acid strengths of ferrocenecarboxylic acid, 1,1'-ferrocenylenedicarboxylic acid and benzoic acid, which were found to be very similar.[7] The pKa value of the monocarboxylic acid is raised by electron donating and lowered by electron withdrawing substituents, even when these are attached to the other ring, thus showing that such effects are transmitted across the metal atom.[81,82]

Lack of olefinic character in the cyclopentadienyl rings was shown by their failure to react with maleic anhydride, or to hydrogenate with Adams' platinum oxide catalyst.

Ferrocene undergoes reactions typical of aromatic systems. Other related compounds which have been shown to undergo electrophilic (and free radical) substitution reactions, are ruthenocene,[29] osmocene,[83] cyclopentadienylmanganese tricarbonyl,[84-87] cyclopentadienylvanadium tetracarbonyl[88,89] and lately dibenzenechromium.[90] The other π-cyclopentadienyl derivatives must also be regarded as aromatic, although instability frequently prevents this being shown by means of electrophilic substitution reactions.

No nucleophilic substitution[91] of ferrocene, or any of its derivatives has ever been achieved.

Attempts at direct nitration[95] and bromination[91,94] with such positive reagents as NO_2^+ and Br^+ respectively, only resulted in oxidation to the ferricinium cation, and complete rupture of the molecule, therefore indirect routes to nitro-, nitroso-,[95-97] and halo- ferrocenes[91-94,151] had to be found.

Since the first successful aromatic substitution reaction, achieved by Woodward and his co-workers[7] with Friedel-Crafts acylation,[29,31,51,84,98-102] ferrocene has been shown to undergo Friedel-Crafts alkylation,[103-105] sulphonation,[102,106-10] metalation by mercuration,[110] sodiation[111-112] and lithiation,[110,113-115] arylation,[110,116-119] formylation[61,66,23,120,121] aminomethylation[125,126] (Mannich reaction) as well as various condensation with aldehydes.[61,102,122-125] Recently we have carried out a successful direct boronation by a Friedel-Crafts type reaction.

Competitive experiments carried out by Kozikowski et al.,[84] showed the reactivity order: ferrocene ≫anisole> methylcyclopentadienylmanganese tricarbonyl >cyclopentadienylmanganese tricarbonyl >benzene. Furthermore, of the three compounds,-ferrocene, ruthenocene and osmocene[29] - the most reactive is ferrocene and the least reactive is osmocene.

These results show then, that ferrocene is the most aromatic of the organometallic compounds so far investigated, and the Russian workers have, on several occasions, described it as being 'superaromatic'.

The Bonding in Ferrocene.

The search for a satisfactory explanation of the nature of the bonding in ferrocene, has led to numerous publications. These have been condensed in several excellent reviews,[10,12,14,17,127,128] and two main concepts of the nature of this bonding have become apparent.

Fischer and his collaborators[23,129] regard ferrocene as a new type of penetration complex, with the iron atom attaining the inert gas configuration by interaction of the Fe^{2+} ion with each of the three pairs of π-electrons in each of the cyclopentadienyl anions. This results in the formation of six coordinate covalences (d^2sp^3) almost octahedrally arranged.

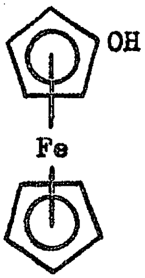
The alternative molecular orbital treatment has had many contributions, the most successful of which were proposed by Dunitz and Orgel,[26,130,131] and Moffitt.[132] This theory prescribes a single covalent $(d_\pi - p_\pi)$ bond from the metal atom to each ring as a whole, and any additional bonding is regarded as being very weak.

The incompatibility however, of the two concepts, may be less than expected at first sight, as Linnett[133] has stated that, 'the attainment of the inert gas configuration is essential'.

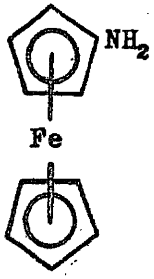
DISCUSSION

Electrophilic substitution reactions of ferrocene have been known now for the past ten years, but the findings from considerable research efforts of many workers have shown that as yet, the nature of electronic transmission within and across the aromatic rings is incompletely understood. A general substitution pattern however became apparent from these experiments, and the main purpose of this study therefore was to investigate further, the directive effects operative in certain substituted ferrocenes.

Ideally, substitution reactions on substituted ferrocenes can be thought of as falling into two main categories, depending on whether the directing substituent is electron donating (activating), or electron withdrawing (deactivating). To obtain the best possible results, the substituent should have a minimum steric effect, but a maximum activating influence. The choice of substitution reaction is also governed by certain factors. The reaction should give high yields, the products should be separable by any method which will give nearly quantitative results, and the reagent used should be as selective as possible. The choice of substituted ferrocene may also be limited by another factor, namely instability. Because of this, such ideal derivatives as hydroxyferrocene[134,136] (XIII) and aminoferrocene[136-138] (XIV), which satisfy the other



XIII

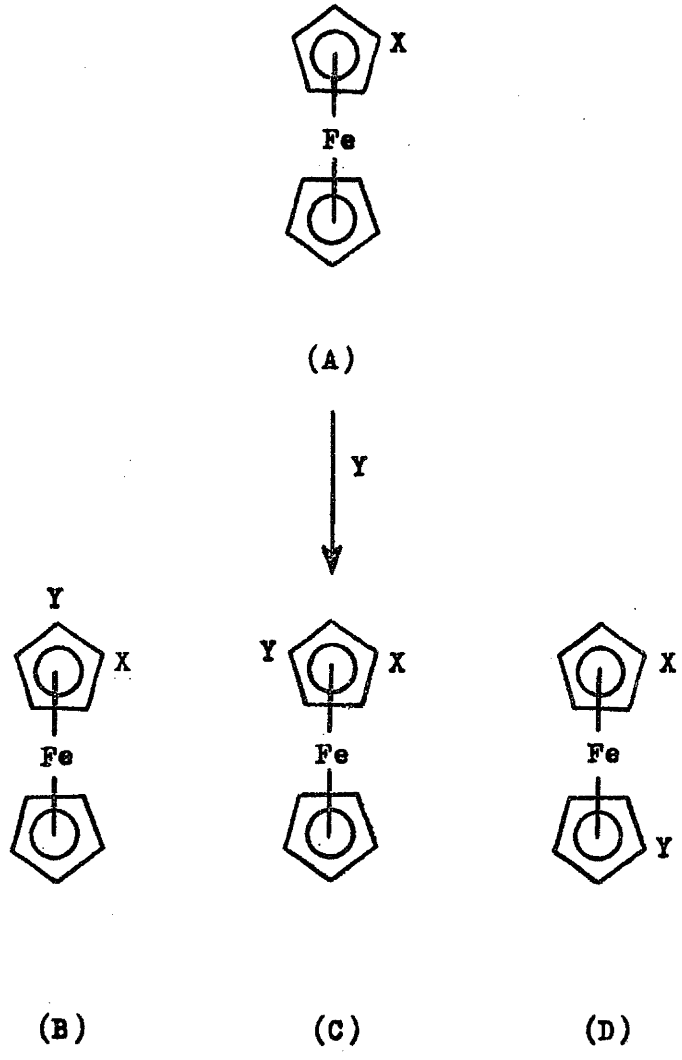


XIV

conditions, have never been investigated in any detailed manner.

From the monosubstitution of a ferrocene (A) already bearing a substituent, the maximum number of isomeric products expected would be three, namely (B), (C) and (D). Under the controlled conditions normally employed for these reactions, introduction of two Y groups is extremely unlikely.

In the majority of cases, the isomer ratios will be deduced from the weight ratios of the isomers or simple derivatives thereof. Chromatography times must therefore be minimised to prevent excessive decomposition on the column, as any one isomer may be preferentially decomposed.

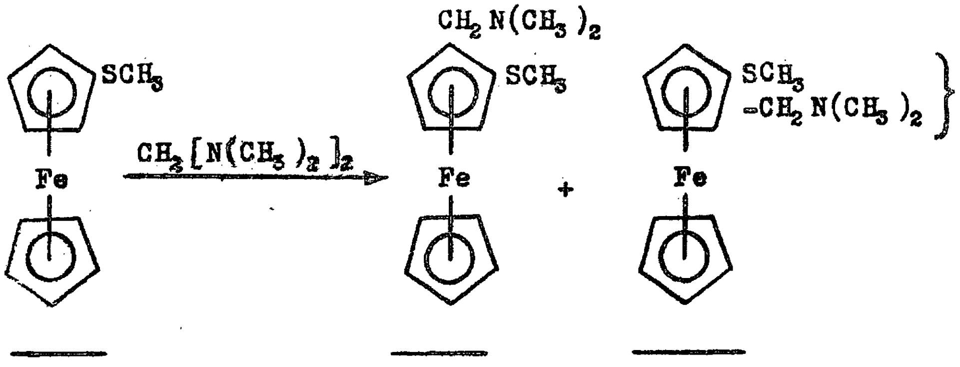

X
Fe
(A)
Y
Y
X
Fe
(B)
Y
X
Fe
(C)
X
Fe
Y
(D)

Methylthioferrocene.

The aminomethylation of methylthioferrocene (XV) with methylene bis-dimethylamine was reported[139] in 1959. The results however proved to be rather unexpected, so a reinvestigation was undertaken.

Thioanisole readily undergoes electrophilic substitution, and acetylation,[140] bromination and sulphonation are reported to proceed in high yields. Nitration however, leads to oxidation of the sulphur atom.[141] Now the methylthio group in thioanisole, is known to exert a marked activating influence, and this same effect would be anticipated in the ferrocene series.

From the aminomethylation (Mannich reaction) of methylthioferrocene (XV) Knox isolated two compounds (XVI) and (XVII) whicn analysed correctly for monosubstituted isomers.



XV   XVI   XVII

The structure of the first isomer, 1-methylthio-2-dimethylaminomethylferrocene (XVI) a brown crystalline solid, m.p. 81.5°, was established unequivocally by consideration of the following evidence:

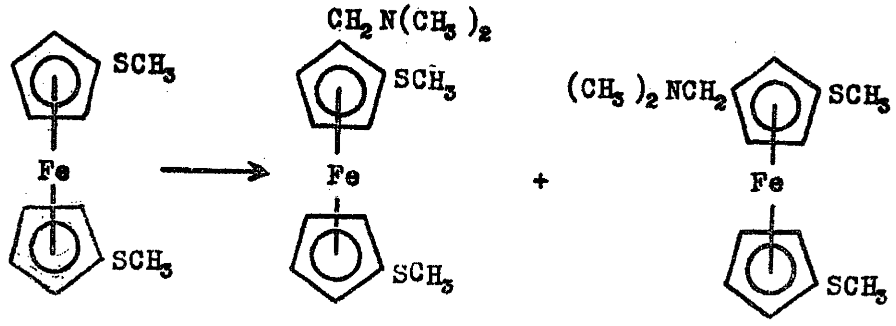
(i) It eluted first on a chromatography column, the general order of elution being 1,2 isomer, before 1,1', before 1,3. Although this is only a qualitative basis for assigning structure, no exceptions to this rule had ever been reported.

(ii) The infrared spectrum showed bands at 9μ and 10μ showing the presence of an unsubstituted cyclopentadienyl ring (Rosenblum's "9,10" rule).

(iii) The nuclear magnetic resonance spectrum[139,142] revealed that the two substituents were adjacent.

In an attempt to clarify the situation, Knox carried out the aminomethylation of di(methylthio)ferrocene[142] (XVIII), and isolated the two expected monosubstituted isomers (XIX) and (XX). They were identified unambiguously by means of their nuclear magnetic resonance spectra, and elution order on chromatography. NMR. spectral comparisons between (XIX) and (XVI) supplied further proof of the identity of the latter.

A detailed investigation of the second compound (XVII), was undertaken to establish its purity. This however failed to yield the 1,3 isomer.

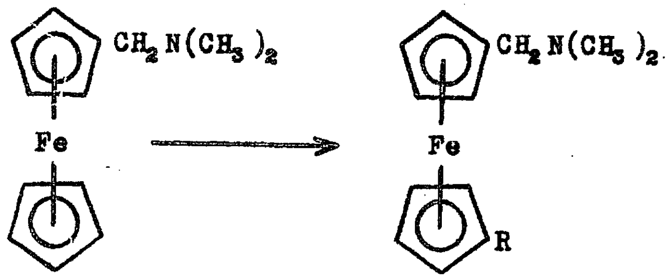


XVIII XIX XX

From the evidence available then, Knox concluded that the second product was the 1,1' isomer, 1-methylthio-1'-dimethylaminomethylferrocene. One anomaly however which could not be explained was the presence in the infrared spectrum of medium strong bands at 9μ and 10μ. These bands were still present after several attempted purifications, thus raising the problem of deciding whether they were due to a free cyclopentadienyl ring, or whether in fact they were an integral part of the infrared spectrum of the 1,1' isomer

Synthesis of Di-(1'-methylferrocenyl)disulphide.

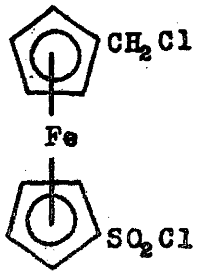
As careful chromatography had failed to resolve the second compound (XVII), the best mode of approach to the problem appeared to be that of synthesising unambiguously, the 1,1' isomer or a simple derivative of it. Several attempts were thus made to synthesise the necessary type of ferrocene derivatives from which it would be possible to prepare the desired isomer. In an attempt to prepare 1-dimethylaminomethylferrocene-1'-sulphonic acid (XXII, R = SO_3H), dimethylaminomethylferrocene (XXI) was treated in one instance with chlorosulphonic[106] acid and in another with dioxan-sulphur trioxide.[107] Neither method proved successful.



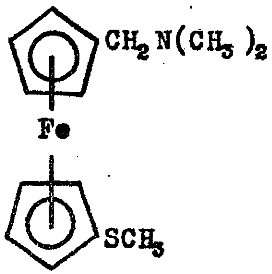
XXI

XXII

With a view to establishing the conditions for the preparation of 1-chloromethylferrocene-1'-sulphonyl chloride (XXIII) from which a synthesis of the-1,1' isomer (XXIV) appeared possible, the preparation of (XXII, R = CH_2Cl) was attempted. The free amine (XXI), was treated with chloromethyl ether and stannic chloride catalyst, but this only resulted in the formation of di-(ferrocenylmethyl-) ether[144] (XXVIII). A repeat

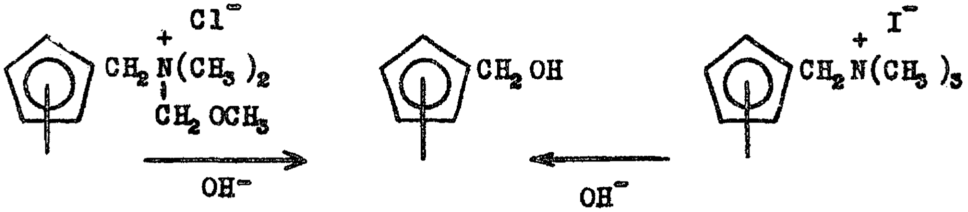


XXIII

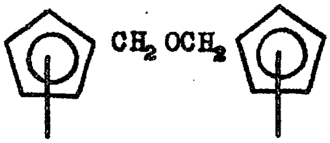


XXIV

experiment incorporating a hydrochloric acid solution of titanous chloride in the work up, yielded ferrocenylmethanol (XXVII) as the only recognisable product. The production of the ferrocenylmethanol would thus appear to proceed *via* a quaternary ammonium salt of the type (XXV) which could then undergo hydrolysis



XXV XXVII XXVI



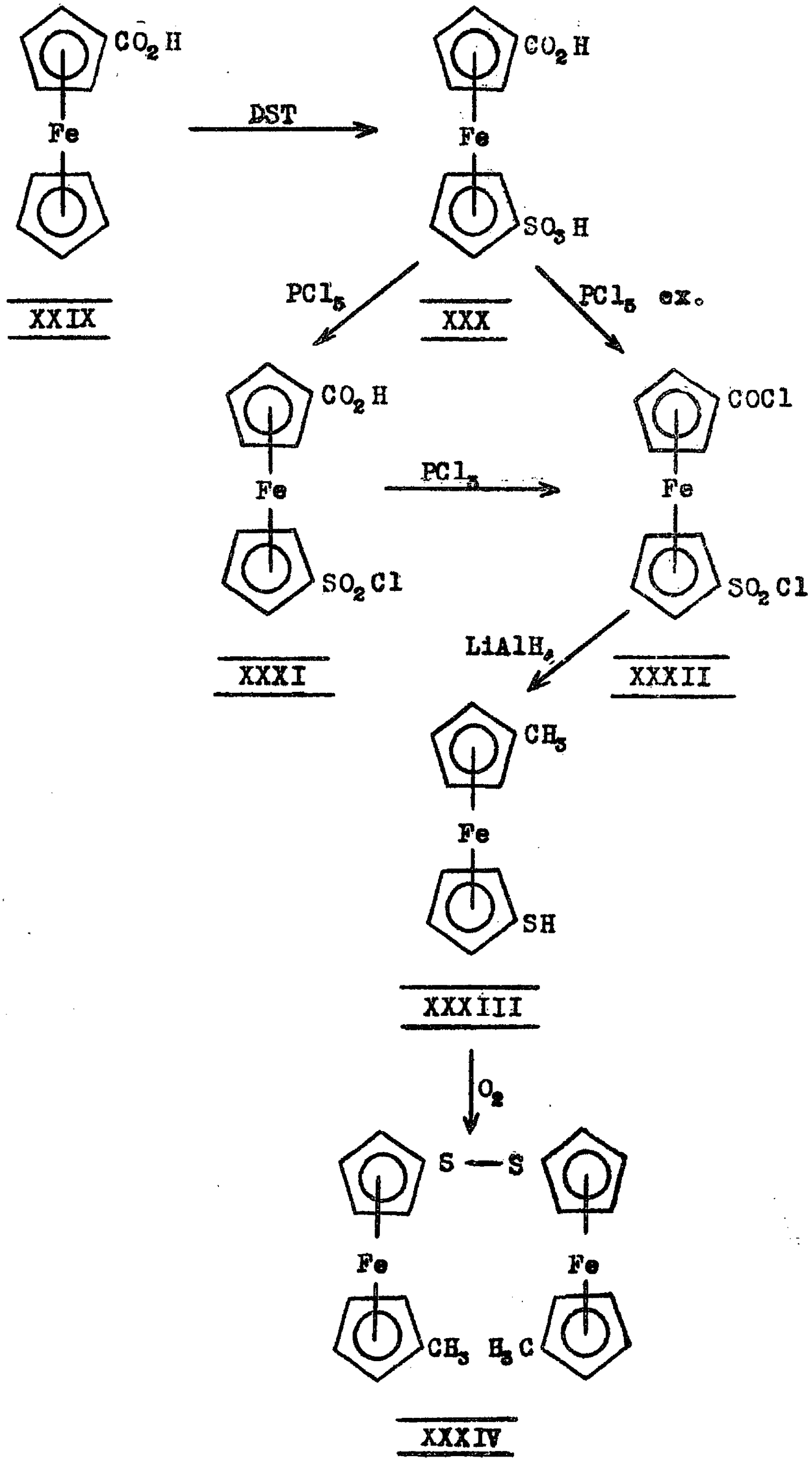
XXVIII

to the alcohol (XXVII), as in the alkaline hydrolysis of (ferrocenylmethyl)trimethylammonium iodide[145] (XXVI). The mode of formation of the di-(ferrocenylmethyl-)ether however, is less clearly understood.

The chloromethylation was then attempted on the methiodide of the amine (XXI) in acetic acid as solvent, but without any success whatsoever.

