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Ferrocenophanes

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The review deals with unusual cyclophanes of the ferrocene series, which are known as ferrocenophanes. The methods of synthesis of ferrocenophane systems are described and the dependence of their properties and structures on the type and length of the bridge is discussed. Special attention has been devoted to the employment of ferrocenophane models for the solution of a number of theoretical problems in ferrocene chemistry. The stereochemistry and practical applications of ferrocenophanes are discussed. Other organometallic analogues of cyclophanes, only a limited number of examples of which are so far known, are also described. The literature up to 1973 inclusive has been covered.
The bibliography includes 231 references.

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I. INTRODUCTION

Ferrocenophanes are ferrocenes in which the two cyclopentadienyl rings are linked by a bridge consisting of several carbon atoms or atoms of other elements. However, the name ferrocenophane is also sometimes given to compounds in which the carbon atoms of the same cyclopentadienyl ring are linked by a bridge. The properties of such compounds differ little from those of disubstituted homoannular ferrocenes and are not dealt with in the present review.

Attempts to synthesise the ferrocenophane system were undertaken soon after the discovery of ferrocene since, it was evident that a bridge between the two rings should introduce interesting modifications into the properties of the molecule. The first ferrocenophane was synthesised in 1957 and since then studies in this field are continually attracting attention, since ferrocenophanes proved to be useful models for the investigation of the structural, stereochemical, and certain theoretical problems. The synthesis of ferrocenophanes with a single bridge has developed fairly widely so that the simplest of them are quite readily available and have been tested for practical purposes. On the other hand, the synthesis of ferrocenophanes with a number of bridges presents considerable difficulties.

The study of the properties of ferrocenophanes has shown that among them compounds with small bridges are particularly interesting. Such ferrocenes do not simply combine the characteristics of ferrocenes and cyclophanes, the properties of both being transformed in a specific manner. In contrast to ferrocenophanes, the analogous compounds with other transition metals (titanium, cobalt, nickel, and chromium) are so far represented only by isolated examples. They too are discussed in the present review.

The only previous review on ferrocenophanes[1] deals with the literature up to 1966, but since then many new ferrocenophanes have been synthesised and the range of interest shown in this field has greatly expanded; there is therefore no doubt about the need for a new review. We may note that isolated data on ferrocenophanes for the period 1964–1972 may be found in annual reviews of literature on ferrocene[2-10].

According to the proposed nomenclature[1,11], all ferrocenophanes can be divided into two groups. The first includes compounds where within the limits of one ferrocene nucleus the rings are linked by one or several bridges. Derivatives where two or more ferrocene nuclei are linked by chains of atoms, so that each ferrocene fragment constitutes as it were a bridge in relation to the other, may be assigned to the second group. For compounds of the first type, the length of the bridge is represented by a number in square brackets or by several numbers in square brackets if there are several bridges. The positions of the bridges are indicated by numbers in round brackets. The numbering begins with the longest bridge, proceeds along the bridge and completely around the ring, and then along the next bridge (in order of decreasing length of the bridges). The heteroatoms are designated by a number indicating their position in the bridge. For compounds of the second type, a set of numbers indicating the lengths of all the bridges joining the ferrocene nuclei is indicated within a single set of square brackets. A new nomenclature, common to all phanes (cyclophanes and metallocenophanes), was proposed recently[12].

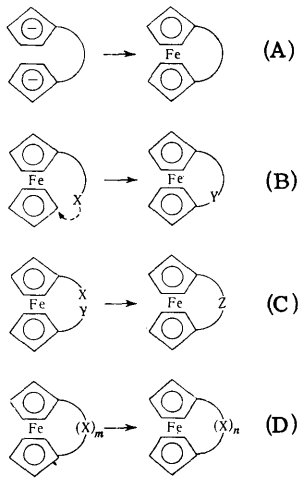
II. METHODS OF SYNTHESIS OF FERROCENOPHANE SYSTEMS†

There are several fundamental approaches to the synthesis of ferrocenophanes. The first makes it possible to obtain a ferrocenophane together with the synthesis of the

† A. A. Pogrebnyak, a Diploma student at Moscow State University, took part in writing this chapter.

ferrocene nucleus and may be called the direct method (see Scheme 1, A).

Scheme 1



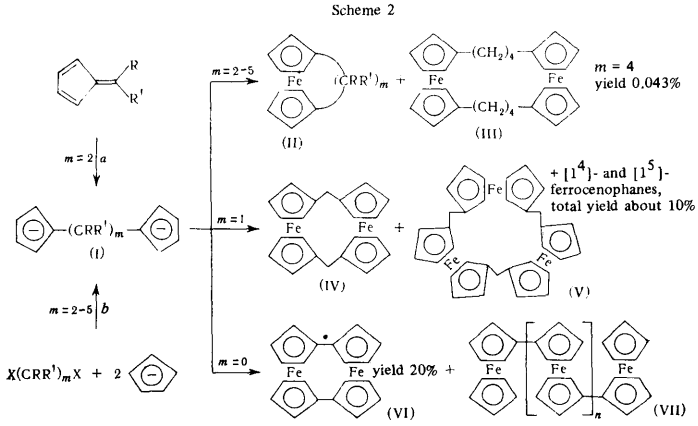
Another method consists of intramolecular substitution in the second cyclopentadienyl (CPD) ring; a group entering into the composition of a substituent in the first ring (B) is then involved in the substitution. In the third method the bridge may be formed by the closure of two heteroannular substituents (C). Finally there is a possibility of a transition from [*m*]- to [*n*]-ferrocenophanes ($m < n$ or $m > n$) by the expansion or contraction of the bridge (D). In addition other special methods used in specific instances are also known.

Naturally each of the fundamental approaches described has many different versions. In the present review all the methods are classified according to these four fundamental types.

A. DIRECT SYNTHESIS

Direct synthesis is understood as the formation of the ferrocenophane system from dicyclopentadienide dianions of type I (Scheme 2) where both cyclopentadienyl rings are linked by a bridge beforehand. In this case ferrocenophanes are obtained by the same method as the usual ferrocenes (the reaction is most often carried out in the presence of anhydrous $FeCl_2$).

Scheme 2



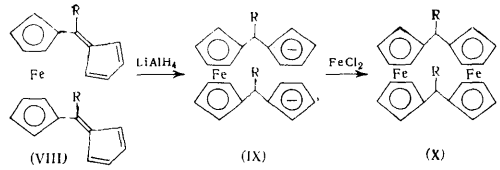
Type (I) dianions are usually obtained by the reaction of the cyclopentadienide anion with the corresponding dihalogeno-compounds (Scheme 2, method *b*). Thus the reaction of the cyclopentadienide anion with $\alpha\omega$-dihalogenoalkanes ($m = 2-5$) yields hydrocarbons in which the two cyclopentadiene rings are linked by a chain of methylene units and which are converted into the dianions (I) after appropriate treatment. The reaction of (I) with $FeCl_2$ makes it possible to synthesise bridged ferrocenes but the yields in this process are very low (with the exception of the case where $m = 2$) and therefore only the synthesis of [2] ferrocenophane is of preparative importance. Naturally the yields of [*m*] ferrocenophanes fall sharply with increase of chain length (Table 1), while the amount of polymeric products increases.

Table 1. Type (II) ferrocenophanes.

No.	*m*	R	R′	Method of synthesis	Yield, %	M.p. (b.p.), °C	Refs.
1	2	CH_3	CH_3	*a*	low	168—169	13,14,16
2	2	CH_3	$CH(CH_3)_2$	*a*		(150—160/1.2)	14
3	2	CH_3	$CH_2CH(CH_3)_2$	*a*		(170—180/2—4)	14
4	2	CH_3	$CH(C_2H_5)(CH_2)_3CH_3$	*a*		(113—123/5)	14
5	2	CH_3	C_6H_5	*a*		(138—165/3—5)	14
6	2	H	H	*b*	50	104—107	15,16
7	3	H	H	*b*	2.5	106—107	17
8	4	H	H	*b*	0.053	58—59	17
9	5	H	H	*b*	0.025	61—62	17

A convenient method for the preparation of dianions with $m = 2$ consists of the interaction of fulvenes with sodium (Scheme 2, method *a*). A whole series of [2] ferrocenophanes containing various substituents in the bridge (Table 1), particularly the widely investigated 1,1,2,2-tetramethyl[2]ferrocenophane, have been synthesised by this procedure.

For $m = 1$ [dianion (I) is obtained from methylene dihalide and the cyclopentadienide anion], the reaction does not lead to [1] ferrocenophane, since the unduly large strain and the mutual inclination of the rings must have an effect on the molecule of this compound; the product is a mixture of [1^n]ferrocenophanes, the lowest members of which are (IV) and (V) (Scheme 2)[18-20]. The molecular weights of all these compounds have been determined mass-spectrometrically. The dianion (IX), which can also be obtained from difulvene (VIII) on treatment with $LiAlH_4$, is formed as an intermediate in this reaction. The interaction of (IX) with $FeCl_2$ yields [1,1]ferrocenophane (X).[21]



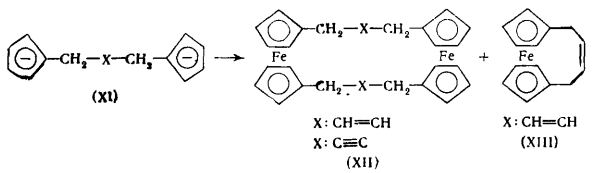
When $m = 0$, the reaction of the dicyclopentadienide dianion (I) with $FeCl_2$ in tetrahydrofuran (THF) gives [0,0]ferrocenophane (VI) together with the polymeric polyferrocenyl (VII).[22]

[4,4]Ferrocenophanes containing double and triple bonds in the bridges [compounds (XII)] have been obtained recently[19]. When *trans*-1,4-dichlorobut-2-ene is used as

the starting material, the monomeric derivative (XIII) is formed in addition to (XII). It is interesting that the ^1H NMR spectra indicate a *cis*-disposition of the methylene groups of the bridge relative to the double bond (the spin–spin splitting of the olefinic protons is 10.4 Hz).