In 1959, Nesmeyanov et al,[108] showed that ferrocenecarboxylic acid (XXIX) could be sulphonated specifically in the 1' position, by treatment with dioxan-sulphur trioxide, to give 1-carboxyferrocene-1'-sulphonic acid (XXX). This di-acid (XXX) with phosphorus pentachloride, yielded the di-acid chloride, 1-chlorocarbonylferrocene-1'-sulphonyl chloride (XXXII), which appeared to be a suitable starting point for the envisaged synthesis.

Along with the di-acid chloride (XXXII) we isolated a compound not reported by the earlier workers.[108] This was identified as 1-carboxyferrocene-1'-sulphonyl chloride (XXXI). When it was allowed to react with excess phosphorus pentachloride, a 41% yield of the di- acid chloride was obtained. Reduction of (XXXII) with lithium aluminium hydride produced the obnoxious smelling mercaptan (XXXIII) which was isolated after air oxidation as di-(1'-methylferrocenyl)disulphide (XXXIV), a yellow crystalline solid, m.p.101.5-102.5°.



XXIX

XXX

XXXI

XXXII

XXXIII

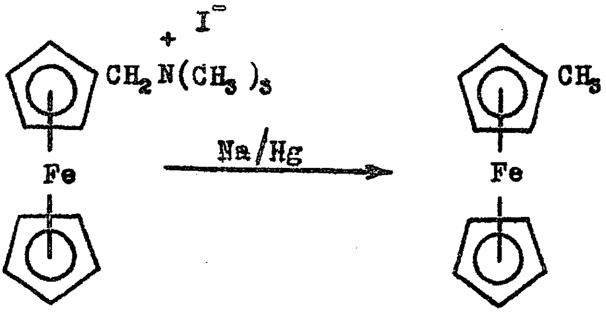
XXXIV

Having thus prepared a suitable derivative of the 1,1' isomer, attention was returned to the aminomethylated products of methylthioferrocene.

Examination of the Aminomethyl-Methylthioferrocenes.

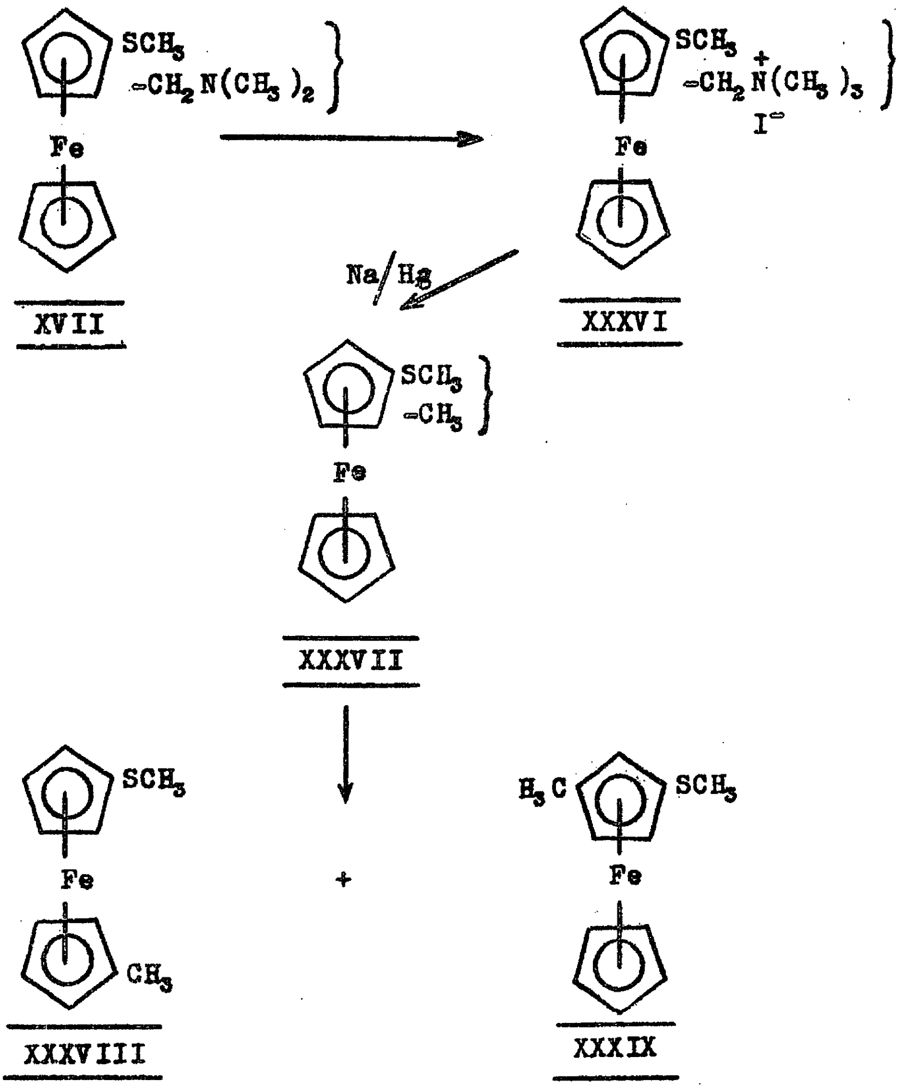
The aminomethylation of methylthioferrocene was repeated and the two compounds (XVI) and (XVII) isolated.

Following the method utilised by Nesmeyanov *et al.*,[148] for the reduction of (ferrocenylmethyl)trimethylammonium iodide (XXVI) to methylferrocene (XXXV) with sodium amalgam, the

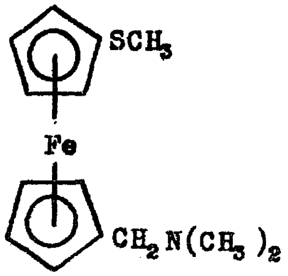


XXVI XXXV

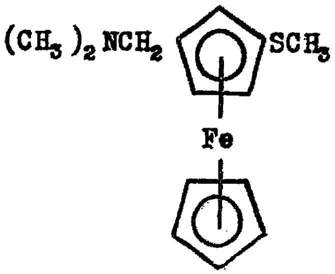
methiodide (XXXVI) of the second compound (XVII) was prepared and reduced without purification to the corresponding methyl derivative, (XXXVII). Since this material contained medium bands at 9μ and 10μ it was submitted to a series of careful chromatographies from which the two virtually pure isomers, (XXXVIII) and (XXXIX) were isolated. Unlike their parent amines which eluted with ether mixtures, the methyl-derivatives eluted in ligroin, thus facilitating the chromatography. Both isomers analysed correctly, the first one



to elute having no bands at 9μ and $10\ \mu$. This therefore was the reduction product of 1-methylthio-1'-dimethylaminomethylferrocene (XXIV), and the other had to be the reduction product of 1-methylthio-3-dimethylaminomethylferrocene (XL). (XXXIX) possessed large "9,10" bands in the infrared.

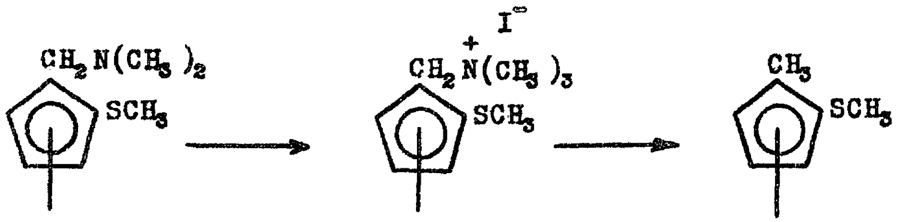


XXIV



XL

To show conclusively that (XXXIX) and 1-methylthio-2-methylferrocene (XLII) were different, a sample of the latter compound was prepared to effect a direct comparison. The crystalline methiodide (XLI) m.p. 182-183°, of 1-methylthio-2-dimethylaminomethylferrocene (XVI) was reduced with sodium amalgam in water as before to give the methyl-derivative (XLII).



XVI XLI XLII

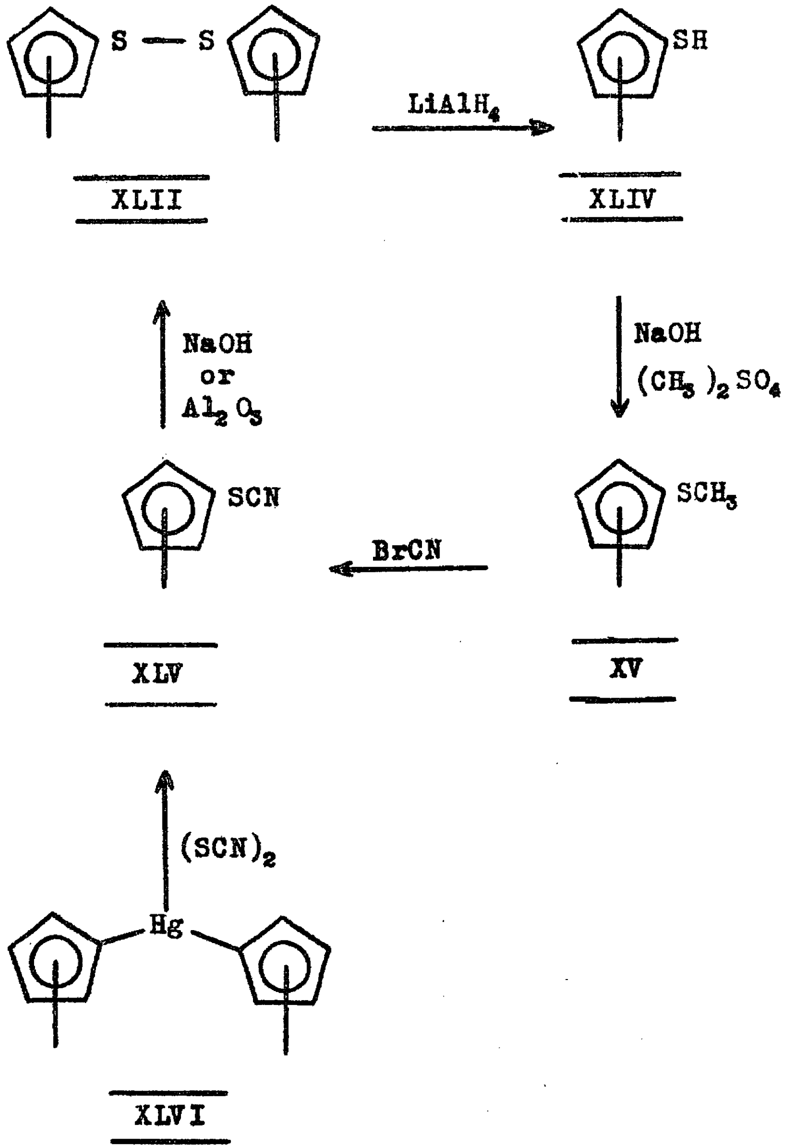
The infrared spectra of (XXXIX) and (XLII) although very similar, were different, thus confirming our previous findings.

By chromatographing a mixture of (XLII) and (XXXVIII), it was found that (XLII) eluted first as expected. Now, since in the initial separation of (XXXIX) from (XXXVIII), the latter eluted first, the general order of elution of 1,2 isomer before 1,1' before 1,3 was realised.

When a small quantity of (XVII) was chromatographed on a large column, eight fractions were collected. The first possessed large bands in the infrared in the regions of 9µ and 10 µ, while the last had only minute bands in those regions. Even though no complete separation of the amines could be achieved, these results indicate an elution order of 1,2 isomer before 1,3 before 1,1' for the three dimethylaminomethyl-methylthioferrocenes. This is the first time an exception to the normal chromatographic elution order has been observed, and as already mentioned, the reduction products from the methiodides of these amines have the normal elution order.

The infrared maxima of all three methiodides are tabulated on p.120.

The problem was now essentially one of converting the 1-methylthio-1'-methylferrocene isomer (XXXVII) to the synthesised di-(1'-methylferrocenyl)disulphide (XXXIV) or vice versa, as both routes appeared feasible. Lithium aluminium hydride reduction of diferrocenyl disulphide[106] (XLIII) has been shown to produce the intermediate ferrocenethiol (XLIV) which can be methylated with dimethyl sulphate in presence of sodium



hydroxide to give methylthioferrocene (XV). The preparation of diferrocenyl disulphide in 32% yield from demethylation of methylthioferrocene with aluminium trichloride had also been reported.[139]

Even though the demethylation proceeded in only 32% yield, this latter method was chosen for the following reasons:

(i) 1-methylthio-1'-methylferrocene is an oil and comparisons of small amounts of oils are undesirable.

(ii) Only a small quantity of the disulphide (XXXIV) was available for conversion to 1-methylthio-1'-methylferrocene (XXXVII).

(iii) The disulphide (XXXIV) is highly crystalline thus facilitating comparison.

Since only a limited amount of 1-methylthio-1'-methylferrocene (XXXVIII) was available for conversion to the disulphide (XXXIV), trial demethylations with aluminium trichloride under the conditions reported by Knox[139] were attempted on methylthioferrocene (XV). No diferrocenyl disulphide was obtained however, and repetition of the reaction under air and under nitrogen, in various solvents and at different temperatures failed to produce any. Traces of ferrocene however were isolated from these reactions but this will be discussed in a later section.

Another route to the diferrocenyl disulphide was now required, and the method used by von Braun and Engelbertz[146] for the cleavage of the sulphur-carbon bond in thio-ethers appeared to offer the best possibilities. These workers showed that cyanogen bromide, when allowed to react with various di-alkyl and alkyl-aryl sulphides, formed the corresponding thiocyanates as shown.

$$R.S.R' + BrCN \longrightarrow R.SCN + R'Br$$

When methylthioferrocene (XV) was treated with cyanogen bromide, ferrocenylthiocyanate (XLV) was isolated as yellow needles, m.p. 104°, in 66% yield. This material showed characteristic $-C\equiv N$ absorption in the infrared at 2169 $cm.^{-1}$ When Nesmeyanov _et al._,[147] treated diferrocenylmercury (XLVI) with thiocyanogen and then with an aqueous solution of sodium thiosulphate they obtained ferrocene and diferrocenyl disulphide (XLIII). The diferrocenyl disulphide, they suggested, was formed from the intermediate ferrocenylthiocyanate (XLV) by the reducing action of the thiosulphate. (XLV) however, failed to react with sodium thiosulphate solution, so diferrocenylmercury was treated with an alcoholic solution of thiocyanogen as described by Nesmeyanov _et al._ Stannous chloride was used to reduce the oxidised material, and chromatography of the extract on deactivated alumina yielded ferrocenylthiocyanate in 23% yield. The only other product obtained was ferrocene which accounted for 68% of the diferrocenylmercury employed, and therefore the total diferrocenylmercury accounted for was 89%.

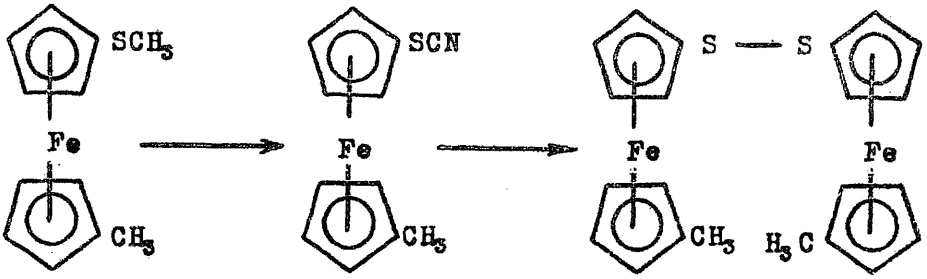
It seems almost certain then that the Russian workers did prepare the ferrocenylthiocyanate (XLV), but the sodium thiosulphate reduction appears to be highly unlikely. At a later date, we discovered that alumina converts thiocyanate derivatives to their corresponding disulphides in near quantitative yields. Furthermore, the more active the alumina, the quicker the reaction proceeds. As the Russian workers had separated the ferrocene from the diferrocenyl disulphide by chromatography on alumina, this might explain why they obtained diferrocenyl disulphide (XLII) and not ferrocenylthiocyanate.

Now alkyl-and aryl-thiocyanates are reported[148] to react with aqueous or alcoholic sodium hydroxide solutions to give the corresponding disulphide, sodium cyanide, sodium cyanate and water.

$$2R.SCN + 2NaOH \longrightarrow R.SS.R + NaCN + NaOCN + H_2O$$

Ferrocenylthiocyanate (XLV) was accordingly refluxed with 2N aqueous sodium hydroxide in methanol and diferrocenyl disulphide was obtained in 92% yield.

Having thus established a method for the preparation of disulphides from methylthioferrocenes, di-(1'-methylferrocenyl) disulphide (XLVIII) m.p. 101-102° was prepared from (XXXVIII) by the same series of reactions, via the intermediate thiocyanate (XLVII) which was obtained as an oil.

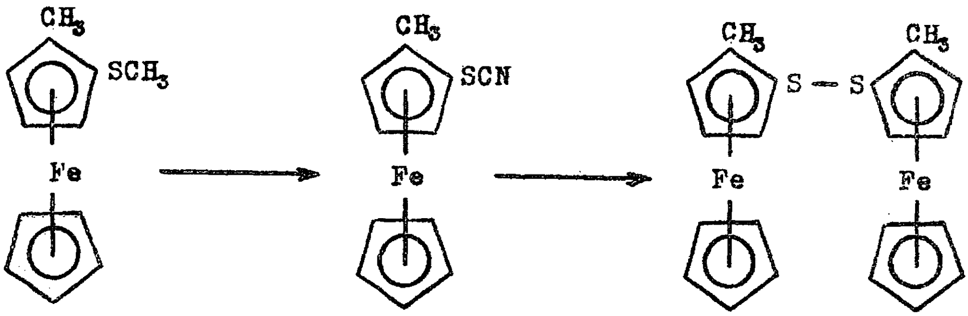


XXXVIII   XLVII   XLVIII

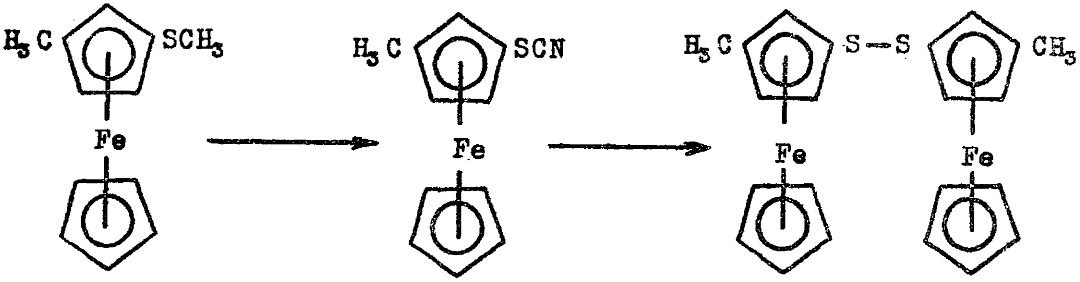
The infrared spectra, melting points and mixed melting points of (XXXIV) and (XLVIII) were identical, so the synthesised disulphide, and that obtained from degradation reactions on the amine, must be the same compound, namely, di-(1'-methylferrocenyl) disulphide.

We have therefore established that the second component from the aminomethylation of methylthioferrocene, contains 1-methylthio-1'-dimethylaminomethylferrocene (XXIV) as the major constituent, and the third isomer, 1-methylthio-3-dimethylaminomethylferrocene (XL) as the other constituent.

The corresponding thiocyanates and disulphides of the 1,2 and 1,3 isomer were prepared by the same reactions described above and it was found that the only crystalline compounds were



XLII XLIX L



XXXIX LI LII

1-thiocyanato-2-methylferrocene (XLIX) m.p. 79° and di-(2-methylferrocenyl)disulphide (L) m.p. 151-153°.

N.B. Near quantitative yields of the disulphides (L) and (LII) were obtained when their corresponding thiocyanates (XLIX) and (LI) were absorbed on normal active alumina in organic solvents.

Competitive Aminomethylation.

A competitive aminomethylation between ferrocene and methylthioferrocene, using similar conditions to those employed for the aminomethylation of methylthioferrocene, was attempted, but the results were inconclusive since the only product which could be separated by chromatography was 1-methylthio-2-dimethylaminomethylferrocene (XVI).

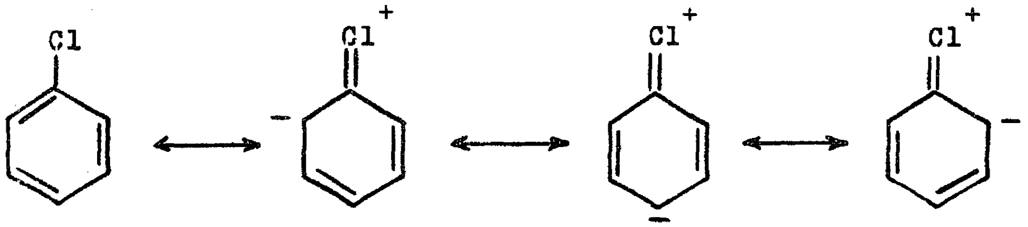
Since it seemed strange that dimethylaminomethylferrocene should elute after (XVI), a mixture of these compounds alone was chromatographed in benzene. As our previous findings indicated, (XVI) eluted first.

Calculations, based on the assumption that there was no serious decomposition, showed that more ferrocene than methylthioferrocene had entered into the reaction. Now taking into account the fact that ferrocene has ten available positions for substitution while methylthioferrocene has only nine, the reactivity of methylthioferrocene compared to that of ferrocene is 0.86, taking ferrocene as unity. These results suggest that any activating effect can only be very slight, but to draw any definite conclusions from such an unsatisfactory experiment would be dangerous.

Substitution of Chloroferrocene.

Since the chloro substituent is reasonably small and thus presents no appreciable steric hindrance, the substitution of chloroferrocene appeared to be worth investigating.

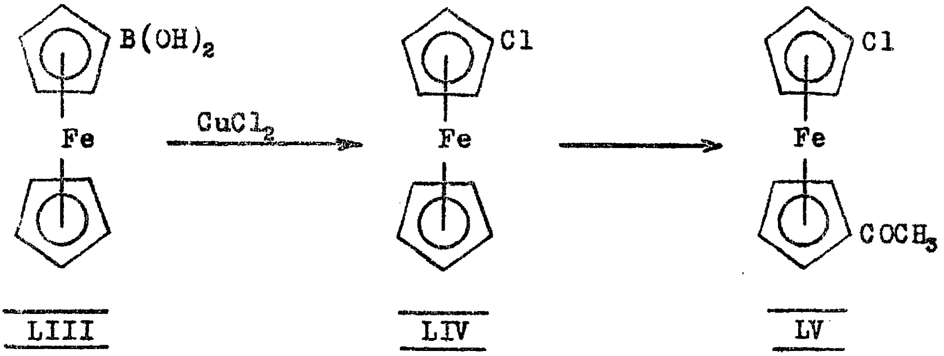
The dipole moment of chlorobenzene indicates the electron attracting (inductive deactivating) nature of the chloro substituent. Normally deactivating groups orient an entering group to the meta position, but halogen substituents are ortho-para directing like the activating (electron releasing) amino and hydroxyl groups. This apparent anomaly is explained, however, by regarding chlorobenzene as a resonance hybrid of four structures.



Chlorobenzene can be nitrated and sulphonated with relative ease. Nitration[149] gives a mixture of ortho and para isomers in the ratio 3:7, while the reversible sulphonation[150] proceeds exclusively in the para position. The deactivating influence of halogen substituents is demonstrated by the fact that dibromination of benzene requires more forcing conditions than monobromination.

One immediate difficulty was the preparation of pure chloroferrocene (LIV), free from ferrocene, by the procedure[151] of treating ferrocenylboronic acid (LIII) with cupric chloride in boiling water. Some ferrocene was nearly always produced and as this could not be removed by chromatography, sublimation or fractional crystallisation, the purity of the chloroferrocene was established by vapour phase chromatography.

When chloroferrocene was subjected to Friedel-Crafts acetylation, a 57% yield of 1-chloro-1'-acetylferrocene (LV), m.p. 53.5-54.5° was obtained. A mixture of ferrocene and chloroferrocene was also recovered, and vapour phase chromatography showed that ferrocene constituted 75% of this mixture.



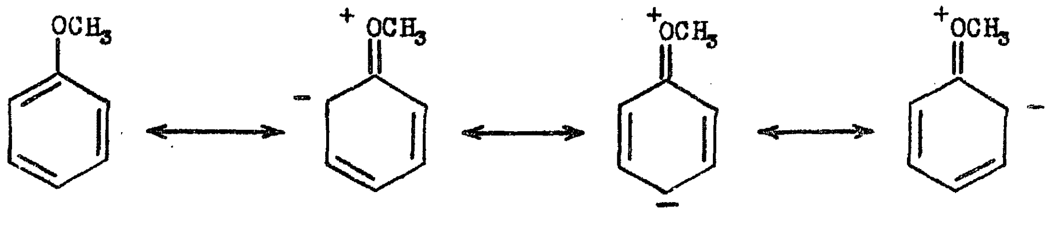
A surprising fact was the complete absence of acetylferrocene, m.p. 84°, although in one preparation the crude 1-chloro-1'-acetylferrocene had m.p. 55-62°. This suggests the presence of acetylferrocene, but vapour phase chromatography failed to give confirmation.

After the completion of these studies, Russian workers[152] published details of the acetylation of bromoferrocene, using acetic anhydride and phosphoric acid. Their results agreed with ours in that the only product they isolated was 1-bromo-1'-acetylferrocene.

Substitution Reactions of Methoxyferrocene.

With the failure of chloroferrocene to throw any appreciable light on the directive effects, the more reactive methoxyferrocene (LXVI) was investigated.

The benzene analogue, anisole, like chlorobenzene, directs ortho- para, but unlike the chloro substituent, the methoxy group has a considerable electron releasing property. It is clear that the tendency to release electrons will be greater with the electron-replete, negative oxygen which can be formed from the hydroxyl group, than with the neutral oxygen atom, i.e. $-\overline{\underline{O}}|^{-} \longrightarrow =\overline{\underline{O}}$ proceeds more readily than does $-\overline{\underline{O}}-R \longrightarrow =\overset{+}{O}-R$, this latter electromeric change compelling oxygen to hold a positive charge. However, the orienting of entering groups in anisole can be explained by considering it to



be a resonance hybrid of four structures.

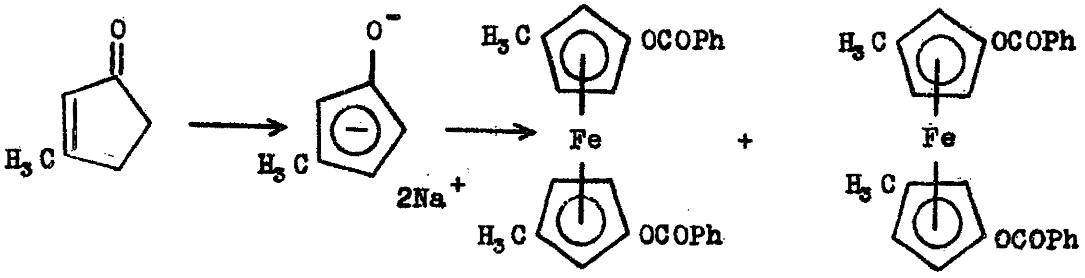
Anisole readily undergoes Friedel-Crafts acetylation,[153] and anisaldehyde (p-formylanisole) is reported to be formed in nearly quantitative yield by the Gatterman synthesis. Both of these reactions give the para product, but nitration[154] proceeds predominantly in the ortho position, (See page 66).

Now while methoxyferrocene should be similar in reactivity to methylthioferrocene, the former compound has the additional advantage of causing less steric interference to further substitution.

Preparation of Methoxyferrocenes.

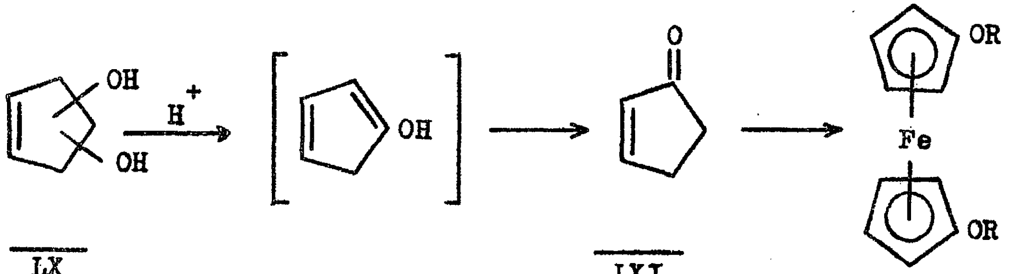
As the preparation of methoxyferrocenes by normal procedures *via* the ferrocenylboronic acids is very time consuming, giving poor yields, one of our first concerns was the investigation of more direct routes to these compounds.

1. In 1957, Benson and Lindsey[32] successfully prepared "hydroxymetallocenes" and their derivatives from the corresponding cyclopentenones. This was achieved by converting 3-methylcyclopentenone (LVI) with excess sodium amide in liquid ammonia into the doubly charged anion (LVII) which then reacts with ferrous chloride to give the corresponding ferrocene derivatives, isolated after benzoylation as the stereoisomeric benzoates (LVIII) and (LIX).



LVI LVII LVIII LIX

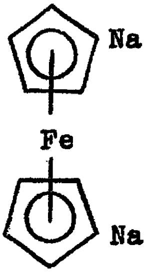
By substituting dimethyl sulphate for benzoyl chloride and using cyclopentenone (LXI)prepared from cyclopentadienol (LX) by the method of DePuy and Eilers,[155] the preparation of



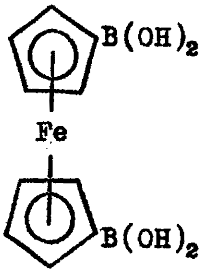
LX LXI LXII

1,1'-dimethoxyferrocene (LXII, R = CH_3) appeared feasible. Unfortunately, however, neither (LXII, R = CH_3)nor (LXII, R = CO.Ph) could be prepared by this method.

2. The preparation of 1,1'-ferrocenylenediboronic acid (LXIV) from 1,1'-disodioferrocene (LXIII) was also attempted, but without success. The disodioferrocene failed to react with either boron trichloride or tri-n-butyl borate.



LXIII



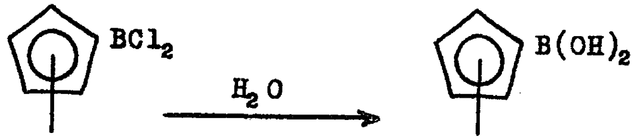
LXIV

3. Following the method reported by Muetterties[156] for the borodihalogenation of benzene and toluene, it proved possible to boronate ferrocene directly, by allowing it to react with boron trichloride, in the presence of aluminium powder, aluminium trichloride and methyl iodide in ligroin, in a Friedel-Crafts type reaction. Muetterties formulated the reaction as:

$$3ArH + Al + 3BX_3 \longrightarrow 3ArBX_2 + AlX_3 + \frac{1}{2}H_2$$

and stated that the methyl iodide acted as initiator.

In the ferrocene series, we found that the quantity of aluminium trichloride employed was of vital importance. Small amounts of aluminium trichloride gave high yields of ferrocenylboronic acid (LIII) and little 1,1'-ferrocenylenediboronic acid (LXIV), whereas a large excess of aluminium trichloride drastically reduced the yield of ferrocenylboronic acid and only slightly increased the yield of diboronic acid. No attempt was made to isolate the ferrocenylboronyl dichloride (LXV) since it hydrolysed immediately on contact with moist air.



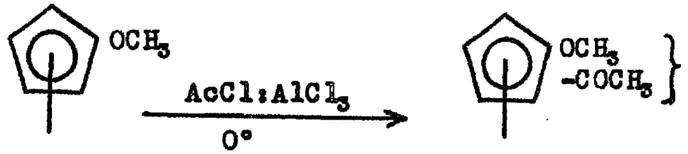
LXV LIII

This method is excellent for preparing fairly large quantities of ferrocenylboronic acid in good yield.

When preparing methoxyferrocenes,[135,170] from mixtures of ferrocenylboronic acids (mono- and di-), *via* the haloferrocenes and ferrocenylacetates, no intermediate purification was attempted. It was found that the haloferrocenes were unresolvable on alumina and that the acetates, although separable on a column, tended to decompose. Chromatography, however, easily separated ferrocene, methoxy- and 1,1'-dimethoxy- ferrocene.

Acetylation of Methoxyferrocene.

Friedel-Crafts acetylation of methoxyferrocene using one mole of Perrier complex[157] ($AlCl_3$:AcCl) per mole of methoxyferrocene, gave a 46% yield of acetylated product. To prevent demethoxylation, the reaction time must be kept to a minimum, and thus the low yield encountered in this reaction may be due to either demethoxylation or the short reaction time.

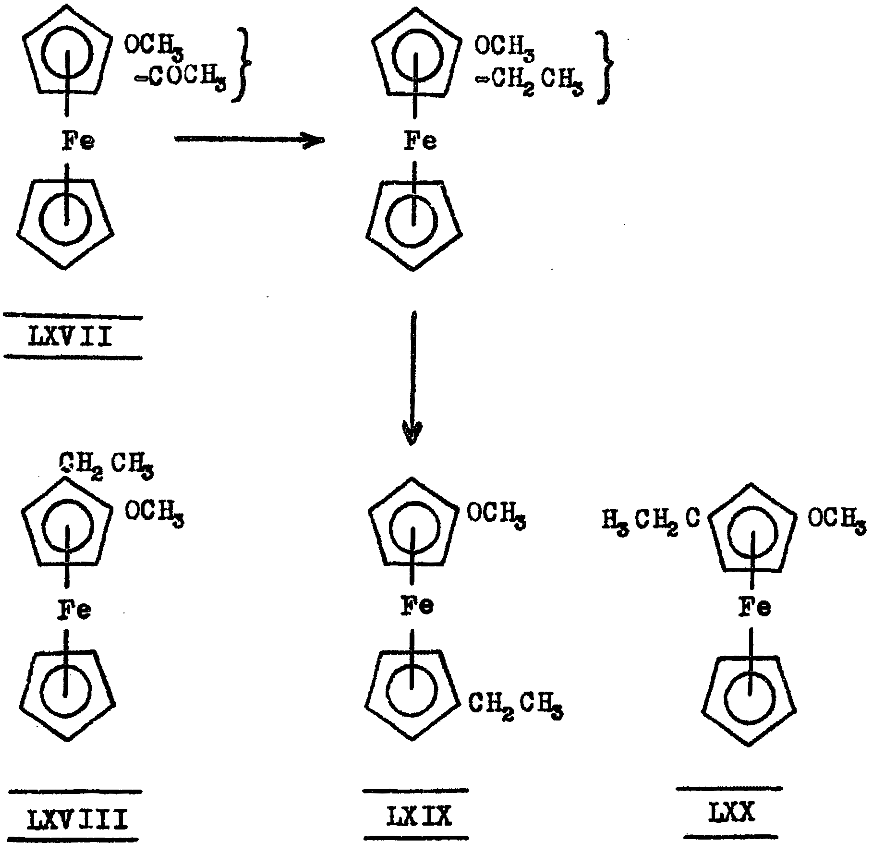


LXVI LXVII

Chromatography of the reaction product furnished methoxyferrocene, two isomeric dimethoxyferrocenes, acetylferrocene and a mixture of three isomeric acetylated methoxyferrocenes (LXVII) in that order. The isomeric dimethoxyferrocenes will be discussed later along with the mode of formation of acetylferrocene.

When the mixture of isomeric acetyl-methoxyferrocenes was subjected to careful chromatography, no resolution was obtained. On one occasion, however, when a very small amount was chromatographed on a large column, 1-methoxy-2-acetylferrocene m.p. 35-36° was obtained from the first part of the diffuse band. Nevertheless, this was not a practical method for determining the isomer ratios, so reduction to the corresponding ethyl- methoxyferrocenes was effected.

On reducing the acetyl-methoxyferrocenes (LXXI) with lithium aluminium hydride-aluminium trichloride, - a method reported by Schlögl for near quantitative reduction of acylferrocenes - only a 54% yield of reduction product was obtained along with two other bands. (See page 50). Reduction using lithium aluminium hydride alone, only produced the corresponding mixture of alcohols. As it had proved possible to separate the three isomers (LXVIII), (LXIX) and (LXX), a better reduction method


LXVII

LXVIII

LXIX

LXX

appeared to offer the best possibilities of obtaining good isomer ratio values.

The Clemmensen reduction procedure which Nesmeyanov et al,[158] showed proceeded in 67% yield for acetylferrocene, has recently been used by Watts[61] who obtained ethylferrocene in 87% yield in the same reaction. This method was accordingly adopted but since the reduction only gave a 60% yield, isomer ratios were calculated for each method.

Structural Assignments to Ethyl-Methoxyferrocenes.

Structural assignments were made on the following basis.

(i) Only (LXIX) of the three isomers isolated, showed no bands at 9 μ. and 10 μ. in the infrared. This was therefore the 1,1' isomer, 1-methoxy-1'-ethylferrocene.

(ii) The first isomer (LXVIII) to elute from the column was assigned the 1,2 structure on the merits of its nuclear magnetic resonance spectrum. This showed a splitting of the methylene peaks, attributed to the adjacent methoxy group. A splitting of the methylene peak in 1-methylthio-2-dimethylaminomethylferrocene[142] has been explained on the grounds of steric hindrance by the adjacent methylthio group, which forces the methylene hydrogens to occupy different positions in space around the ferrocene nucleus. The steric hindrance present in 1-methoxy-2-ethylferrocene would be expected to be less, and in fact the splitting was just visible.

The remaining isomer (LXX) must therefore be 1-methoxy-3-ethylferrocene.

Displacement of Ferrocene Substituents by Protons.

In an effort to clarify the apparent dehalogenation and demethoxylation occurring during the acetylation of chloro- (LXXI, $X = Cl$) and methoxy- (LXXI, $X = OCH_3$) ferrocene, dry hydrogen chloride gas was passed through a chloroform solution of chloroferrocene. No reaction took place. When, however, solutions of chloroferrocene and methoxyferrocene in methylene chloride at room temperature under nitrogen, were stirred with freshly ground aluminium trichloride, ferrocene was quickly generated in each case. In the latter case, apart from formation of ferrocene and recovery of unchanged methoxyferrocene, at least two other bands were eluted close together in the chromatography. The infrared spectra of these compounds which possessed bands at 9 µ. and 10 µ. were identical to the infrared spectra of the products obtained in the preparation of the acetyl-methoxyferrocenes. These spectra were also similar to those of the by-products from the lithium aluminium hydride-aluminium trichloride reduction of the acetyl- methoxyferrocenes. The similarity between these spectra and the spectrum of methoxy-ferrocene (Table No.15. page 122), suggests that these compounds are isomeric dimethoxy- ferrocenes.