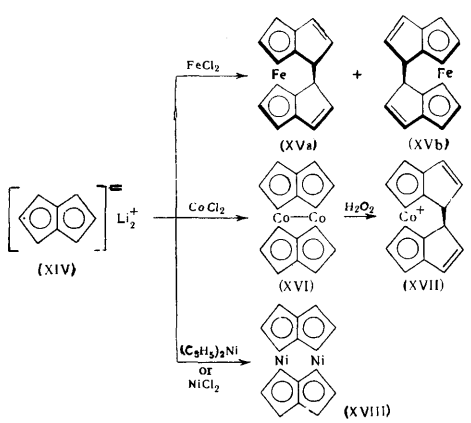
Ferrocenophanes containing silicon atoms in the bridge have been obtained from the corresponding dianions, for example from $[C_5H_5(CH_3)_2SiSi(CH_3)_2C_5H_5]^{2-}$.[23,24]

The direct method has also been used for the synthesis of titanocenophane. The reaction of the dianion (I) ($m = 1$, R = R′ = H) with $TiCl_4$ gave a 30% yield of 1,1′-methylenetitanocene dichloride[19]. The cyclopentadiene rings in this compound are inclined relative to one another, but the non-bridged initial titanocene dichloride has the same structure and therefore the introduction of the monomethylene bridge does not distort the geometry of the molecule, in contrast to [1]ferrocenophane (which has still not been synthesised). Bridged derivatives of titanocene with a silicon or germanium atom in the bridge have been recently synthesised by a similar procedure[25].



Several different bridged metallocene derivatives have been synthesised by Katz and coworkers[26,27] using the dianion (XIV) (Scheme 3).

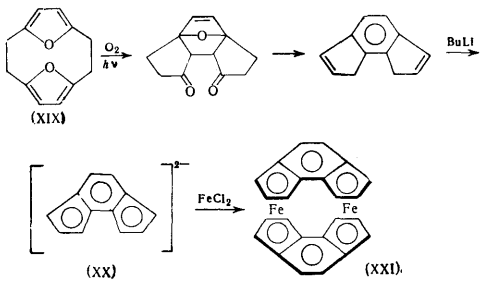
Scheme 3



The structures of compound (XV)[28] and (XVII) are similar to that of "bis-(π-azulene)iron"[29,30] (see below).

The two cyclopentadienide anions from which [*m*,*n*]-ferrocenophanes are obtained may be linked not by one but by two chains[31] and by condensed benzene [the dianion (XX)][32] or naphthalene[33] rings. The dianion (XX), obtained by the photochemical oxidation of furanocyclophane (XIX), gives rise to the interesting ferrocenophane (XXI) on treatment with $FeCl_2$.[32] The corresponding nickel compound was obtained similarly[34]. A dicobalt derivative analogous to the ferrocenophane (VI) has been synthesised recently[35].

A single instance of the synthesis of bisarenemetal π-complexes, in which two benzene rings are linked by a bridge, is known. The reaction of *trans*-stilbene with $CrCl_3$ in the presence of triethylaluminium results in the formation of 1,1′-tetramethylene-βγ-diphenylbisbenzenechromium, which has been isolated as the iodide salt. Its pyrolysis yields 1,2,3,4-tetraphenylbutane, which confirms the proposed structure[36].



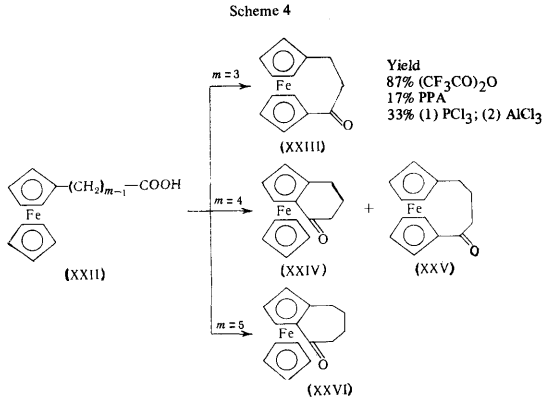
B. INTRAMOLECULAR SUBSTITUTION IN THE CYCLOPENTADIENE RING

This procedure has many different versions and leads both to ferrocenophanes containing a purely hydrocarbon bridge and to [*m*,*n*]ferrocenophanes. The intramolecular cyclisation of ferrocenylpropionic acids, whereby [3]ferrocenophanes can be obtained, has been developed in greatest detail[37–72].

1. Intramolecular Acylation

Rinehart and Curby obtained the first ferrocenophane (XXIII)[37] by the cyclisation of β-ferrocenylpropionic acid (XXII) in the presence of polyphosphoric acid (PPA). However, it was found that the method has a very limited applicability and is suitable only for the synthesis of [3]ferrocenophanes[39,40]. Thus, whereas the cyclisation of γ-ferrocenylbutyric acid still gives a small yield of the corresponding [4]ferrocenophan-1-one[41], acids with a longer methylene chain yield exclusively products of homoannular cyclisation or polymers (Scheme 4)[42–46].