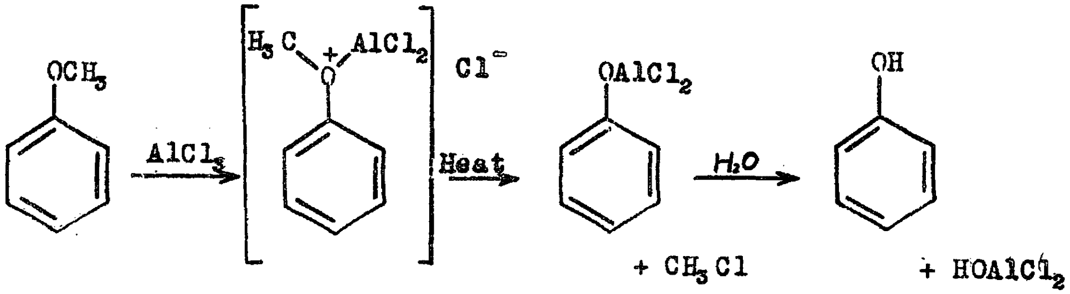
Similar treatments of acetyl- and ethyl-ferrocene in methylene chloride with aluminium trichloride, indicated that the acetyl group was very difficult to remove and that de-ethylation requires longer reaction time than demethoxylation. This evidence therefore suggests that the largest contributary cause for the poor yields obtained in the reduction with $LiAlH_4$-$AlCl_3$ is that of demethoxylation.

When methylthioferrocene in methylene chloride was stirred in the cold with excess freshly ground aluminium trichloride, 30% ferrocene was obtained along with unchanged starting material and at least two other bands. From infrared spectral comparisons, these minor bands appear to be isomeric di(methylthio)- ferrocenes. (Table No.16. page123).

In the acetylation of phenylferrocene, Rosenblum[159] reported the isolation of traces of acetylferrocene. Formation of the latter may have come about, either by dephenylation of phenylferrocene followed by acetylation of the ferrocene produced, or by the dephenylation of the three isomeric acetyl-phenylferrocenes. If the latter mode of reaction were followed, preferential dephenylation of any one isomer would alter the isomer ratios. These remarks are naturally also relevant to our acylations. Recently, Rosenblum and Howells[160] have repeated Rosenblum's previous work, but they do not mention if acetylferrocene was isolated.

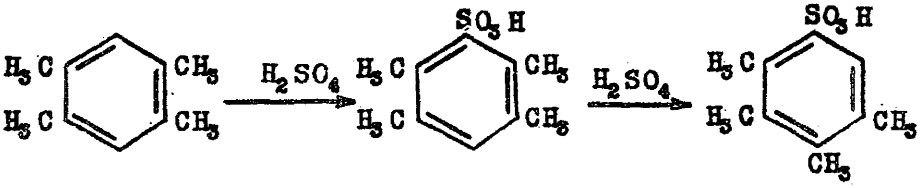
A protonation reaction similar to those already discussed, has been reported by Bruce.[171] He observed an 11% conversion of ferrocenylamine to ferrocene, when the former compound was treated with acetic acid and sodium acetate.

It has long been known that anisole, as well as thioanisole,[161] can be dealkylated with aluminium trichloride. Normal procedures require heating these compounds either with aluminium trichloride alone at 120°, or in a solvent such as benzene or carbon disulphide. The reaction has been represented thus:



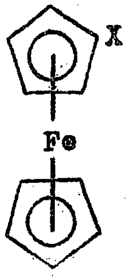
If analogous reactions occurred in the ferrocene series, hydroxyferrocene and ferrocene thiol would be produced. The former compound would decompose while the latter would oxidise in air to diferrocenyl disulphide. However, no disulphide was isolated.

Certain electrophilic substitutions of aromatic systems e.g. sulphonation and Friedel-Crafts reactions, are known to be reversible. These " reverse " substitutions involve electrophilic displacement of a substituent by a proton. Examples of this type of reaction include the Jacobsen reaction[162] in which alkyl

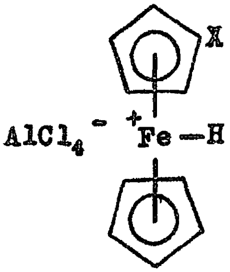


groups or halogen atoms are displaced during sulphonation, and the " detritiation" and " protodesilylation" studies by Eaborn and his co-workers.[163]

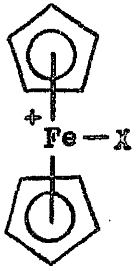
The evidence suggests that ferrocene is a likely intermediate in all the reactions described, and although dry hydrogen chloride itself failed to dechlorinate chloroferrocene, hydrogen chloride (formed in sufficient quantities from traces of moisture) must play a part in the reaction. It is thus tempting to assume[164] that the known type[101] of complex (LXXII) is directly involved. If this can exchange X and H to give the cation (LXXIII),



LXXI



LXXII



LXXIII

this may then react further according to one or both of the alternative schemes.

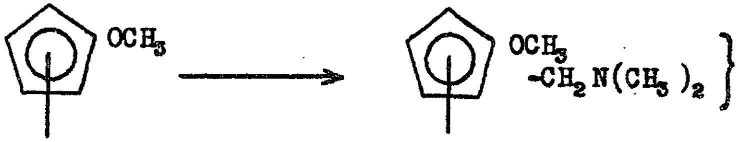
$$(1)\quad \underset{\underline{\text{LXXIII}}}{(C_5H_5)_2Fe^{+}X} + \underset{\underline{\text{LXXI}}}{(C_5H_4X)(C_5H_5)Fe} \longrightarrow (C_5H_5)_2Fe^{+} + (C_5H_4X)(C_5H_5)Fe^{+} + X^{-}$$

$$(2)\quad (C_5H_5)_2Fe^{+}X + (C_5H_4X)(C_5H_5)Fe \longrightarrow (C_5H_5)_2Fe + C_{10}H_8X_2Fe + H^{+}$$

In the case of chloroferrocene, no dichloro derivative was isolated and course (1) or some related mode of reaction must be followed. Methoxy- and methylthio- ferrocene on the other hand afforded not only ferrocene, but also mixtures of the isomeric dimethoxy- and di(methylthio)- ferrocenes. The second course must therefore be followed at least in part, and the overall process may be described as a disproportionation.

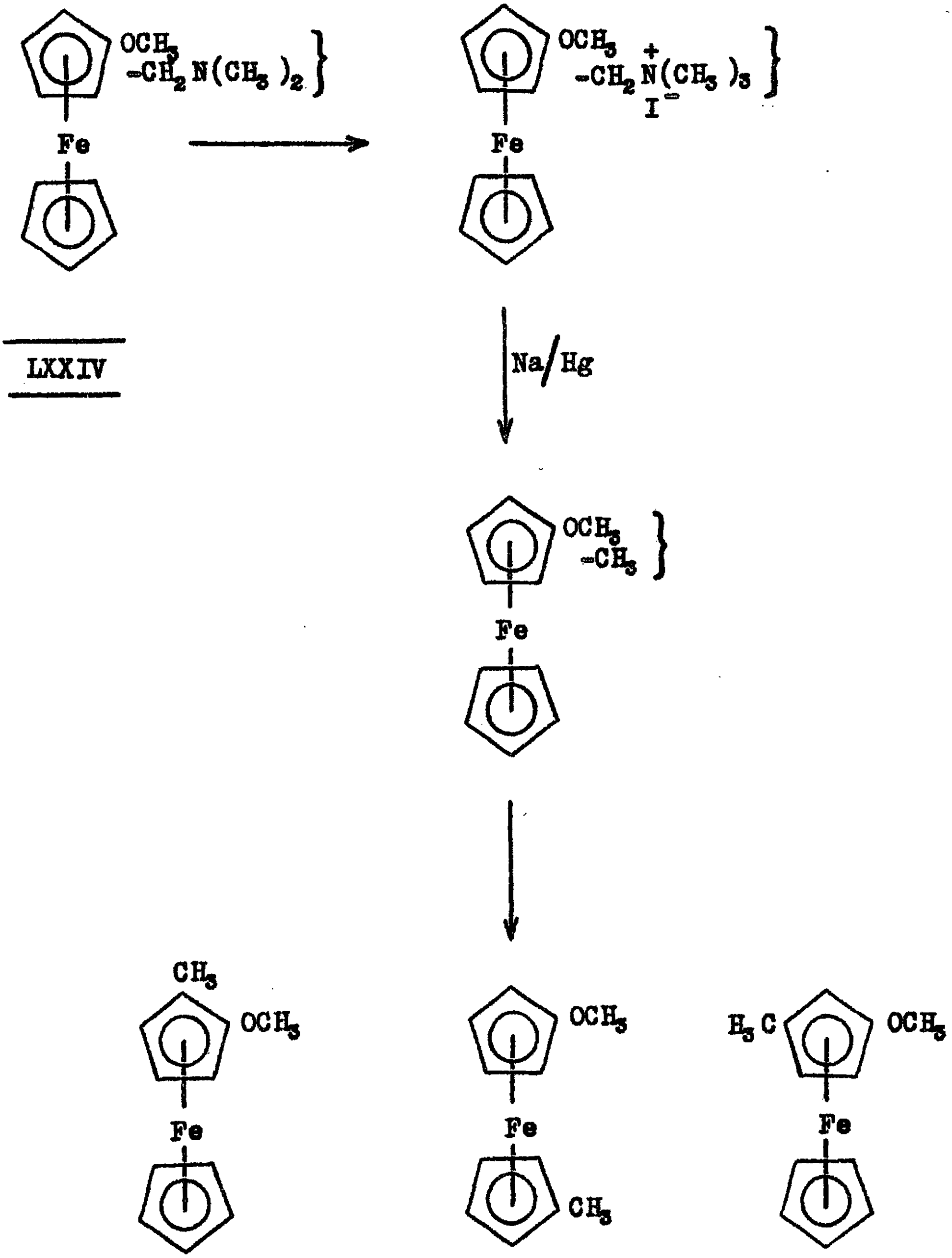
Aminomethylation of Methoxyferrocene.

The aminomethylation of methoxyferrocene (LXVI) proceeded very smoothly in 82% yield (conversion) with a reaction time of 6 hr., compared to 24 hr. for the **aminomethylation** of methylthioferrocene. Chromatography failed to separate any of the three expected isomers. The mixture of isomers (LXXIV) was therefore converted to the methiodides and reduced with sodium amalgam in water to the mixture of methyl derivatives. Since the overall reduction was achieved in 90% yield, the isomer ratios obtained for the methyl compounds should be valid for the parent amine isomers.



LXVI LXXIV

Careful chromatography now led to separation of the three methyl isomers (LXXV), (LXXVI) and (LXXVII). It was found most advantageous to run infrared spectra between 8.5 μ. and 11.5 μ. on fractions where visible separation of bands was doubtful, e.g., between the 1,1' and 1,3 isomers. The "9,10" bands could thus be used as a criterion of purity.



LXXIV

LXXV

LXXVI

LXXVII

Structural Assignments to Methyl-Methoxyferrocenes.

Initial structural assignments were based on the following evidence:

(i) Of the three isomers obtained, only (LXXVI) had no bands in the infrared at 9 µ. and 10 µ. This was therefore the 1,1' isomer.

(ii) Both the remaining (LXXV) and (LXXVII) had bands in the infrared at 9 µ. and 10 µ. Since the normal order of elution is isomer 1,2 before 1,1' before 1,3, (LXXV) was assigned the 1,2 structure and (LXXIV) must be the 1,3 isomer.

N.B. N.M.R. spectra of these isomers failed to confirm our structural assignments.

Correlation of Methyl- and Ethyl- Methoxyferrocenes.

Since N.M.R. spectra did not supply conclusive evidence for distinguishing between the 1,2 and 1,3 isomers in the methyl-methoxyferrocene series, some other confirmation of structure was desirable.

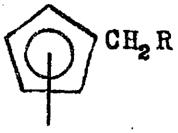
The following points on structure elucidation have been established:-

(i) The three isomeric ethyl-methoxyferrocenes have the normal elution order; 1,2 before 1,1' before 1,3.

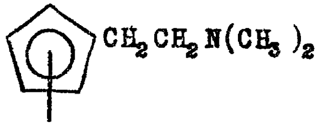
(ii) Of the three reduction products, (A), (B) and (C) from the three isomeric dimethylaminomethyl-methoxyferrocenes, (B) is 1-methoxy-1'-methylferrocenes.

Now, if the the first of the amines to elute from the column gives (A) on reduction and this amine could be converted to 1-methoxy-2-ethylferrocene, (A) must be 1-methoxy-2-methyl-ferrocene. A normal elution order would therefore be obtained.

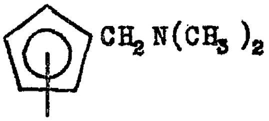
The possibilities of converting a dimethylaminomethyl grouping to an ethyl group were thus investigated using dimethylaminomethylferrocene (XXI) as a model compound. Since however, ethylferrocene is an oil, the preparation of the crystalline benzylferrocene was attempted first. When the (ferrocenylmethyl) trimethylammonium iodide (XXVI) was heated with 30% excess phenyllithium in a tetrahydrofuran-ether solvent system, 25% benzylferrocene (LXXVIII, R = Ph), 5% N,N-dimethyl-β-ferrocenylethylamine (LXXIX) and 13% dimethylaminomethylferrocene (XXI) were obtained. Similar treatment of the methiodide with



LXXVIII

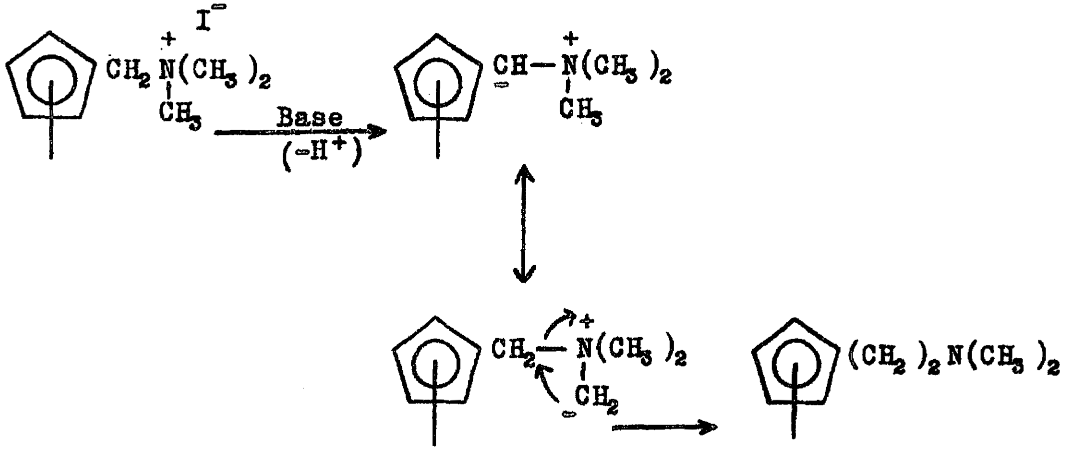


LXXIX



XXI

methyllithium furnished 27% ethylferrocene (LXXVIII, R = CH_3), 29% of (LXXIX) and 9% of (XXI). This rearrangement which has also been observed by Watts,[61] has been formulated as follows:[165,166]



To minimise the side-reaction, the methiodide was treated with the less basic corresponding Grignard reagents, but only 9% of benzylferrocene was obtained, and no ethylferrocene was isolated.

$$\mathrm{Fe\cdot CH_2\overset{+}{N}(CH_3)_3X^-} \xrightarrow{\mathrm{RMgX}} \mathrm{Fe\cdot CH_2\cdot R + N(CH_3)_3 + MgX_2} \quad [\mathrm{Fe = C_{10}H_9Fe}]$$

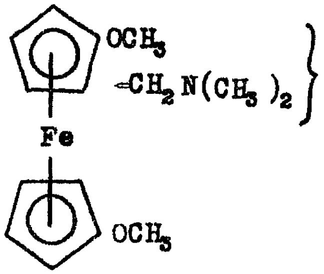
At this time, Russian workers[167] described the reactions of this methiodide with several Grignard reagents including the aforementioned. Using considerably higher temperatures and a four fold excess of Grignard reagent they obtained ethyl- and benzylferrocene in 59% and 27% yield respectively.

Unfortunately however, when the mixture of aminoferrocenes was chromatographed and several fractions taken, each fraction had "9,10" bands in the infrared. As we could not be absolutely certain that the first fraction to elute from the column was predominantly the 1,2 isomer, any conversion to the corresponding ethyl- methoxyferrocene would be worthless.

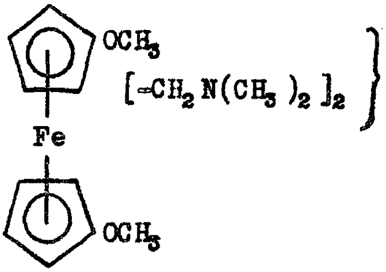
On the other hand, comparisons of the infrared spectra of the ethyl- and methyl- methoxyferrocenes proved more successful. The infrared spectrum (See Table No.14 page 121) of the supposed 1-methoxy- 2 -methylferrocene was very similar to that of 1-methoxy-2-ethylferrocene. These compounds have absorptions at 704 cm.$^{-1}$ and 697 cm.$^{-1}$ respectively, while none of the four remaining isomers absorb near this region. In fact, an excellent correlation between the corresponding isomer of each series, is obtained in the region below 1000 cm.$^{-1}$ The structural assignments made to the methyl- methoxyferrocenes from elution order data, are thus substantiated.

Aminomethylation of 1,1'-Dimethoxyferrocene.

From the aminomethylation of 1,1'-dimethoxyferrocene, two products were isolated. The major product analysed for a di-(dimethylaminomethyl) derivative (LXXXI) of 1,1'-dimethoxyferrocene, and was presumably a mixture of isomers. The other product (LXXX), was probably a mixture of the two isomeric dimethylaminomethyl-dimethoxyferrocenes, but too little was obtained for further investigation.



LXXX



LXXXI

Some Directive Effects Present in Substituted Ferrocenes.

The following two tables summarise the results from previous studies in this field, all site reactivities having been corrected for statistical factors.[168]

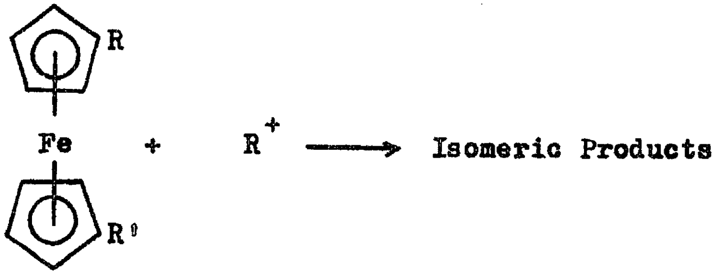


Table No. 1.

Site reactivities for electron withdrawing (deactivating) groups.

	Directing Groups	Reagent	Site Reactivities 2	3	1'	*p*	Ref.
1	$R=COCH_3$; $R'=H$	$ClCOCH_3+AlCl_3$	1.00	-	24	-	31, 169
2	$R=C_6H_5$; $R'=H$	"	1.64	1.00	2.13	0.49	160
3	$R=p\text{-}CH_3OC_6H_4$; $R'=H$	"	1.94	1.00	1.68	-	160
4	$R=R'=C_6H_5$	"	1.65	1.00	-	0.50	160
5	$R=R'=p\text{-}CH_3OC_6H_4$	"	1.95	1.00	-	-	160
6	$R=R'=p\text{-}BrC_6H_4$	"	1.11	1.00	-	-	160
7	$R=Br$; $R'=H$	$Ac_2O+H_3PO_4$	-	-	Ex.[a]	-	152
8	$R=C_6H_5$; $R'=H$	$CH_2[N(CH_3)_2]_2+H^+$	-	-	"	-	173
9	$R=C_6H_5$; $R'=H$	$O(CH_2CH_2)_2O.SO_3$	-	-	"	-	173
10	$R=COCH_3$; $R'=H$	"	-	-	"	-	109

[a] The 1,1' product was formed exclusively (Ex.).

Table No. 2.