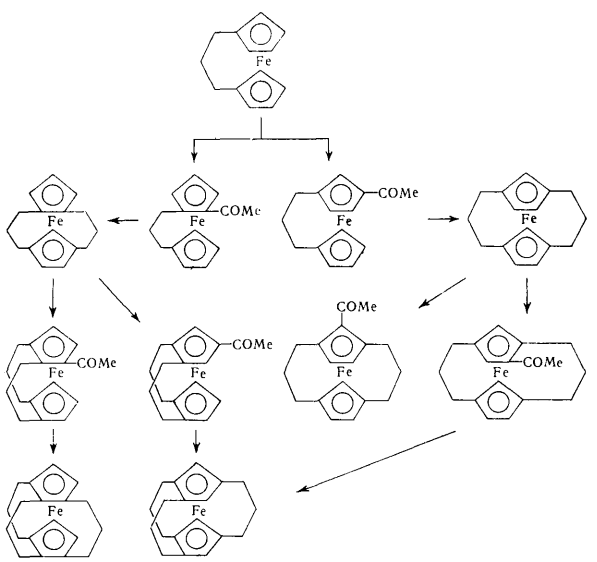
Scheme 4



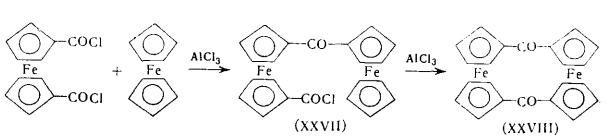
The reaction does not proceed via a heteroannular mechanism in all cases, even for $m = 3$. Thus, when there is a fairly bulky substituent in the cyclopentadiene ring or in the propionic acid chain, a considerable amount of the homoacylation product is formed[47–51]. Nevertheless [3]ferrocenophanes have been obtained mainly by this

method hitherto. The initial β-ferrocenylpropionic acid (XXII, $m = 3$) can be conveniently synthesised from acetylferrocene[39] or ferrocenealdehyde[47,52-54] according to the following schemes respectively: $FcCOCH_3 \rightarrow FcCOCH_2COOC_2H_5 \rightarrow FcCH_2CH_2COOH$ or $FcCHO \rightarrow FcCH=CHCOOH \rightarrow FcCH_2CH_2COOH$. The [3]ferrocenophan-1-one obtained by the cyclisation of β-ferrocenylpropionic acid is readily reduced to [3]ferrocenophane by a mixture of $LiAlH_4$ and $AlCl_3$.[55] By consecutive application of the above stages and of reduction, Rinehart et al.[47] obtained ferrocenophanes with two and three bridges. One of the possible syntheses is illustrated in Scheme 5. [3]Ferrocenophanes with a number of bridges were obtained similarly by Schlögl and coworkers[53,56-58]. Two-bridge ferrocenophanes containing three-, four-, and five-membered bridges in various combinations have been described[59-61]. It is noteworthy that the synthesis of multibridge ferrocenophanes consists of many stages and is very laborious. French chemists have made a detailed study of the cyclisation of substituted β-ferrocenylpropionic acid[45,46,48-51,62-72].

Scheme 5



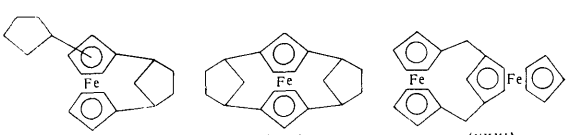
The synthesis of [1,1]ferrocenophanes (XXVIII) by the Friedel–Crafts reaction is closely related to the cyclisation of aliphatic ω-ferrocenyl acids discussed above[73,74]. This reaction proceeds via the formation of the intermediate (XXVII)[75], whose geometry promotes electrophilic attack on the second ring. Compound (XXVIII) has also been obtained from ferrocenecarboxylic acid chloride[76]. The cyclisation of *o*-carboxybenzeneferrocene [probably *o*-carboxybenzoylferrocene [Ed. of Translation)] does not lead to ferrocenophanes[43,44].



(XXVII) (XXVIII)

2. Other Examples of Substitution in the Cyclopentadiene Ring

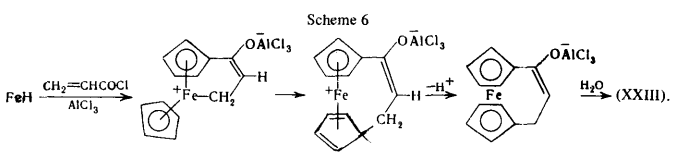
Bridged ferrocenes can be formed not only in intramolecular acylation but also in the heteroannular alkylation of ferrocene by olefins. The ferrocene molecule is cleaved by hydrogen fluoride[77] or phosphoric acid[78] with liberation of cyclopentadiene, which then alkylates other ferrocene molecules. In the simultaneous intramolecular alkylation of both rings the product is a ferrocenophane which can also be obtained by the reaction of ferrocene with anhydrous $AlCl_3$ in benzene[79] or in methylene dichloride[80], or by treating ferrocene with zinc chloride[81,82]. Apart from the ferrocene with a single bridge, the derivative (XXIX) and the ferrocene (XXX) with two bridges are also formed[83]. The structures of these compounds have been demonstrated by chemical methods and by ^1H NMR[83]. By alkylating ferrocene with methylene dichloride, Neuse and coworkers obtained the ferrocenophane (XXXI) together with polymeric products[80]. Apart from other products, the reaction of ferrocene with formaldehyde in the presence of acids gives the ferrocenophane (IV).[84]



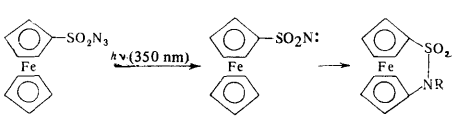
(XXIX) (XXX) (XXXI)

An interesting and synthetically important reaction was recently described by Turbitt and Watts[85]. When ferrocene reacts with acryloyl chloride, [3]ferrocenophan-1-one (XXIII) and propionylferrocene are formed, the ratio of the products depending on the reaction temperature. When the reaction is carried out at −78°C, compound (XXIII) is obtained in 40–60% yield. The sequence of stages leading to (XXIII) proposed by the authors is illustrated in Scheme 6.

Scheme 6



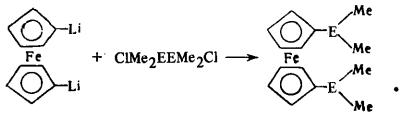
The nitrene (XXIII) formed when compound (XXXII) is irradiated in benzene attacks the second ring, giving the ferrocenophane (XXXIV) with two heteroatoms in the bridge[86]:



(XXXII) (XXXIII) (XXXIV)

Organometallic and halogeno-derivatives of ferrocene have been used to synthesise ferrocenophanes. Thus several bridged compounds containing silicon or germanium atoms in the bridge [for example (XXXVI) with E = Si or Ge] have been obtained by the reaction[23,87] of 1,1-dilithioferrocene (XXXV) with the corresponding dichlorides.

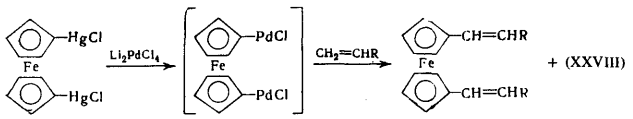
Some of these ferrocenophanes have also been obtained by the direct method (A).



(XXXV) (XXXVI)

The interesting 1,2,3-trithia[3]ferrocenophane is formed when compound (XXXV) reacts with sulphur[88]. Treatment of dibenzylferrocenylacetonitrile with butyllithium leads to the substitution of one of the hydrogen atoms of the free cyclopentadiene ring by lithium, and, after intramolecular attack on the CN group, 1-aza-3,3-dibenzyl[3]ferrocenophan-1-ene is formed[89]. [0,0]Ferrocenophane (VI) has been obtained by the reaction of (XXXV) with cobalt chloride, or of 1,1'-diodoferrocene with copper[90], or by heating a mercury derivative of ferrocene with silver[91]. A copper derivative of 1-bromo-1'-ethynylferrocene was also used to synthesise [2,2]ferrocenophane-1,13-diyne[92]. In a study of the addition of ferrocene to olefins in the presence of palladium salts, Kasahara et al. observed the formation of [0,0]ferrocenophane (VI).[93] When this reaction is carried out in the presence of carbon monoxide, [1,1]ferrocenophane-1,12-dione (XXVIII) is formed[94] (Scheme 7).

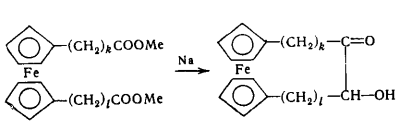
Scheme 7



C. CYCLISATION INVOLVING TWO HETEROANNULAR SUBSTITUENTS IN THE FERROCENE NUCLEUS

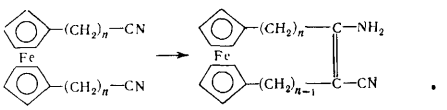
1. Cyclisation of 1,1'-Disubstituted Alkylferrocenes with ω-Functional Groups

The acyloin cyclisation developed by Schlögl and Seiler[95,96] is a universal method for the preparation of ferrocenophanes with a bridge of any length. In this procedure a 1,1'-di-(ω-methoxycarbonylalkyl)ferrocene (XXXVII) is condensed in the presence of finely divided sodium in boiling xylene. Acyloin [*m*]ferrocenophanes with $m = 4$, 6, 8, 9, or 10 have been obtained. This method is less suitable for the synthesis of ferrocenophanes with an odd number of carbon atoms in the bridge, since in this case the required starting materials are the asymmetric diesters (XXXVII, $k \neq l$), which are difficult to obtain.



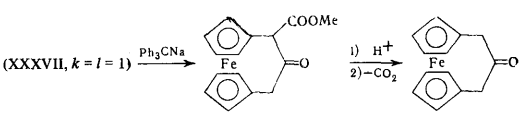
(XXXVII) (XXXVIII)

The cyclisation of the corresponding symmetrical dinitriles (XXXIX, $n = 1$, 2, 5, or 7)[97,98], which can be obtained by various methods[98-101], has been suggested for the synthesis of ferrocenophanes with an odd value of *m*. The sodio-derivative of *N*-methylaniline or (for $n = 1$) methylmagnesium iodide were used as catalysts. This method made it possible to synthesise macrocyclic [11]- and [15]-ferrocenophanes[98]:



(XXXIX) (XL)

The possibility of employing the Dieckmanncyclisation for synthesising ferrocenophanes has so far been demonstrated in only one instance[102]. Under the influence of triphenylmethylsodium, the diester (XXXVII, $k = l = 1$) is converted into the bridged ferrocene (XLI), which decarboxylates to the ketone (XLII) after hydrolysis:

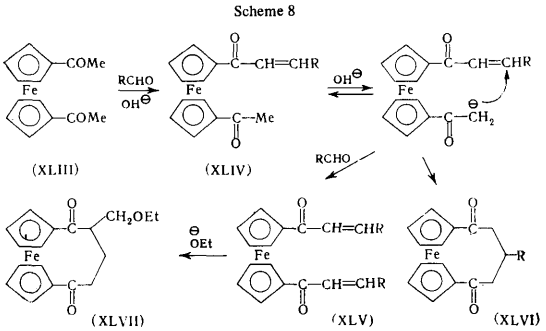


(XLI) (XLII)

2. Cyclisation with the Intermediate Formation of a Carbanion and Its Attack on a Double Bond

In 1960 Hauser and coworkers isolated two products after the reaction of 1,1'-diacetylferrocene (XLIII) with benzaldehyde in the presence of alkali: the red 1,1'-dicinnamoylferrocene (XLV, $R = C_6H_5$) and a yellow product to which the structure of a bridged diketone (XLVI, $R = C_6H_5$) was attributed (Scheme 8).[103] The ratio of the products depends on the amount of benzaldehyde introduced into the reaction. Thus, when 1 mole of benzaldehyde per mole of (XLIII) is used, the yield of (XLV) is 6–13% and the yield of the ferrocenophane (XLVI) is fairly high (66–68%).

Scheme 8



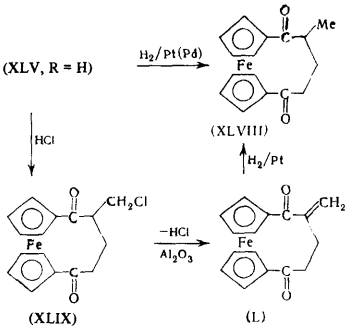
With increase of the amount of aldehyde to 6 moles, the yield of (XLVI) falls to 5% and the amount of (XLV) increases to 75%. Furdik et al. soon showed that not only benzaldehyde but also other aromatic[104-106] and aliphatic aldehydes[107] can be used in this reaction. It was found that, for aliphatic aldehydes and *m*-nitrobenzaldehyde, the yields of ferrocenophanes are significantly lower (about 10%) and that only the dicinnamoyl derivatives (XLV) are formed in the reactions with *o*- and *p*-nitrobenzaldehydes. The condensation also occurs under the influence of acid catalysts[108].

The formation of ferrocenophanes from various 1,1-diacylferrocenes was investigated in later studies[109-111].

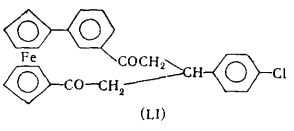
The ferrocenophane (XLVI, R = H) has also been obtained from 1-acetyl-1′-acryloylferrocene (XLIV, R = H)[112,113] or from 1-acetyl-1′-β-chloropropionylferrocene[114], which confirms the scheme proposed for the formation of the ferrocenophane. It was also found[115] that 1,1′-dicinnamoylferrocene (XLV, R = C_6H_5) undergoes retroaldol condensation under the influence of a base with formation of compound (XLIV, R = C_6H_5), which then condenses to (XLVI, R = C_6H_5) in 92% yield. Barr and Watts showed[113] that the reaction of 1,1′-diacetylferrocene with formaldehyde in aqueous ethanol solution of sodium hydroxide yields as the main product the ferrocenophane (XLVII), formed by the condensation of 1,1′-diacryloylferrocene (XLV, R = H).

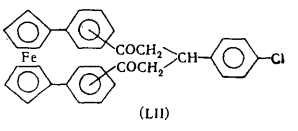
It is interesting that the catalytic hydrogenation of 1,1-diacryloylferrocene (XLV, R = H) over platinum or palladium leads to the formation of a new C–C bond and of the ferrocenophane (XLVIII). The same product was synthesised by the cyclisation of (XLV, R = H) under the influence of HCl with subsequent dehydrochlorination of the product (XLIX) to (L) and catalytic hydrogenation of the latter (Scheme 9).[116]

Scheme 9



An instance of the formation of 4,methyl[4]ferrocenophan-1-one by the intramolecular attack of the carbonion on the double bond of 1-acetyl-1′-isopropenylferrocene[117,118] is also known. Treatment of difulvene (VIII, R = CH_3) with sodamide leads to the formation of a ferrocenophane with a three-membered bridge[74,119]. Toma and Salisova recently employed the method involving addition to an activated double bond in order to synthesise ferrocenophanes with different bridge lengths[120,121]. 3-Phenylacyl[3]ferrocenophan-1-one, 2-(*p*-chlorophenyl)-1-cyano[4]ferrocenophan-1-one, and 3-(*p*-chlorophenyl)[7]ferrocenophane-1,5-dione were obtained in this way[120]. The method proved to be convenient for the synthesis of compounds (LI) and (LII).[121]



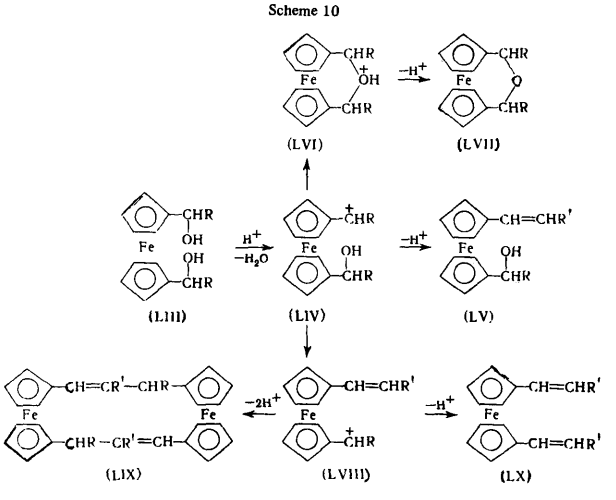


Finally one should note that the polymerisation of 1,1′-divinylferrocene[122] and 1,1′-di-isopropenylferrocene[123] yields high-molecular-weight products containing ferrocenophane rings.