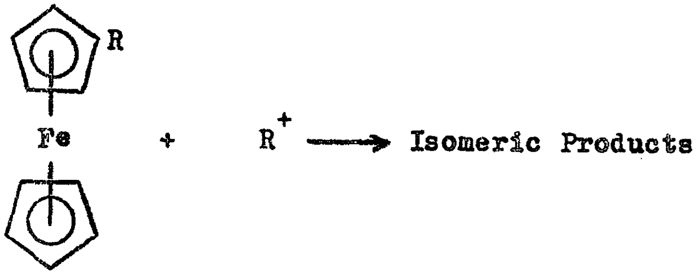
Site reactivities for electron donating (activating) groups.

	Directing Group	Reagent	Site Reactivities 2	3	1'	Ref.
1	$R=CH_2CH_3$; $R'=H$	$ClCO.CH_3 + AlCl_3$	0.33	1.00	0.24	172
2	$R=R'=CH_3$	$Ac_2O + AlCl_3$	0.44	1.00	-	79
3	R=R'=i Pr	"	0.23	1.00	-	79
4	$R=R'=S.CH_3$	$CH_2[N.(CH_3)_2]_2 + H^+$	1.95	1.00	-	142

Numerous other substitution reactions have been carried out, but such complicating factors as inability to separate the products, and polysubstitution, have made the calculation of site reactivities impossible.

The findings from this study are summarised in Table No.3. below, and again site reactivities are corrected for statistical factors.

Table No. 3.



Directing Group R	Reagent	Site Reactivities		
		2	3	1'
$-S.CH_3$	$CH_2[N(CH_3)_2]_2$ [a]	1.41	1.00	0.62
"	" [b]	1.50	1.00	0.57
$-O.CH_3$	$CH_2[N(CH_3)_2]_2$ [a]	1.60	1.00	0.43
"	$Cl.COCH_3 + AlCl_3$ [c]	2.14	1.00	2.70
"	" [d]	0.80	1.00	0.94
"	" [e]	0.73	1.00	0.87
$-Cl$	$Cl.COCH_3 + AlCl_3$	-	-	Ex. [f]

[a] Calculated from isomer weights of reduced amines.

[b] Determined from infrared spectral data of reduced amines.

[c] Calculated from isomer weights of reduced acetyl isomers (Reduction by $LiAlH_4-AlCl_3$).

[d] Calculated from isomer weights of reduced acetyl isomers (Clemmensen reduction).

[e] Determined from infrared spectral data of reduced acetyl isomers (Clemmensen reduction).

[f] 1,1' isomer exclusively.

The results tabulated above, indicate that methylthio and methoxy groups are activating in nature, allowing preferential aminomethylation in the already substituted ring. The predominance of the 1,2 isomer in each case, agrees with molecular orbital calculations of localisation energies by Richards,[175] and Rosenblum and Howells.[160] These calculations predict a higher reactivity for the 2 position in ferrocenes bearing either an electron withdrawing or an electron donating substituent.

In the aminomethylation of 1,1'-di(methylthio)ferrocene,[142] (Table No. 2.), the ratio of the 2 to 3 isomer was found to be 1.95:1. This order of substitution agrees with that obtained from the aminomethylation of methylthioferrocene although the 2:3 isomer ratios do not correspond exactly. It also agrees with the predictions based on the molecular orbital calculations. However, if the methylthio group is electron donating in nature, the site reactivities present in 1,1'-di(methylthio)ferrocene should be similar to those present in 1,1'-dimethylferrocene. As can be seen from the table, this is not so.

Although steric effects are undoubtedly present, they are necessarily less important in the 5-membered cyclopentadienyl ring than in the six-membered benzene ring, and arguments along these lines do not satisfactorily explain the discrepancy between the reactivities of these compounds.

A descriptive resonance treatment,[71] in which the primary covalent iron to ring bond is regarded as being a position variable single bond, also predicts preferential substitution in the 2 position. Contrary to molecular orbital calculations however, this treatment suggests that highly electron attracting groups direct predominantly into the 3 position.

What may be an important factor in certain substitution reactions is the possibility of interaction between the electrophile and the directing group. This interaction has been established as being present in the nitration of anisole[154] and related aromatic ethers, causing preferential ortho nitration. The discrepancy in site reactivities between the aminomethylation of 1,1'-di(methylthio)ferrocene and the acetylation of 1,1'-dimethylferrocene may therefore be explained by the presence of this effect in the former reaction. This interaction between electrophile and directing group might also explain why such vastly different results were obtained from the acetylation and aminomethylation of methoxyferrocene. A further complicating factor however, is the poor reduction yields of isomeric ethyl-methoxyferrocenes obtained. Two different types of reduction gave entirely different results and since the reduction was small (55-60 % in each case) preferential decomposition of any one isomer cannot be discounted. The site reactivities obtained from the acetylation of methoxyferrocene must therefore be unreliable, and further research into this problem would be advantageous.

An obvious answer to the problem would be the determining of isomer ratios from the parent acetyl-methoxyferrocenes, possibly by vapour phase chromatographic methods.

Chloroferrocene was found to be highly deactivated as expected, giving exclusively the 1,1' isomer on acetylation.

EXPERIMENTAL

The majority of reactions described in the following experimental were conducted under nitrogen which had been deoxygenated and dried by passing it through Fieser's solution and then concentrated sulphuric acid.

Unless otherwise stated, all chromatographies were carried out on Spence's grade H alumina which had been partially deactivated by exposure to the air for 6 hr.

Ferrous chloride was prepared by refluxing anhydrous ferric chloride and chlorobenzene for 2 hr. The mixture was then filtered through a sintered glass funnel and the ferrous chloride washed well with ether.

Melting points are uncorrected and were measured in capillary tubes evacuated to 20 m.m. pressure.

Ligroin refers to petroleum ether, b.p. 60-80°.

Attempted Preparation of 1-Dimethylaminomethylferrocene-1'-sulphonic Acid. - (a) **From Dimethylaminomethylferrocene and Chlorosulphonic Acid.** - To a rapidly stirred solution of dimethylaminomethylferrocene (5.25 g., 0.022 mole) in dry acetic anhydride (30 ml.) under nitrogen, was added from a micro burette over a period of 10 min., technical chlorosulphonic acid (2.5 g., 0.022 mole). An immediate darkening in colour accompanied the addition. After being left 24 hr. at room temperature, the reaction mixture was filtered with care into ice-cold water (75 ml.). Basification with 5N sodium hydroxide solution followed by ether extraction to remove starting material, yielded no extract. Similar extraction under neutral and acid conditions also gave negative results. Further attempts to isolate the required product, including evaporation to dryness of the original filtrate before basification, proved futile.

(b) **From Dimethylaminomethylferrocene and Dioxan-Sulphur Trioxide.** - A suspension of dioxan-sulphur trioxide (4.2 g., 0.025 mole) [prepared by distillation of sulphur trioxide (2 g.) from 65% oleum into a stirred solution of dry dioxan (2.2 g.) in dry dichloroethylene (25 ml.) under nitrogen at 0°] was added gradually to a stirred solution of dimethylaminomethylferrocene (5.25 g., 0.0216 mole) in dry dichloroethylene (20 ml.) under nitrogen at 0°. After 0.5 hr. at 0-15° and a further 1.5 hr.

at room temperature, the solvent was evaporated under reduced pressure at room temperature to prevent excessive decomposition. Unsuccessful attempts were made to isolate the lead, barium and S-benzyl-thiouronium salts of the required product.

Further sulphonations with dioxan-sulphur trioxide on (ferrocenylmethyl)trimethylammonium iodide were equally unsuccessful.

Attempted Preparation of 1-Dimethylaminomethyl-1'-chloromethylferrocene. - Anhydrous stannic chloride (2.0 g., 0.0077 mole) was added over a period of 20 min. to a stirred solution of dimethylaminomethylferrocene (4.80 g., 0.0198 mole) and chlorodimethylether (3.2 g., 0.04 mole) in dry carbon disulphide (35 ml.) under nitrogen at 0°. After a further 15 min., ice-water (100 ml.) was added and the yellow precipitate which separated out was filtered off. The organic layer was removed and evaporated to dryness to yield a solid residue, which, together with the previous precipitate, was extracted with ligroin. Evaporation afforded the yellow crystalline di-(ferrocenylmethyl-) ether (0.90 g.), m.p. 127°, which was recrystallised from ligroin to constant m.p. 132° (Lit.,[144] m.p. 132-134°) (Found: C,63.9; H,5.4. Calc. for $C_{22}H_{22}Fe_2O$. C,63.8; H,5.4%). The melting point was undepressed on admixture with an authentic sample, and the infrared spectra corresponded exactly.

In an experiment, identical to the one described above, employing the same reactants under the same conditions, the only product identified was ferrocenylmethanol (0.4157 g.) which crystallised from ligroin, in yellow needles, m.p. 79° (Lit.,[148] m.p. 81-82°). The infrared spectra of this material and of an authentic sample were identical, and the mixed melting point was undepressed.

Attempted chloromethylation of (ferrocenylmethyl) trimethylammonium iodide in acetic acid as solvent, only resulted in isolation of starting material.

1-Chlorocarbonylferrocene-1'-sulphonyl chloride and 1-Carboxyferrocene-1'-sulphonyl chloride. - Phosphorus pentachloride (8 g., 38.3 mmole) in dry chloroform (50 ml.), was added to a stirred suspension of 1-carboxyferrocene-1'-sulphonic acid (3.5 g., 11.3 mmole) in chloroform (100 ml.) maintained under a nitrogen atmosphere at 40-50°. The phosphorus pentachloride was added in several equal portions after similar intervals of time, and as the reaction progressed, dissolution of the acid chlorides was observed. After 4 hr., the reaction mixture was filtered, the filtrate washed several times with water and then dried over calcium chloride. Evaporation of the chloroform using a rotary evaporator with the minimum of heating, afforded a reddish crystalline residue (2 g.) which was triturated with warm ligroin and filtered. After removal of excess solvent as before, cherry-red crystals (1.03 g.; 27%) of the di-acid chloride, m.p. 103° (Lit.[108] m.p. 103-104°) were obtained on cooling. The ligroin insoluble brown crystalline mass from the trituration, crystallised from methanol in brown plates. This material decomposed without melting at 137°, (Found: C, 40.6; H, 3.0; S, 9.5; Cl, 10.9. $C_{11}H_9FeSO_4Cl$ requires C, 40.2; H, 2.8; S, 9.8; Cl, 10.8%) and infrared spectral comparisons between the di-acid chloride and other related compounds (See table No.11 p.118) indicated that this compound was <u>1-carboxyferrocene-1'-sulphonyl chloride</u>.

<u>1-Chlorocarbonylferrocene-1'-sulphonyl chloride from 1-Carboxyferrocene-1'-sulphonyl chloride.</u> - A large excess of phosphorus pentachloride (2 g.; 9.6 mmole) in chloroform (30 ml.) was added to the stirred 1-carboxyferrocene-1'-sulphonyl chloride (0.176 g.; 0.54 mmole) in chloroform (70 ml.) under nitrogen, and kept at 40-50° for 4 hr. The reaction mixture was worked up as before to yield the red crystalline 1-chlorocarbonylferroceno-1'-sulphonyl chloride (0.076 g.; 41%) m.p. 103-104° as the only product.

<u>Di-(1'-methylferrocenyl)disulphide.</u> - To a stirred suspension of lithium aluminium hydride (0.355 g., 8.8 mmole) in anhydrous ether (45 ml.) under nitrogen, 1-chlorocarbonylferrocene-1'-sulphonyl chloride (0.37 g., 1.1 mmole) in ether

(35 ml.) was added over a period of 10 min. After refluxing for 18 hr., the excess lithium aluminium hydride was destroyed by dropwise addition of ethyl acetate followed by wet ether, and 4N sulphuric acid (5 ml.). The ether layer was separated and evaporated under reduced pressure to yield an obnoxious smelling brown residue, which was dissolved in ethanol (10 ml.), water (25 ml.) and ammonia (10 ml., d,0.88). A stream of air was passed through the solution overnight and the disulphide which had separated out, was extracted with benzene. Removal of the washed and dried ($CaCl_2$) solvent under reduced pressure, gave a yellow solid which was chromatographed in ligroin to yield one main band and three others in trace amounts.

The main band, di-(1'-methylferrocenyl)disulphide (0.1312 g., 53%) crystallised from ligroin in golden brown needles, m.p. 101.5-102.5° (Found: C,57.0; H,4.5; S,13.7. $C_{22}H_{22}Fe_2S_2$ requires C,57.2; H,4.8; S,13.9%).

Aminomethylation of Methylthioferrocene. - Employing the conditions established by Knox[139], methylthioferrocene and 100% excess methylene bis-dimethylamine in glacial acetic acid, were stirred at 100° under nitrogen for 24 hr. The results from two such aminomethylations, together with the results from two carried out by Knox, are summarised below.

Table No.4.

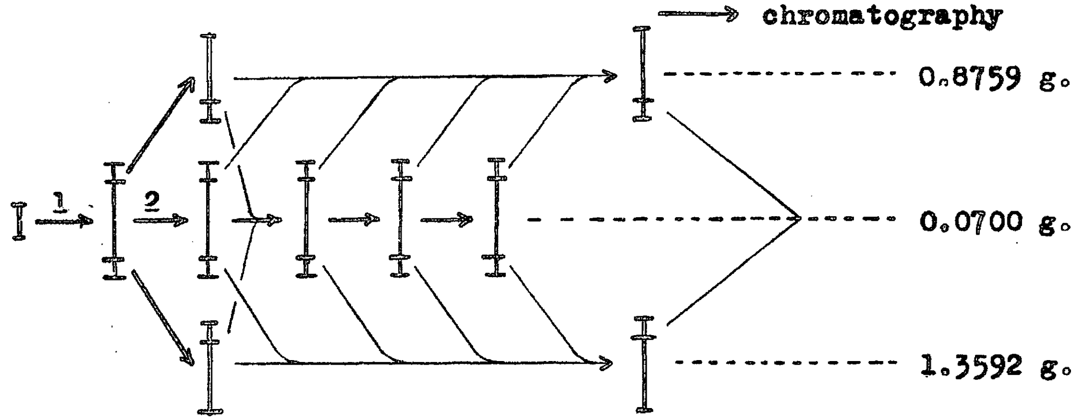
a	Recovered Fc.SCH_3 %	Yields % b	c	Isomer Weights g. 1,2	1,1'+1,3	Isomer Ratio 1,1' + 1,3/1,2
1[d]	28	54.8	76.5	1.455	2.504	1.72
2[d,e]	18	74.5	91.0	1.997	3.394	1.70
3	28.6	54.2	76.0	1.509	2.415	1.61
4[e]	8.7	79.0	87.0	5.262	9.507	1.81

[a] All runs carried out on 5.8 g. methylthioferrocene except No.4, where 15 g. was used. [b] Conversion yield. [c] Yield based on unrecovered methylthioferrocene. [d] Runs carried out by Knox. [e] Catalytic amounts of 85% phosphoric acid used; 0.05 g. for No.2 and 0.15 g. for No.4.

(3-Methylthioferrocenylmethyl)trimethylammonium Iodide and (1'-Methylthioferrocenylmethyl)trimethylammonium Iodide. - A mixture (from run No. 4) of 1-methylthio-1'-dimethylaminomethylferrocene and 1-methylthio-3-dimethylaminomethylferrocene (0.6 g.) was chromatographed in a column (23" x 0.8") in a benzene-ether mixture (49:1). From the resulting diffuse yellow band, eight approximately equal fractions were collected, and an infrared spectrum between 8.5 μ and 11.5 μ, was obtained for each. The first fraction showed large bands at 9μ and 10μ and was therefore mainly 1-methylthio-3-dimethylaminomethylferrocene, while the last fraction only had minute bands at 9μ and 10µ and was thus predominantly 1-methylthio-1'-dimethylaminomethylferrocene. Dropwise addition over a period of 10 min., of methyl iodide in benzene, to a solution of the amines in benzene, followed by refrigeration of the mixtures for 1 hr. at 8°, afforded the yellow solid methiodides. Filtration and successive crystallisations from acetone furnished (3-methylthioferrocenylmethyl)trimethylammonium iodide, m.p. 178° (Found: N, 3.0. $C_{15}H_{22}FeINS$ requires N, 3.2%), and (1'-methylthioferrocenylmethyl)trimethylammoniun iodide, m.p. 154.5-5° (Found: N, 3.0. $C_{15}H_{22}FeINS$ requires N, 3.2%).

1-Methylthio-1'-methylferrocene and 1-Methylthio-3-methylferrocene. - A mixture (from run No. 4) of 1-methylthio-1'-dimethylaminomethylferrocene and 1-methyl-3-dimethylaminomethylferrocene (3.00 g., 10.4 mmole) in dry benzene (60 ml.) was quaternised by portionwise addition of methyl iodide (1.841 g., 13.0 mmole) in dry benzene (10 ml.). The solution was shaken vigorously after each addition and then the mixture was refrigerated for 2 hr. after the final addition. The mixture of methiodides (4.473 g., 10.4 mmole) which separated out as an oil, was dissolved in water (110 ml.) and added, with cooling in an ice-bath, to freshly crushed sodium amalgam (655 g., 6.8%) made from sodium (45 g.) and mercury (45 ml.). Benzene (50 ml.) was added and the reaction mixture heated for 3 hr. on a steam bath. During this time the benzene extracted the reduced product as it formed, and evolution of trimethylamine was observed. When cool, the benzene extract was washed, dried ($CaCl_2$) and evaporated to yield a brown oil which, when chromatographed in ligroin afforded an unresolvable diffuse yellow band (2.420 g., 95%).

Infrared spectra of several fractions of this band, showed that two compounds were present, and the following chromatographic scheme, incorporating infrared spectroscopy, was used. Chromatograms 1 and 2 were carried out in a column 41" x 0.8" while the remainder only required a column 23" x 0.8". A total of nine chromatographies were thus required to achieve separation of the isomers.



The first isomer to elute had no bands at 9µ and 10µ and was therefore 1-methylthio-1'-methylferrocene. (Found C, 58.5; H, 5.8. $C_{12}H_{14}FeS$ requires C, 58.6; H, 5.7%). The other compound must then be 1-methylthio-3-methylferrocene, (Found: C, 58.7; H, 6.0. $C_{12}H_{14}FeS$ requires C, 58.6; H, 5.7%)

Both analyses samples were deep orange-red oils purified by distillation at 0.02 mm.

N.B Vapour phase chromatography failed to resolve the mixture of isomers.

Determination of Isomer Ratios. - The infrared spectrum of the middle fraction (0.070 g.) had medium size '9,10' bands and was assumed to contain approximately equal amounts of each isomer.

Weight of 1,1' isomer = 1.3593 + 0.0350 = 1.3628 g.

and Weight of 1,3 isomer = 0.8757 + 0.0350 = 0.8792 g.

1,1' Isomer : 1,3 isomer = 1.3628 : 0.8792 = 1.55 : 1.

Since the aminomethylation of methylthioferrocene (run No.4) provided 9.507 g. of the 1,1' + 1,3 isomers and 5.262 g. of the 1,2 isomer

$$1,1' + 1,3 : 1,2 = 9.507 : 5.262 = 1.81 : 1$$

$$1,2 \equiv 35.6\%$$

and

$$1,1' + 1,3 \equiv 64.4\%$$

$$1,1' \equiv \frac{1.55}{2.55} \times 64.4 \equiv 39.2\%$$

$$1,3 \equiv \frac{1}{2.55} \times 64.4 \equiv 25.2\%$$

The complete isomer ratios are shown in the table on p. 79.

Determination of the Isomer Ratios from the Aminomethylation of Methylthioferrocene, by means of Infrared Spectroscopy.

Methylthioferrocene (5.80 g., 25 mmole) was aminomethylated (run No.3) under the conditions employed before,[≋] and the products isolated were

(i) 1-methylthio-2-dimethylaminomethylferrocene (1.510 g.)