3. Cyclisation with the Intermediate Formation of a Carbonium Ion

Cyclisation with the intermediate formation of a carbonium ion with the charge in the α-position relative to the ferrocene nucleus is widely used to synthesise [3]ferrocenophanes. The ease of formation of these carbonium ions is well known. Carbonium ions such as (LIV) (Scheme 10) are formed following the elimination of the hydroxy-group from α-ferrocenylmethanols (LIII) under the influence of acids. The reaction can proceed further in several ways. When R is not a powerful electron acceptor (R = alkyl, aryl, or hydrogen), the next stage involves attack by the hydroxyl of the α-carbonium centre with subsequent elimination of a proton from (LVI), which results in the formation of 2-oxa[3]ferrocenophane (LVII, R = Alkyl, aryl, or H)[13,124-135]. When R′ in the β-position relative to the ferrocene ring is a powerful electron acceptor, for example CN or $COOC_2H_5$ (then R = CH_2CN or $CH_2COOC_2H_5$), the carbonium ion (LIV) eliminates a proton from the β-position particularly easily and is converted into the olefin (LV), which then gives rise to the diolefin (LX) via the same mechanism[98,101]. Species of the type of (LVIII) can dimerise following intermolecular attack by the carbonium ion on the double bond with formation of the ferrocenophane (LIX, R = CH_3, R′ = H).[133] We may note that intramolecular attack on the double bond, leading to [3]ferrocenophane, is also possible.

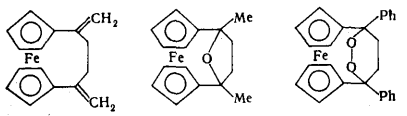
Scheme 10



The α-carbonium ion can also be formed by the hydrolysis of the quaternary salt $N^+Me_3I^-$, which has in fact been used in the synthesis of 2-oxa[3]ferrocenophane[129,133,135].

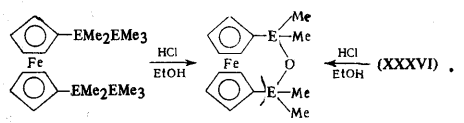
Hisatome and Yamakawa[136] found recently that, on treatment with HCl in benzene, 1,1′-di-(α-hydroxyisopropyl)ferrocene undergoes an unusual condensation leading to the [4]ferrocenophanes (LXI) and (LXII) apart from the uncylised ferrocenes. The analogous reaction of 1,1′-di-(α-hydroxy-α-phenylethyl)ferrocene yielded[137] a series of [4]ferrocenophanes, including the peroxide (LVIII) whose structure was confirmed mass-spectrometrically. The acid-catalysed dimerisation of 2-ferrocenylpropene

results in the formation of a [3]ferrocenophane containing the ferrocenyl group in the 1-position[138].



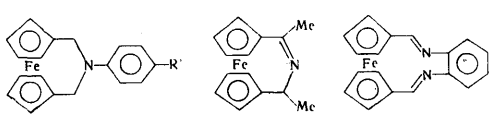
(LXI) (LXII) (LXIII)

Hydrolysis or alcoholysis of various 1,1′-disubstituted ferrocenes whose substituents consist of silicon or germanium atoms has been used to synthesise the corresponding ferrocenophanes with an oxygen atom in the bridge[24,139-142]. Thus Kumada et al.[141] obtained the bridged ethers (LXV) from both uncylised ferrocene (LXIV) and from the ferrocenophane (XXXVI, E = Si or Ge):



(LXIV) (LXV) (XXXVI).

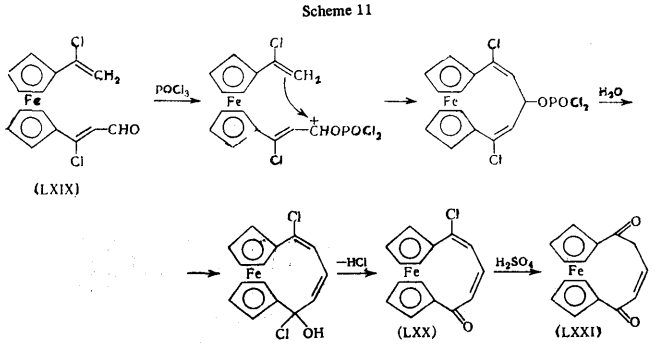
The dicarbinol (LIII, R = H) was used[143,144] to obtain 2-aryl-2-aza[3]ferrocenophanes (LXVI), which are formed when (LIII) is treated with aryl isocyanates (R′ = H, OCH_3, or NO_2). It is noteworthy that another three-membered ferrocenophane (LXVII) with a nitrogen atom in the bridge was synthesised by the reduction of 1,1′-diacetylferrocene monoxime[145]. Condensation of ferrocene-1,1′-dialdehyde with *o*-phenylenediamine[146] resulted in a product to which the authors attributed the structure (LXVIII). The condensation of ferrocene-1,1′-dicarboxylic acid dichloride with hydrazine leads to a polymer in which [3]ferrocenophane rings were detected[147].