(ii) 1-methylthio-1'-dimethylaminomethylferrocene and
 1-methylthio-3-dimethylaminomethylferrocene (2.415 g.)

The total yield was 3.925 g. (76%) and the isomer ratio of 1,1' + 1,3 : 1,2 = 1.61 : 1

Infrared spectra of the pure 1,2 isomer and of the 1,1' + 1,3 mixture of isomers were obtained in carbon tetrachloride solution, and standardisation of the spectra was effected by comparison of the areas under the aromatic C-H stretching frequency band at 3086 cm.$^{-1}$ A further comparison of the areas under the band at 1105 cm.$^{-1}$ ('9' band) gave an estimate of the amount of 1,3 isomer present in the mixture and hence the complete isomer ratio was calculated. The base-line for calculation of the areas was taken as the average of the background absorption of the spectra.

[≋] No phosphoric acid was employed as catalyst, otherwise conditions were identical to those already described. Phosphoric acid, while not altering the ratio of isomers formed, increases the overall yield from 77% to 91%.

	1,2 isomer	1,1' + 1,3 isomers	$\frac{1,1' + 1,3}{1,2}$
Area under band at 3086 cm.$^{-1}$	148	165	1.11 (correction factor)
Area under band at 1105 cm.$^{-1}$	302	142	

Corrected area for 1,2 isomer = 302 x 1.11 = 336

1,2 : 1,1' + 1,3 = 336 : 142 = 1 : 0.422

i.e. 42.2% of the mixture of 1,1' + 1,3 isomers is the 1,3 isomer.

Now, since 1,1' + 1,3 : 1,2 = 1.61 See above (weight ratio)

The 1,2 isomer ≡ 38.3% of total aminomethylated product.

∴ 1,3 isomer ≡ 61.7 x 0.422 = 25.5%

and 1,1' isomer ≡ 61.7 - 25.5 = 36.2%

Table No.5.

	Dimethylaminomethyl - Methylthioferrocenes					
	1,2		1,3		1,1'	
	a	b	a	b	a	b
%	35.6	38.3	25.2	25.5	39.2	36.2
Isomer Ratio	1.41	1.50	1.00	1.00	1.55	1.42
Weighted Ratio	1.41	1.50	1.00	1.00	0.62	0.57

a As calculated from isomer weights of reduced amines.

b Determined from infrared spectral data of reduced amines.

Competititve Aminomethylation Between Methylthioferrocene and Ferrocene. - Ferrocene (0.789 g., 4.24 mmole), methylthioferrocene (0.984 g., 4.24 mmole), methylene bis-dimethylamine (0.432 g., 4.24 mmole) and a catalytic amount of 85% phosphoric acid in glacial acetic acid (30 ml.) were stirred at 100° under nitrogen for 24 hr. The solvent was then distilled off, water (35 ml.) added, and the solution basified at 0° to pH10 with 10N sodium hydroxide solution. Continuous ether extraction for 30 hr. afforded after drying (KOH pellets) and evaporation, a semi-solid residue (1.6876 g.). Chromatography yielded,

(i) ferrocene (0.4970 g., 63%) m.p. 171° and

(ii) methylthioferrocene (0.702 g., 71.3%) eluted with ligroin.

(iii) 1-methylthio-2-dimethylaminomethylferrocene (0.050 g., 4.1%) m.p. 81° eluted with a benzene-ether mixture (19:1),

(iv) a diffuse yellow band (0.324 g.) eluted with a benzene-ether mixture (9:1).

Rechromatography of the last band failed to produce any further resolution and thus the experiment failed in its direct objective. Assuming however, that no serious decomposition occurred, the recovery figures for ferrocene and methylthioferrocene show that ferrocene (0.292 g.; 1.57 mmole) and methylthioferrocene (0.282 g.; 1.21 mmole) reacted.

Since ferrocene has ten available places for substitution compared to methylthioferrocene's nine, the statistical value for the reactivity of methylthioferrocene is 0.86, taking ferrocene as unity.

Reaction of Methylthioferrocene with Aluminium Halides. - (a) To a stirred suspension of aluminium trichloride (0.40 g., 3 mmole) in dry methylene chloride (35 ml.) under a nitrogen atmosphere, was added methylthioferrocene (0.41 g., 1.70 mmole) in methylene chloride (10 ml.). After refluxing for 6 hr., decomposition of the reaction mass was achieved by addition of ice (5 g.), concentrated hydrochloric acid (2 ml.) and titanous chloride solution. The chloroform extract was washed with water, dried ($CaCl_2$) and evaporated under reduced pressure to give a residue which on chromatography in ligroin yielded a brown oil (0.065 g.). Comparisons of the infrared spectra of this oil and of methylthioferrocene in carbon disulphide solutions, showed them to be different but no serious attempt was made to elucidate the structure of this oil. It showed absorption in the infrared at 758 $cm.^{-1}$ which could be attributed to a carbon-chlorine bond. All attempts to crystallise this oil failed, and no disulphide was obtained.

Further demethylations were attempted using:

(i) aluminium bromide in methylene chloride under nitrogen,
(ii) aluminium chloride in methylene chloride in air,
(iii) aluminium chloride in carbon disulphide under nitrogen,
(iv) aluminium chloride in carbon disulphide in air,
but no diferrocenyl disulphide was obtained, even when the reflux times were varied. Traces of ferrocene however, were isolated in each case.

(b) To a stirred solution of methylthioferrocene (1.00 g., 4.3 mmole) in methylene chloride (15 ml.) under nitrogen, was added excess freshly ground aluminium trichloride. After 2hr., the excess aluminium trichloride was decomposed with ice-water and titanous chloride solution. The organic layer was separated, washed, dried ($CaCl_2$) and evaporated to yield a dark brown residue which was chromatographed in ligroin. Ferrocene (0.2392 g., 30%), m.p. 173-175° was quickly eluted from the column, followed by methylthioferrocene (0.2440g., 24.4%) and two isomeric di(methylthio)- ferrocenes. These last two compounds were identified by means of their infrared spectra which were very similar to the spectrum of methylthioferrocene. (See Table No.16. page 123). Less than 0.040 g. of each compound was isolated.

Ferrocenylthiocyanate. - (a) A mixture of methylthioferrocene (0.227 g., 0.98 mmole) and cyanogen bromide (2 g., 18.9 mmole) under nitrogen was heated for 3 hr. at 60-70° and left a further 4 hr. at room temperature. After the excess cyanogen bromide had been removed by repeated addition of ether and evaporation under reduced pressure, the reaction mixture was extracted with warm dry benzene and warm dry ether. To the residue, from the evaporation of the combined extracts was added dry ether (10 ml.) which in turn was evaporated to remove the last traces of cyanogen bromide. Initial chromatography in benzene followed by rechromatography in a ligroin- benzene mixture (1:1) yielded ferrocenylthiocyanate (0.157 g., 66%), which crystallised from ligroin in yellow feathery leaflets m.p. 104°: $\nu_{max.}$ (in CCl_4 solution) 2169 cm.$^{-1}$ ($C\equiv N$) (Found: C, 54.7; H, 4.05; N, 5.95; S, 12.7. $C_{11}H_{12}FeNS$ requires C, 54.3; H, 3.7; N, 5.8; S, 13.2%).

(b) Diferrocenylmercury (0.78 g., 1.36 mmole) was triturated in an evaporating basin with a methanolic solution of thiocyanogen, prepared by extracting with methanol, an equimolar mixture of cupric sulphate and potassium thiocyanate which had been ground together in a mortar. The filtered alcoholic solution of thiocyanogen was added in small amounts until an excess was present, then the reaction mass was heated for 20 min. Filtration of the green reaction mixture afforded (a), a filtrate which was diluted with an equal volume of water and (b), a green residue which was dissolved in 50% aqueous methanol (200 ml.). A hydrochloric acid solution of stannous chloride was added to each solution which was then filtered and ether extracted (x 3). The combined extracts were washed carefully with water, dried ($CaCl_2$) and evaporated. Chromatography of the residue in ligroin yielded ferrocene (0.346 g.) m.p. 172°, ferrocenylthiocyanate (0.141 g., 23%) eluted by a ligroin-benzene mixture (3:2) and two other unidentified compounds present only in trace amounts. The ferrocenylthiocyanate recrystallised from ligroin in yellow leaflets m.p. 104° and the melting point was undepressed on admixture with an authentic sample. The infrared spectrum was also identical in every respect to that of the ferrocenylthiocyanate previously prepared.

Ferrocene (0.346 g.) and ferrocenylthiocyanate (0.141 g. account for 68% and 21% respectively of the diferrocenylmercury employed in the reaction.

<u>Attempted Preparation of Diferrocenyl Disulphide.</u> - A saturated solution of sodium thiosulphate (40 ml.) was added to ferrocenylthiocyanate (0.040 g., 0.164 mmole) in methanol (30 ml.) at room temperature and left for 2.5 hr. After

dilution with water (40 ml.), the reaction mixture was extracted with ligroin which was carefully washed, dried ($CaCl_2$) and evaporated <u>in vacuo</u>. Chromatography yielded a yellow band eluted with a ligroin-benzene mixture (1:1), and removal of solvent gave a residue (0.036 g.) which crystallised from ligroin in yellow leaflets m.p. 103°. The infrared spectrum was identical with that of the starting material.

<u>Diferrocenyl Disulphide.</u> - 2N Sodium hydroxide solution (30 ml.) was added to a stirred solution of ferrocenyl-thiocyanate (0.030 g., 0.123 mmole) in methanol (20 ml.) under nitrogen, and the mixture was refluxed for 4 hr. in an oil bath at 90°. The cooled reaction mixture was extracted with ether, and the extract was dried ($CaCl_2$) and evaporated to afford a solid residue. This was chromatographed on alumina yielding a single yellow band eluted with a ligroin-benzene mixture (1:1). Evaporation of the solvent gave a residue (0.025 g., 92%) which crystallised from ligroin in golden yellow plates, m.p. 192° (Lit.[106] m.p. 192°). There was no depression of the melting point on admixture with an authentic sample of diferrocenyl disulphide, and the infrared spectra corresponded exactly.

<u>1-Thiocyanato-1'-methylferrocene.</u> - 1-Methylthio-1'-methylferrocene (0.205 g., 0.83 mmole) and cyanogen bromide

(2 g., 18.9 mmole), were fused together at 70-75° under nitrogen for 2.5 hr. and left standing a further 2 hr. at room temperature. Excess cyanogen bromide was removed by co-distillation with ether as before, and the reaction mixture extracted with warm dry benzene and warm dry ether. Evaporation of the combined extracts furnished a residue which was treated with dry ether (10 ml.) and distilled under reduced pressure to remove any remaining cyanogen bromide. Chromatography in benzene gave a brown oil (0.117 g.) which was rechromatographed in petrol and eluted with a ligroin-benzene mixture (3:2). Removal of solvent afforded a brown oil (0.074 g.; 35%), $\nu_{max.}$ (in CCl_4 solution) 2179 cm.$^{-1}$ ($C\equiv N$). No. '9,10' bands were present in the infrared. This is therefore the required 1-thiocyanato-1'-methylferrocene which distilled readily at 0.02 mm. to give a golden brown oil. (Found: C, 56.3; H, 4.4; N, 5.8. $C_{12}H_{11}FeNS$ requires C, 56.05; H, 4.3; N, 5.45%).

Di-(1'-methylferrocenyl)disulphide. - To a stirred solution of 1-thiocyanato-1'-methylferrocene (0.069 g., 0.268 mmole) in methanol (20 ml.) under nitrogen, was added 2N sodium hydroxide solution (30 ml.). After refluxing for 4.5 hr. in an oil bath at 90°, the mixture was cooled, extracted with ether which was dried ($CaCl_2$) and evaporated under reduced pressure. Chromatography in ligroin of the solid residue obtained, yielded a trace amount of a yellow compound (probably starting material) followed by the main yellow band. Removal of solvent and crystallisation of the residue (0.060 g., 97%) from ligroin produced golden yellow plates, m.p. 101-102°. This material proved to be identical to the synthesised sample previously described, as:-

(i) the melting points were the same,

(ii) there was no depression of the melting point on admixture with the unambiguously synthesised sample,

(iii) the infrared spectra were identical in both carbon disulphide and carbon tetrachloride.

(2-Methylthioferrocenylmethyl)trimethylammonium Iodide. - To a solution of 1-methylthio-2-dimethylaminomethylferrocene (2.00 g., 6.91 mmole) indry benzene (50 ml.) methyl iodide (1.23 g., 8.64 mmole) in dry benzene (10 ml.) was added portionwise over a period of 15 min. After each addition, the solution was shaken vigorously until the methiodide began to crystallise out, and when the final addition was completed, the solution was cooled to about 8° for 3 hr. to ensure complete quaternisation. Filtration and recrystallisation of the precipitate from acetone afforded yellow rectangular prisms, m.p. 182-183°, of (2-methylthioferrocenylmethyl)trimethylammonium iodide, (Found: C, 41.2;

H, 5.0; I, 29.2; N, 3.0; S, 6.8. $C_{15}H_{22}FeINS$ requires C, 41.8; H, 5.1; I, 29.4; N, 3.2; S, 7.4%).

On one occasion, the methiodide appeared to soften or melt at 157°, recrystallise, and remelt at 183°.

1-Methylthio-2-methylferrocene. - To powdered sodium amalgam (438 g.) made from sodium (30 g.) and mercury (30 ml.) was added with cooling in an ice bath, a solution of the above methiodide (2.982 g., 6.91 mmole) in water (80 ml.). The reaction mixture was then heated for 2 hr. on a steam bath, and after cooling, the oil which had separated out was extracted with benzene. Evaporation of the dried ($CaCl_2$) extract gave a residue (1.685 g.) which was chromatographed in ligroin to yield 1-methylthio-2-methylferrocene, as a brown oil (1.630 g., 96%). Distillation at 0.02 mm. furnished an orange-red oil (Found: C, 58.9; H, 5.8; S, 12.4. $C_{12}H_{14}FeS$ requires C, 58.6; H, 5.7; S, 13.0%).

1-Thiocyanato-2-methylferrocene. - 1-Methylthio-2-methylferrocene (0.209 g., 0.85 mmole) was treated with cyanogen bromide (2 g., 18.9 mmole) as previously described, furnishing after extraction, a residue (0.110 g.) of 1-thiocyanato-2-methylferrocene. Chromatography in a ligroin-benzene mixture (2:1) afforded a yellow solid (0.081 g., 39%), which crystallised from ligroin in plates, m.p. 79°; $\nu_{max.}$ (in CCl_4 solution) 2169 cm.$^{-1}$ ($C{\equiv}N$). (Found: C,55.9; H,3.9; N,5.25. $C_{12}H_{11}FeNS$ requires C,56.05; H,4.3; N,5.45%).

Di-(2-methylferrocenyl)disulphide. - (a) 1-Thiocyanato-2-methylferrocene [prepared by fusing 1-methylthio-2-methylferrocene (0.700 g., 2.85 mmole) and freshly made cyanogen bromide (6 g., 56.7 mmole) at 75° for 2 hr. under nitrogen] in a ligroin-benzene mixture (2:1), was absorbed on an alumina column and left standing overnight. When elution was continued after 16 hr., two bands were resolved, the first being di-(2-methylferrocenyl)disulphide (0.453 g., 69%), crystallising from ligroin in brown leaflets, m.p. 151-153°. The disulphide was further purified by sublimation at 140°/0.02 mm. (Found: C,57.2; H,4.9. $C_{22}H_{22}Fe_2S_2$ requires C,57.2; H,4.8%). The second band, 1-thiocyanato-2-methylferrocene (0.050 g., 8.5%) m.p. 77-79°, eluted with a ligroin-benzene mixture (1:1).

(b) 1-Thiocyanato-2-methylferrocene (0.040 g., 0.156 mmole) in methanol (10 ml.) was refluxed with 2N sodium hydroxide (15 ml.) for 4 hr. and the reaction mixture worked up as before to yield a brown residue (0.030 g.). This was chromatographed in a ligroin-benzene mixture (5:2) to give the required disulphide (0.024 g., 67%), m.p. 149-151°.

1-Thiocyanato-3-methylferrocene. - Cyanogen bromide (3 g., 28.4 mmole) and 1-methylthio-3-methylferrocene (0.380 g., 1.54 mmole) were fused together at 70° for 1 hr. under a nitrogen atmosphere. The reaction and work up were executed as before taking care to remove any residual cyanogen bromide. Chromatography of the extract in a ligroin-benzene mixture (7:3) afforded 1-thiocyanato-3-methylferrocene, a golden brown oil (0.124 g., 43%); $\nu_{max.}$ (in CCl_4 solution) 2188 cm.$^{-1}$ ($C\equiv N$), which distilled at 0.02 mm. (Found: C, 56.4; H, 4.2; N, 5.6. $C_{12}H_{11}FeNS$ requires C, 56.05; H, 4.3; N, 5.5%). The infrared spectrum also possessed "9,10" bands.

Di-(3-methylferrocenyl)disulphide. - (a) Hydrolysis of 1-thiocyanato-3-methylferrocene (0.114 g., 0.445 mmole) in methanol (20 ml.) was achieved as before by refluxing in 2N sodium hydroxide solution (30 ml.), and after a similar work up, an oil (0.096 g.) was obtained. Chromatography in a ligroin-benzene mixture (4:1) yielded di-(3-methylferrocenyl)disulphide, a viscous brown oil (0.076 g., 74%) (Found: C, 57.6; H, 5.1. $C_{22}H_{22}Fe_2S_2$ requires C, 57.2; H, 4.8%). No $-C\equiv N$ absorption was present in the infrared.

(b) A solution of 1-thiocyanato-3-methylferrocene (0.1650 g., 0.642 mmole) in a ligroin-benzene mixture (4:1) was absorbed on normal active alumina, packed in ligroin in a chromatography colomn (14" x 0.75" I.D.), and left for 2 days. Continued elution with benzene, afforded, on evaporation of the solvent a deep orange oil which was rechromatographed on 6 hr. deactivated alumina in a ligroin-benzene mixture (9:1). The only product obtained was the required disulphide (0.144 g., 97%) which was distilled with difficulty at 0.08 mm. A certain amount of decomposition occurred during the distillation.

N.B. In one experiment employing alumina which had been deactivated for >20 hr., the hydrolysis was noticeably slower.

1-Chloro-1'-acetylferrocene. - To a stirred solution of chloroferrocene (2.0540 g., 9.3 mmole) in dry, methanol free chloroform (20 ml.) under nitrogen at 0°, was added an excess of Perrier complex over a period of 15 min. The complex was prepared by stirring a solution of acetyl chloride (1.42 g., 18.16 mmole) in pure chloroform (30 ml.) with excess freshly ground aluminium trichloride for 2 hr., followed by filtration through a sintered glass funnel. After stirring for 2.5 hr., the reaction mixture was left overnight. Decomposition was achieved by addition of ice and titanous chloride solution. The organic layer was separated, washed, dried ($CaCl_2$) and evaporated affording a residue which was chromatographed in a ligroin-benzene mixture (1:1) to yield:-

(a), a mixture of ferrocene and chloroferrocene (0.7654 g.) eluted by the above solvent, present in the ratio of 3:1 as determined from vapour phase chromatography. Since the vapour phase chromatogram showed no ferrocene in starting material, ferrocene formed in the reaction was 0.75 x 0.7654 g. = 0.574 g. (33%) and chloroferrocene recovered was 0.25 x 0.7654 g. = 0.191 g. (9%); (b), 1-chloro-1'-acetylferrocene (1.2272 g., 57% based on unrecovered chloroferrocene, - 50% conversion) m.p. 53.5-54.5° after crystallising twice from hexane (Found: C, 54.8; H, 4.4; Cl, 13.2. $C_{12}H_{11}FeClO$ requires C, 54.9; H, 4.2; Cl, 13.5%).

V.P.C. showed that no acetylferrocene was present.

In one preparation of 1-chloro-1'-acetylferrocene the crude product before crystallisation had m.p. 55-62° but again vapour phase chromatography showed there was no acetylferrocene present, although its presence would be expected.

Two other bands were present in trace amounts but identification was not attempted.

Attempted Dechlorination of Chloroferrocene. - Through a solution of chloroferrocene (0.272 g., 1.23 mmole) in dry chloroform (10 ml.) under nitrogen, was passed dry hydrogen chloride gas for 20 min. The reaction mixture was left standing overnight then treated with water (15 ml.) and titanous chloride solution (3 drops). The organic layer was separated, washed carefully with water, dried ($CaCl_2$) and evaporated to furnish a residue (0.163 g.) which was chromatographed in ligroin to remove impurities. Vapour phase chromatograms[≡] of the starting material and chromatographed product proved to be identical, both showing small peaks due to ferrocene.

[≡] The column employed was one packed with silicone grease on celite. The conditions used are outlined below.

Inlet pressure 700 mm.
Outlet pressure 195 mm.
Flow rate (N_2) 1.8 l/hr.
Temperature 228°C.

Dechlorination of Chloroferrocene. - To a solution of chloroferrocene (0.1984 g., 0.90 mmole) in dry chloroform (10 ml.) under nitrogen in a 25 ml. two necked flask, fitted with gas inlet tube and calcium chloride outlet tube, was added freshly ground aluminium trichloride (2 g.). Nitrogen was passed through the solution a further 45 min. as it grew progressively greener, then the mixture was decomposed by careful addition of ice, ice-water and titanous chloride solution. The organic layer was separated, washed with water, dried ($CaCl_2$) and evaporated to yield a residue, which when chromatographed on alumina using ligroin, as solvent, afforded a yellow-brown crystalline material (0.100 g.) on removal of the solvent.

Vapour phase chromatograms, (under the condition employed before) of the starting material and chromatographed product showed that :-

(i) The starting material was comprised of chloroferrocene 93%
and ferrocene 7%

(ii) The chromatographed product consisted of chloroferrocene 50%
and ferrocene 50%

Attempted Acetylation of 1,1'-Dichloroferrocene. - A solution of Perrier complex [prepared from acetyl chloride (1.0 g., 12.7 mmole) and excess freshly ground aluminium trichloride in in chloroform (30 ml.)] was added over a period of 10 min. to a stirred solution of 1,1'-dichloroferrocene (0.84 g., 3.3 mmole) in chloroform (20 ml.) under nitrogen at 0°. The mixture was stirred a further 1.5 hr. and left standing overnight. Decomposition of the complex was effected by addition of ice, ice-water and titanous chloride solution, and the organic layer was separated, washed dried ($CaCl_2$) and evaporated. The residue so obtained was chromatographed on alumina and ligroin soon eluted a yellow crystalline solid (0.105 g.), m.p. 55-75° which was presumably a mixture of 1,1'-dichloroferrocene, chloroferrocene and ferrocene. At least three other compounds were eluted from the column, the first of which was a brown oil, possessing C=O absorption in the infrared. This material however, was too unstable to characterise. The last two compounds to elute were only present in trace amounts and thus could not be identified.

Attempted Preparation of 1,1'-Dimethoxyferrocene. - To a stirred suspension of sodium amide in liquid ammonia [made from sodium (9.4 g., 0.4 g.atom) freshly distilled liquid ammonia (250 ml.) and ferric nitrate as catalyst] under nitrogen, was added cyclopentenone (16.4 g., 0.2 mole) over a period of 20 min. After 3 hr., freshly prepared anhydrous ferrous chloride (12.7 g., 0.1 mole) was added in small portions over 0.5 hr. When most of the ammonia had evaporated after a further 2 hr., anhydrous tetrahydrofuran (200 ml.) was added and the reaction mixture left overnight. A solution of sodium hydroxide (5 g.) in water (250 ml.) was added carefully and the mixture stirred for approximately 25 min. The solid material was removed by filtration and the filtrate was treated with dimethylsulphate (25.2 g., 0.2 mole) for 0.5 hr. Extraction with chloroform, which was washed, dried and evaporated, yielded a yellow-brown gummy solid which only dissolved in tetrahydrofuran and glacial acetic acid.

The same preparation was attempted using dispersed sodium in anhydrous T.H.F. with similar results.

1,1'-Dibenzoyloxyferrocene. - The identical preparations given above were carried out using benzoyl chloride (under Schotten-Baumann conditions) in place of dimethylsulphate, but none of the desired products was obtained.

Attempted Preparations of 1,1'-Ferrocenylenediboronic Acid.-

(a) From Disodioferrocene and Boron Trichloride. - To a stirred solution of boron trichloride (100 g., 0.852 mole) in anhydrous petroleum ether (500 ml., 40/60°) under nitrogen at -70°, was added portionwise, a suspension of disodioferrocene [prepared from dispersed sodium (10 g., 0.435 g. atom), chlorobenzene (21 g., 0.188 mole) and ferrocene (18.6 g., 0.10 mole) in benzene (100 ml.)] 15 ml. at a time over a period of 45 min. The reaction mixture was allowed to warm up to room temperature over 1.5 hr., then stirred a further 2 hr. Excess boron trichloride was distilled off under reduced pressure (30 mm.) using a receiving vessel and trap immersed in carbon dioxide-acetone baths, and the reaction mixture was decomposed at -60° by careful addition of methanol (70 ml.) followed by 10% sodium hydroxide solution (200 ml.). Filtration through kieselguhr afforded an alkaline extract, which on acidification at 0° with 10% sulphuric acid together with titanous chloride solution, yielded no precipitate of 1,1'-ferrocenylenediboronic acid.

(b) From Disodioferrocene and Tri-n-butyl Borate. - To a stirred solution of tri-n-butyl borate (196 g., 0.852 mole) in anhydrous ether (400 ml.) under nitrogen at -40°, was added portionwise, a suspension of disodioferrocene (prepared from the quantities of reagents previously mentioned) in 15 ml. aliquots, over a period of 45 minutes. Stirring was continued a further 21 hr. at room temperature, and the reaction mixture decomposed at -40° with methanol (70 ml.), and 10% sodium hydroxide solution (200 ml.). Filtration through kieselguhr furnished an alkaline layer, which when combined with further alkaline extracts and acidified with 10% sulphuric acid solution together with titanous chloride solution, gave no precipitate of diboronic acid.

Ferrocenylboronic Acid and 1,1'-Ferrocenylenediboronic Acid.- To a stirred slurry of ferrocene (37.2 g., 0.2 mole), fine aluminium powder (50 g., 1.85 mole), freshly ground aluminium trichloride (3 g., 0.0225 mole) and methyl iodide (1 ml.) in dry ligroin (350 ml.) under nitrogen at -30°, was added dropwise over a period of 40 min., boron trichloride (100 g., 0.852 mole). The reaction mixture was then stirred a further 4 days at 8° and the remaining boron trichloride distilled off under reduced pressure (20 mm.) with the trap and receiving flask immersed in carbon dioxide-acetone baths. The reaction mass was then suction filtered (caution-fire) through kieselguhr and the aluminium powder washed carefully with dry ligroin.[x] The red coloured filtrate of ferrocene,

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[x] Ether must not be used to wash the aluminium powder as this increases the risk of fire. Solid carbon dioxide was always added to the buchner funnel during the filtration.

ferrocenylboronyl dichloride and 1,1'-ferrocenylenebis(boronyl dichloride) was hydrolysed at 0° by dropwise addition of water, (containing a few drops of titanous chloride), to the stirred solution. After 1 hr., the mixture of boronic acids was filtered off and washed with ligroin until the filtrate was colourless. Evaporation of the filtrate afforded unchanged ferrocene (8.1 g., 22%). The boronic acids were then washed with water to neturality to Congo red paper, and then with ether to remove the ferrocenylboronic acid. Evaporation of the dried ($CaCl_2$) ether extract afforded ferrocenylboronic acid (17.0 g. 37%). The ether insoluble residue after soxhlet extraction, was dried under vacuum over calcium chloride to yield 1,1'-ferrocenylenediboronic acid (2.1 g., 3.9%).

Table No. 6

Numerous runs were carried out under various conditions, and the results are listed below.

	REACTANTS [a]								PRODUCTS	
	FcH Mole	BCl_3 Mole	Al g. atom	$AlCl_3$ mmole	CH_3I ml.	Temp. °C	Time Hr.	FcH Rec. %	$FcB(OH)_2$ %	$Fc[B(OH)_2]_2$ %
1.	0.1	0.38	0.67	3.8	0.5	20 [b]	24	↑	15	-
2.[c]	0.1	0.43	0.89	-	0.5	80	16		-	-
3.	0.05	0.43	0.74	7.5	0.5	70	5	[e]	-	-
4.	0.1	0.43	1.11 [d]	120	0.5	20	3		2	11
5.	0.1	0.43	1.11	224	1.0	10	120	↓	2.5	9.1
6.	0.2	0.85	1.85	15	1.0	8	96	35	22	14.5
7.	0.6	2.56	6.66	30	2.0	11	96	80	7	10
8.	0.2	0.85	1.85	15	1.0	8	96	20	54	2.2
9.[f]	0.2	0.85	1.85	22.5	1.0	8	96	22	37	3.9

[a] The solvent was ligroin in each case. [b] All temperatures except runs 2 and 3 were room temperatures. [c] Reaction carried out in a bomb. Only 4 hr. at 80°. [d] When zinc dust replaced aluminium, only diboronic acid (0.0058 mole., 6%) was isolated. [e] Ferrocene recovered was not weighed. [f] Three experiments using these conditions gave identical results.

<u>Acetylation of Methoxyferrocene</u>. - A solution of Perrier complex [formed by stirring acetyl chloride (1.820 g., 23.2 mmole) with excess freshly ground aluminium trichloride in dry methylene chloride (85 ml.) for 2 hr.] was added dropwise over a period of 40 min. to a stirred solution of methoxyferrocene (4.500 g., 20.8 mmole) in methylene chloride (75 ml.) under nitrogen at 0°. The complex was decomposed with ice, water and titanous chloride solution 5 min. after the final addition, and the organic layer was separated, washed with water, dried ($CaCl_2$) and evaporated to give a brown residue (4.7722 g.). Chromatography in benzene yielded:-

(a) an oily solid (0.7180 g.) eluted by benzene and having no $>C = O$ absorption in the infrared.

(b) acetylferrocene (0.229 g., 4.82%), m.p. 84-85° after sublimation, eluted slowly by benzene.

(c) a deep red oil (2.4795 g., 46.3%) (Found: C,61.4; H,5.8 $C_{13}H_{14}FeO_2$ requires C,60.5; H,5.5%) comprising of the three mono-acetylated methoxyferrocenes, eluted by a benzene-ether mixture (1:1). Yield based on unrecovered starting material was 51.2% .

Rechromatography of (a) in ligroin afforded methoxyferrocene (0.455 g., 10%), and two orange-brown oils (0.104 g.) and (0.155 g.).

When 0.460 g., of (c) was rechromatographed and the band collected in five fractions, the first and last fractions had the largest '9,10' bands. Moreover the first fraction was a low melting solid, 1-methoxy-2-acetylferrocene; $\nu_{max.}$ (liquid film) 1680 cm.$^{-1}$ (C=O), which after being sublimed twice, had m.p. 35-36°.

Reduction of the Isomers of Acetyl-methoxyferrocene.

(a) Lithium aluminium hydride-aluminium trichloride reduction. - A suspension of lithium aluminium hydride (0.500 g., 13.14 mmole) in anhydrous ether (20 ml.) was added carefully with cooling (ice-bath) to a stirred suspension of freshly ground aluminium trichloride (1.75 g., 13.14 mmole) in anhydrous ether (15 ml.) under nitrogen. To this mixture at room temperature, was added dropwise, a solution of the acetylated products of methoxyferrocene (1.70 g., 6.57 mmole) in anhydrous ether (20 ml.). Twenty minutes after the final addition, the reaction mixture was decomposed with ice-water and the ether layer separated, washed with water (x 2), dried ($CaCl_2$) and evaporated to yield a brown oil (1.5125 g.). Chromatography afforded three bands, the first being a brown oil (0.8328 g., 54%) comprising of the ethyl isomers, eluted with ligroin. The second band, also a brown oil (0.2336 g.), eluted with benzene, was followed by another oil (0.0511g.) eluted with ether. Neither of these showed hydroxyl absorption in the infrared.

The first band was rechromatographed in ligroin on a column (44" x 0.75" I.D.) yielding two bands, the first of which was 1-methoxy-2-ethylferrocene (0.1580 g., 10.25%)(Found: C,64.1; H,6.2; O,7.2. $C_{13}H_{16}FeO$ requires C,64.0; H,6.6; O,6.6%). Eleven approximately equal fractions of the second band were collected, and an infrared spectrum of each was obtained in the region 8.5 μ to 11.5 μ, after evaporation of the solvent. The samples were then grouped according to whether or not they had bands at 9 μ and 10 μ, and in this way the chromatography was followed, giving a separation of 1-methoxy-1'-ethylferrocene (0.4996 g., 32.4%) (Found: C,63.6; H,6.5. $C_{13}H_{16}FeO$ requires C,64.0; H,6.6%), and 1-methoxy-3-ethylferrocene (0.0750 g., 4.86%)(Found: C,65.2; H,7.1; O, — . $C_{13}H_{16}FeO$ requires C,64.0; H,6.6; O,6.6%).

Further treatment of band 2 (0.2336 g.) with an excess of the reducing agent, established that this was not a mixture of ethers formed by dehydration of the intermediate alcohols, since only starting material was recovered. The infrared spectrum of this compound however was found to be very similar to the spectra of bands 2 and 3 from the acetylation of methoxyferrocene.

In an effort to improve the reduction yields, further experiments, using various amounts of aluminium trichloride-lithium aluminium hydride complex, were carried out. These are outlined below.

(i) Reduction of acetyl-methoxyferrocenes (0.600 g., 2.32 mmole) with lithium aluminium trichloride (0.088 g., 2.32 mmole) and aluminium trichloride (0.310 g., 2.32 mmole) only resulted in a 54.6% yield of isomeric ethyl-methoxyferrocene.

(ii) A reduction using an excess of lithium aluminium hydride and a catalytic amount of aluminium trichloride resulted in the isolation of a mixture of isomeric alcohols and a trace of the isomeric ethyl- methoxyferrocenes.

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(b) Clemmensen Reduction. - To a solution of the isomeric acetyl-methoxyferrocenes (0.417 g., 1.62 mmole) dissolved in ethanol (20 ml.) was added zinc amalgam [prepared by shaking mossy zinc (7.5 g.) for 5 min. with a dilute hydrochloric acid solution of mercuric chloride (0.75 g.)]. The mixture was brought to reflux and a solution of concentrated hydrochloric acid (4 ml.) in ethanol (5 ml.) added over 10 min. When the mixture had refluxed a further 0.75 hr., the solution was decanted into water (250 ml.) and ether extracted. This extract was washed, dried ($CaCl_2$) and evaporated to furnish an oil which was chromatographed on alumina using ligroin as solvent to yield a mixture of the ethyl-methoxyferrocenes (0.235 g., 60%). Two other oils were obtained in small amounts.

Rechromatography of the ethyl-methoxyferrocenes (0.225 g.) as on p.103, in a column (43" x 0.8") afforded 1-methoxy-2-ethylferrocene (40 mg.), 1-methoxy-1'-ethylferrocene (118 mg.) and 1-methoxy-3-ethylferrocene (50 mg.)

The complete isomer ratios are shown on p.106.

In another Clemmensen reduction of the isomeric acetyl-methoxyferrocenes (0.600 g., 2.33 mmole), 1-methoxy-2-ethylferrocene (52 mg.) and a mixture of the 1,1' and 1,3 isomers (226 mg.) were obtained (total yield 56%). The weights of the 1,1' and 1,3 isomers present were determined from infrared spectral data by the method described on p.78.

	1,2 isomer	1,1' + 1,3 isomer	$\frac{1,1' + 1,3}{1,2}$
Area under band at 3086 cm.$^{-1}$	68	101	1.485 (correction factor)
Area under band at 1003 cm.$^{-1}$	170	81	

Corrected area for 1,2 isomer = 170 x 1.485 = 253

1,2 : 1,1' + 1,3 = 253 : 81 = 1:0.312.

31.2% of the mixture of 1,1' + 1,3 isomers is the 1,3 isomer

1,3 isomer = 31.2 x 226 = 71 mg.

and 1,1' isomer = 226 - 71 = 155 mg.

Isomer Ratios for Acetyl-Methoxyferrocenes

Table No. 7. Results determined from $LiAlH_4$-$AlCl_3$ reduction

	1,2	1,3	1,1'
Weight mg.	158	75	499.6
Isomer ratio	2.14	1.0	6.75
Weighted ratio	2.14	1.0	2.70

Table No. 8. Results determined from Clemmensen Reduction

	1,2		1,3		1,1'	
	a	b	a	b	a	b
Weight mg.	40	52	50	71	118	155
Isomer ratio	0.80	0.73	1.00	1.00	2.36	2.18
Weighted ratio	0.80	0.73	1.00	1.00	0.94	0.87

a. Calculated from isomer weights of reduced acetyl-methoxyferrocenes.

b. Determined from infrared spectral data of reduced acetyl-methoxyferrocenes.

Demethoxylation of Methoxyferrocene.

To a stirred solution of methoxyferrocene (0.50 g., 2.3 mmole) in methylene chloride (10 ml.) under nitrogen, was added freshly ground aluminium trichloride (0.75 g.). After 10 minutes, the excess aluminium trichloride was decomposed with ice-water and titanous chloride solution. The organic layer was separated, washed, dried ($CaCl_2$) and evaporated to yield a residue, which, when chromatographed, afforded ferrocene (0.030 g., 7%) and methoxyferrocene (0.179 g., 36.0%) eluted with ligroin, and two other compounds (0.089 g.) and (0.082 g.) respectively, eluted with benzene. Infrared spectral comparison (Table No.15, page 122) suggested that these compounds were isomeric dimethoxyferrocenes. These infrared spectra were also identical to the spectra of the unidentified oils obtained in the preparation of the acetyl- methoxyferrocenes.

Aminomethylation of Methoxyferrocene. - To a stirred solution of methoxyferrocene (3.50 g., 16.2 mmole) in glacial acetic acid (50 ml.) under nitrogen, was added methylene bis-dimethylamine (2.07 g., 20.3 mmole) and a catalytic amount of 85% phosphoric acid (2 drops). The reaction mixture was stirred 1.5 hr. at room temperature, then heated over a period of 0.5 hr. to 100° and maintained at this temperature for a further 4 hr. Most of the acetic acid was then removed by distillation, water (130 ml.) was added and the solution basified to pH10 with 10N sodium hydroxide solution. Ether extraction gave, after removal of the dried (KOH pellets) solvent, a brown residue (4.160 g.), which was chromatographed on alumina to yield methoxyferrocene (0.142 g., 4.1%) eluted with ligroin, and a brown oil (3.600 g.) which was eluted with a benzene-ether mixture (1:1). This oil, b.p. 150°(bath)/0.02 mm. (Found: C, 61.8; H, 6.8; N, 5.0. $C_{14}H_{19}FeNO$ requires C, 61.6; H, 7.0; N, 5.1%) failed to resolve on rechromatography, but was later shown to consist of the three isomeric mono-aminomethylated methoxyferrocenes. The conversion yield was thus 82%, and the yield based on unrecovered methoxyferrocene was 85%.

A picrate of the mixture, prepared in aqueous ethanol and recrystallised from aqueous acetone, afforded orange-red needles, m.p. 124.5-126° (Found: C, 47.8; H, 4.4; N, 11.2; O, 25.5.

$C_{20}H_{22}FeN_4O_8$ requires C,47.8; H,4.4; N,11.4; O,25.6%). When this picrate was heated in concentrated caustic solution, and then ether extracted, evaporation furnished the free amine. The infrared spectrum of this material was identical to that of the first portion of the main band, and thus the picrate and regenerated amine appeared to consist mainly, if not entirely, of the 1,2 isomer.

Reduction of Aminoethylated Methoxyferrocenes. - To a solution of the aminomethylated products of methoxyferrocene (1.00 g., 3.67 mmole) in dry benzene (50 ml.) was added proportionwise methyl iodide (0.730 g., 5.14 mmole) in dry benzene (10 ml.) over a period of 10 minutes. On each addition the solution was shaken vigorously and after the final addition, the mixture was refrigerated at 8° for 12 hr. The precipitate was filtered off and the filtrate evaporated to dryness giving a combined weight of 1.52 g. (100%) of methiodide.

To freshly ground sodium amalgam (175 g.), made from sodium (12 g.) and mercury (12 ml.), was added with cooling in an ice bath, a solution of the methiodide in water (60 ml.). After addition of benzene (20 ml.) the reaction mixture was heated on a steambath for 3 hr., during which time the evolution of trimethylamine was observed When the reaction mass had cooled, it was extracted with benzene, which after drying ($CaCl_2$) was evaporated to yield a brown oil (0.7872 g.). Chromatography in ligroin yielded the reduced product (0.7605 g., 90.5%) and 0.695 g. of this was rechromatographed in ligroin in a column measuring 44" x 0.75" I.D. Two bands were eluted, the first of which was 1-methoxy-2-methylferrocene (0.2945 g.) (Found: C, 62.8; H, 6.1; $C_{12}H_{14}FeO$ requires C, 62.6; H, 6.1; O, 7.0%).

The second band containing 1-methoxy-1'-methylferrocene and 1-methoxy-3-methylferrocene was collected in ten approximately equal fractions and an infrared spectrum from 8.5 μ.-11.5 μ. obtained for each sample, after evaporation of the solvent. Fractions were then grouped according to whether or not they had bands in 9μ. and 10 μ. Thus 1-methoxy-1'-methylferrocene (0.1983 g.) (Found: C, 62.7; H, 6.6; O, 7.7. $C_{12}H_{14}FeO$ requires C, 62.6; H, 6.1; O, 7.0%) and 1-methoxy-3-methylferrocene (0.1846 g.) (Found: C, —; H, —; O, 7.05. $C_{12}H_{14}FeO$ requires C, 62.6; H, 6.1; O, 7.0%) were obtained. All three isomers were oils, and analyses samples were prepared by distillation at 0.02 mm.

Isomer Ratios for Dimethylaminomethyl-Methoxyferrocenes.

Table No. 9.

	1,2	1,3	1,1'
Weight g.	0.2945	0.1846	0.1983
Isomer ratio	1.60	1.00	1.07
Weighted ratio	1.60	1.00	0.43

Since the reduction was accomplished in >90% yield, it is reasonable to assume that the isomer ratios for the aminomethylated products would not be far removed from that shown on the previous page.

Aminomethylation of 1,1'-Dimethoxyferrocene. - 1,1'-Dimethoxyferrocene (1.30 g., 5.3 mmole), methylene bis-dimethylamine (2.16 g., 21.2 mmole) and a catalytic amount of 85% phosphoric acid in glacial acetic acid (30 ml.) were stirred at 100° for 15 hr. under nitrogen. Most of the acetic acid was distilled off and water (150 ml.) added. The solution was then basified to pH 10 with 10N sodium hydroxide solution and extracted with ether. This extract was dried (KOH pellets) and evaporated to yield an oil (0.856 g.) which was chromatographed on alumina to yield two bands. The first of these bands eluted with ether affording a brown oil (0.146 g.), b.p. 150° (bath)/0.02 m.m. (Found: N, 4.4. $C_{15}H_{21}FeNO_2$ requires N, 4.6%). This oil presumably consists of the 1,1',2 and 1,1',3 isomers and 0.146 g. thus represents a 9.1% conversion yield. An ether-methanol mixture (99:1) eluted the second band which furnished another brown oil (0.687 g.), b.p. 140-145° (bath)/0.02 m.m. (Found: C, 59.9; H, 8.4; N, 7.7. $C_{18}H_{28}FeN_2O_2$ requires C, 60.0; H, 7.8; N, 7.8%). This second compound probably consists of isomeric di-(dimethylaminomethyl)-1,1'-dimethoxyferrocenes, and 0.687 g. represents a 36% conversion yield.

Some Reactions of (Ferrocenylmethyl)trimethylammonium iodide.

(a) With Phenyllithium. - To a stirred solution of phenyllithium prepared under nitrogen from lithium metal (0.28 g., 0.04m) and bromobenzene (2.36 g., 0.015 m.) in dry ether (15 ml.) over a period of 0.75 hr., was added (ferrocenylmethyl)trimethylammonium iodide (2.35 g., 0.006m) followed by ether (20 ml.) and tetrahydrofuran (30 ml.). The solution was then refluxed for 8 hr., during which time evolution of trimethylamine was observed. When the reaction mixture had cooled, methanol (15 ml.) and water (250 ml.) were added. Evaporation of the dried (KOH pellets) ether extract afforded a brown oil which was chromatographed to yield four bands. The first, eluted with ligroin, was diphenyl (0.050 g.) together with a trace amount of some ferrocene derivative (either ferrocene itself or methylferrocene). Purification of the diphenyl was achieved by oxidation of an ether solution of the mixture with a solution of ferric chloride in hydrochloric acid. Removal of the now colourless ether layer furnished pure diphenyl which, after sublimation had m.p. 66-68° (Lit. 69-71°). Benzylferrocene (0.4110 g., 24.5%) m.p. 69-72° (Lit. 70-74°) also eluted with ligroin. Further elution with a benzene-ether mixture (9:1) furnished N,N-dimethyl-β-ferrocenylethylamine (0.076 g., 4.84%) and dimethylaminomethylferrocene (0.194 g., 13.1%) which were characterised as their methiodides.

N.B. The infrared spectra of all these compounds were identical in every respect to those of authentic samples.

In a similar reaction, the same amount of phenyllithium was stirred 2 hr. at room temperature, and 1 hr. at reflux, with (ferrocenylmethyl)trimethylammonium iodide (3.85 g., 0.01m.) in ether (120 ml.) without tetrahydrofuran. Chromatography of the extract in ligroin afforded 9 bands, of which only diphenyl (0.028 g.); benzylferrocene (0.5389 g., 19.6%) m.p. 69-71°; N,N-dimethyl-β-ferrocenylethylamine (0.160 g., 6.2%), and dimethylaminomethylferrocene (0.240 g., 9.9%) were identified.

(b) With Methyllithium. - To a stirred solution of methyllithium prepared under nitrogen from lithium metal (0.28 g., 0.04m.) and methyl iodide (2.14 g., 0.015m.) in dry ether (15 ml.) was added (ferrocenylmethyl) trimethylammonium iodide (3.35 g., 0.0085m.) followed by ether (20 ml.) and tetrahydrofuran (30 ml.). The reaction mixture was refluxed for 16 hr., cooled and extracted with ether after addition of methanol (15 ml.) and water (250 ml.). The dried (KOH pellets) extract was evaporated to give a brown oil which on chromatography in ligroin yielded ethylferrocene (0.490 g., 27%) n_D^{17} 1.6038 (Lit. n_D^{20} 1.6011) eluted by ligroin; N,N-dimethyl-β-ferrocenylethylamine (0.655 g., 29.4%) and dimethaminomethylferrocene (0.197 g., 9.4%) both eluted by a benzene-ether mixture (4:1). All three products were characterised by their infrared spectra which were identical to those of authentic samples.

In another reaction employing methyllithium [prepared from lithium metal (0.28 g., 0.04m.) and methyl iodide (2.14 g., 0.015m.) in dry ether (20 ml.)] and (ferrocenylmethyl) trimethylammonium iodide (3.85 g., 0.01m.), the reactants after addition of tetrahydrofuran (100 ml.), were stirred at 70° for 10 mins. and a further 2 hr. at room temperature. On heating up to 70° the evolution of trimethylamine became more pronounced and the suspension of methiodide dissolved or reacted to give a deep brown coloured solution. After addition of methanol (20 ml.) and ether (250 ml.) the reaction mixture was washed with water to remove unchanged methiodide. Evaporation of the dried (KOH pellets) organic layer furnished a residue which on chromatography in ligroin yielded ethylferrocene (0.7196 g., 26%); N,N-dimethyl-β-ferrocenylethylamine (0.146 g., 5.7%) and dimethylaminomethylferrocene (0.7413 g., 30.5%).

(c) With Phenylmagnesium bromide. - To a stirred solution of phenylmagnesium bromide [prepared under nitrogen from magnesium turnings (0.375 g., 0.0154m.) and bromobenzene (2.36 g., 0.0150m.) in ether (30 ml.)], was added (ferrocenylmethyl)-trimethylammonium iodide (3.85 g., 0.01m.) followed by tetrahydrofuran (100 ml.). Most of the ether was distilled off and the reaction mixture was refluxed for 24 hr. When the reaction mixture had cooled, the excess Grignard reagent was destroyed with methanol (10 ml.) and unchanged methiodide was removed by filtration. The filtrate, diluted with ether (250 ml.), was washed with water to remove the last traces of methiodide, dried ($CaCl_2$) and evaporated to give a brown residue. Chromatography in ligroin afforded a mixture of benzylferrocene and diphenyl which were separated as already described on page111 to yield benzylferrocene (0.260 g., 9.4%), m.p. 68-70° and diphenyl (0.040 g.) m.p. 66-68°. The infrared spectra of both were identical to those of authentic samples.

(d) With Methylmagnesium iodide. - To a stirred solution of methylmagnesium iodide[prepared under nitrogen from magnesium turnings (0.375 g., 0.0154m.) and methyl iodide (2.140 g., 0.0150m.) in ether (25 ml.)] was added (ferrocenylmethyl) trimethylammonium iodide (3.85 g., 0.01m.) followed by tetrahydrofuran (100 ml.). As before, the ether was distilled off and the reaction mixture refluxed for 24 hr. Methanol (10 ml.) was added to destroy the excess Grignard reagent when the reaction had cooled. Filtration removed the unchanged methiodide leaving a colourless filtrate.

APPENDIX

Polarographic Measurements.

Preparation of Supporting Electrolytes. - The supporting electrolyte (i) was prepared by dissolving anhydrous sodium perchlorate[*] (2.4492 g., 0.02 mole) in 0.1M perchloric acid (20 ml.) (made from 71% analar perchloric acid and distilled water) and adding absolute ethanol (80 ml.) When 5 ml. of this solution was mixed with a solution of 0.0080 g. of the ferrocene derivative in absolute ethanol (5 ml.), in the oxidation cell, the overall concentration of the supporting electrolyte was 90% ethanol, 0.1M sodium perchlorate, 0.01M perchloric acid.

Supporting electrolyte (ii)was prepared in a similar manner using 1.0M perchloric acid (20 ml.) to give an overall electrolyte concentration in the oxidation cell of 90% ethanol, 0.1M sodium perchlorate, 0.1M perchloric acid.

Several oxidation potentials are listed below in table No. 10.

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[*] This is best prepared by recrystallising twice from distilled water at 80°, as at this temperature, anhydrous sodium perchlorate crystallises free from chloride contamination. The anhydrous sodium perchlorate was then dried over P_2O_5 in a vacuum desiccator.

APPARATUS.

The experimental measurements were obtained using a Tinsley Model 19/1 polarograph and a divided H-cell, with a saturated calomel reference electrode.

Table No. 10.

	Ferrocene Substituent	Oxidation Potential. Volts	
		0.01M $HClO_4$	0.1M $HClO_4$
1	1,1'-$(Cl)_2$	-	+0.466
2	-Cl	-	0.460
3	-SCH_3	+0.323	0.295
4	-H	0.314	0.288
5	1,1'-$(SCH_3)_2$	0.275	0.261
6	-CH_3	0.272	0.236
7	1,1'-$[C(CH_3)_3]_2$	0.240	0.200
8	1,1'-$(CH_3)_2$	0.227	0.188
9	1,1'-$[CH(CH_3)_2]_2$	0.220	0.202

Table No.11.

Positions of strongest infrared maxima (cm.$^{-1}$) between 2000 cm.$^{-1}$ and 1000 cm.$^{-1}$ from KCl discs.

$\mathrm{Fc.CO_2H}$	$\mathrm{Fc.SO_3H}$	$\mathrm{Fc}<\begin{smallmatrix}\mathrm{CO_2H}\\\mathrm{SO_3H}\end{smallmatrix}$	$\mathrm{Fc.SO_2Cl}$	$\mathrm{Fc.COCl}$[d]	$\mathrm{Fc}<\begin{smallmatrix}\mathrm{SO_2Cl}\\\mathrm{COCl}\end{smallmatrix}$	$\mathrm{Fc}<\begin{smallmatrix}\mathrm{SO_3Cl}\\\mathrm{CO_2H}\end{smallmatrix}$
-	-	-	-	1767	1770	-
-	1715[a]	-	-	-	1712	1712
1660	-	1667	-	-	1689[b]	1695[b]
1471	-	1485	-	-	1477	1479
-	-	-	-	1441	1445	-
1416	1412	-	-	-	-	-
1399	-	1403	-	-	1399	1399
-	-	1366	1374	-	1372	1371
1279	-	1290	-	-	-	-
-	-	-	-	-	1247	1247
-	1185[a]	1190[a]	1203	-	1203	1203
1156	-	-	-	-	-	1164
-	-	-	1143	-	1144	1143
1105[c]	1110[c]	-	1107[c]	1109[c]	-	-
-	1057	1062	-	-	-	-
1048	-	1046	-	-	1046	-
1026	1022	1031	1030	-	1033	1029
-	-	1010	1014	-	1015	1010
1003[c]	1003[c]	-	1000[c]	1000[c]	-	-

[a] Broad band [b] Shoulder [c] "9,10" bands [d] From the literature.[174]

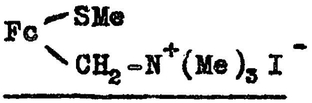
Table No.12.

Positions of infrared maxima ($cm.^{-1}$) below 2000 $cm.^{-1}$ from liquid films.

	$\mathrm{Fc}{<}^{\mathrm{SMe}}_{\mathrm{Me}}$	
1,2	1,3	1,1'
-	1475	1477
1456	1456	1456
1441	1437	1441
1422	1425	1427
-	-	1387
1366	1376	1370
1307	1307	1311
1239	1242	-
-	-	1227
1168	-	1167
1106	1105	-
1076	-	-
-	-	1038
1030	1026	1024
1001	1001	-
966	966	965
952	-	-
-	937	-
-	-	921
-	902	-
-	-	889
833	-	825
-	816	810

Table No.13.

Positions of strongest infrared maxima (cm.$^{-1}$) below 2000 cm.$^{-1}$ from KCl discs.



$$\mathrm{Fc}\begin{cases}\mathrm{SMe}\\ \mathrm{CH_2{-}N^{+}(Me)_3\ I^{-}}\end{cases}$$

1,2	1,3	1,1'
1639	-	-
1481	1481	1481
1468	1471	1468
1443	-	-
1410[a]	1410	1408
-	1395	1383
-	1372	-
-	-	1309
1248	1255	1244
1167	-	1167
1104	1103	-
1035	1047	1036
-	-	1024[b]
-	-	1017[b]
1000	1000	-
-	-	986
969	979	977
-	926	920
909	-	-
-	899	890
874	874	876
841	-	847
-	826	828
814	-	809
-	741	741

[a] Poorly resolved peak [b] Duplet.

Table No. 14.

Positions of infrared maxima (cm.$^{-1}$) below 2000 cm.$^{-1}$ from liquid films.

	$Fc<^{OMe}_{Me}$			$Fc<^{OMe}_{Et}$	
1,2	1,3	1,1'	1,2	1,3	1,1'
1493	1493	1493	1493	1493	1493
1475	–	–	1475	–	–
1456	1460	1456	1451	1452	1452
1416	1414	1425	1416	1418	1425
1381[a]	–	1377	1380	1376	1376
1372[a]	1372	–	–	–	–
–	–	–	1316	1312	1312
–	–	–	1284	–	–
1277	1277	1277	–	1272	–
–	–	1245	–	2145	1245
–	–	1225	–	–	1224
–	–	–	1206	–	–
1138	1140	–	1143	1141	–
–	–	–	1117	–	–
1103	1101	–	1104	1104	–
–	–	1057	–	1058	1058
1048	–	–	1046	–	–
1029	1029	1036	1028	1036	1037
–	–	1020	–	1021	–
1010	–	1010	–	–	1014
1000	998	–	1000	1000	–
–	942	–	–	935	–
–	919	917[a]	–	917	917
–	–	914[a]	–	904	904
813	811	813	815	813	813
–	–	800	–	–	801
792	–	–	791	–	–
704	–	–	697	–	–

[a] Duplet.

Table No.15.

Positions of infrared maxima (cm.$^{-1}$ below 2000 cm.$^{-1}$ from liquid films of products obtained in the demethoxylation of methoxyferrocene. The spectrum of methoxyferrocene was recorded in nujol.

Fc.OMe	Band 3	Band 4
-	-	1739(m)
1493(vs)	1493(vs)	1493(vs)
1466[a](s)	1464[b](m)	1464[b](s)
1456[a](s)	1449[b](m)	1449[b](s)
1429(vs)	-	-
1410(m)	1418(s)	1418(s)
1377(s)	1377(m)	1377(m)
-	-	1299(m)
-	1279(m)	1279(m)
1244(vs)	1244(s)	1244(s)
1227(m)	-	-
-	1209(w)	1209(m)
-	-	1124(s)
1104(s)	1103(s)	1103(s)
1058(vs)	1053(vs)	1053(vs)
-	1020(s)	1020(s)
1012(vs)	1010(s)	1010(s)
1000(s)	1000(m)	1000(m)
914(s)	916(w)	916(m)
832(s)	-	-
821(s)	813(s)	813(vs)
804(vs)	-	-
-	-	676(s)

[a] Duplet [b] Shoulder

Table No.16.

Positions of infrared maxima ($cm.^{-1}$) below 2000 $cm.^{-1}$ from carbon tetrachloride solutions of products obtained in the demethylthiolation of methylthioferrocene.

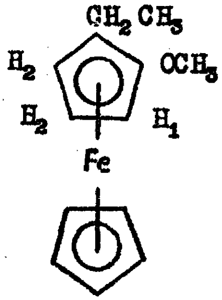
Fc.SMe	Band 3	Band 4
1439[a](m)	1437(s)	1437(s)
1412[a](s)	1425[b](s)	1420[b](s)
1309(m)	1316(w)	1309(m)
-	1256(m)	1256(w)
-	1211(w)	-
1166(s)	-	1166(m)
1103(s)	1104(m)	1104(m)
1050(w)	1036(w)	1036(m)
1019(s)	1021(m)	1021(s)
1000(s)	1000(w)	1000(m)
965(m)	-	965(m)
953(w)	953(w)	955(m)
-	-	927(w)
886(s)	-	889(m)

[a] Multiplets [b] Shoulder

Table No.17.

N.M.R. spectrum for 1-methoxy-2-ethylferrocene.

τ Values		
8.90 8.77 8.65		$-CH_3$
7.64[a] 7.51[a] 7.42[a] 7.24[a]		$-CH_2-$
6.55	-	$-O.CH_3$
6.28	-	ring proton (H_1)
6.16	-	ring protons(H_2)
5.86	-	protons of free ring



[a] Duplet

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