(LXVI) (LXVII) (LXVIII)

The reaction of the $\alpha\beta$-unsaturated aldehyde (LXIX) with $POCl_3$ in dimethylformamide leads[148] to the bridged dienone (LXX), which can be converted into compound (LXXI) by treatment with sulphuric acid[113]. A mechanism has been proposed for the formation of the ferrocenophane (LXX) (Scheme 11)[116]:

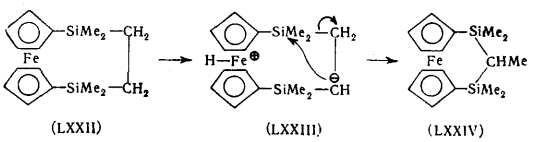
Scheme 11



(LXIX) (LXX) (LXXI)

D. EXPANSION AND CONTRACTION OF THE BRIDGE

Ferrocenophanes can be obtained from other ferrocenophanes with longer or shorter bridges. Thus the reaction of [3]ferrocenophan-1-one (XXIII) with diazomethane results[54] in the expansion of the bridge and the formation of two [4]ferrocenophanes containing carbonyl groups in the 1- and 2-positions. Both ketones can be reduced to [4]ferrocenophane by a mixture of $LiAlH_4$ and $AlCl_3$ or by the Wolff–Kishner method. 1-Aza[4]ferrocenophane has been obtained by the Beckmann rearrangement from [3]-ferrocenophan-1-one[149]. An instance of bridge contraction and conversion from [4]- to [3]-ferrocenophanes is known. On prolonged heating up to 380°C, compound (LXXII) is converted into (LXXIV).[150] The authors suggest that a proton is initially transferred from one of the methylene groups of the bridge to the iron atom with formation of the carbanion (LXXIII), which then rearranges to (LXXIV):

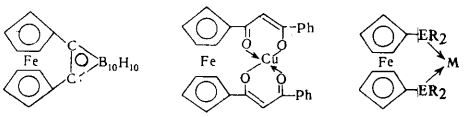


(LXXII) (LXXIII) (LXXIV).

E. OTHER METHODS OF SYNTHESIS

An unusual rearrangement with formation of the interesting [2]ferrocenophane (LXXV) containing a carborane ring in the bridge was described by Zakharkin et al.[151]

Certain 1,1′-disubstituted ferrocenes proved to be convenient bidentate ligands for the formation of complexes with various metals, for example (LXXVI)[152] and (LXXVII) with E = P or As, R = CH_3 or C_6H_5, and M = $Cr(CO)_4$, $Mo(CO)_4$, $W(CO)_4$, $Ni(CO)_2$, $Ni(CO)I_2$, PtX_2, or PdX_2 (X = halogen)[75,153,154].



(LXXV) (LXXVI) (LXXVII)

It is suggested that diacetylferrocene forms complexes with $AlCl_3$[155] and $SnCl_4$[156] in which the metal atom is coordinated to both carbonyl groups simultaneously. The hypothesis has been put forward that the blue compound formed when ferrocene and $AlCl_3$ are dissolved in carbon tetrachloride is a kind of ferrocenophane in which the two ferrocene rings are linked by two aluminium atoms[157]. The interaction of 1,1′-di(acetoacetyl)ferrocene with a nickel(II) salt resulted in the formation of a polynuclear ferrocenophane[158]. Finally the anhydride of ferrocene-1,1′-dicarboxylic acid is apparently a bridged dimer[159].

III. CHEMICAL PROPERTIES

A bridge of any length in ferrocenophanes gives rise to a definite steric hindrance to the approach of the attacking agent towards the cyclopentadiene rings and short bridges ($m = 2$) also distort the ferrocene structure, resulting in an inclination of the rings, to such an extent that the behaviour of ferrocenophanes of this kind differs qualitatively from that of non-bridged 1,1′-disubstituted ferrocenes. This can be illustrated by the following examples.

Whereas the reductive cleavage of ferrocene and its alkyl derivatives by lithium in propylamine results in the formation of the corresponding cyclopentadienes (yield from 45 to 77%), [3]ferrocenophane decomposes only partly under these conditions and [3][3](1,3)ferrocenophane is completely resistant to the reaction of lithium[160].

Table 2. The β/α ratio in the acetylation products[161].

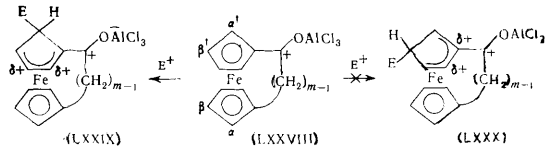
[3]Ferrocenophane	1.57
[4]Ferrocenophane	1.65
[5]Ferrocenophane	2.19
3-Phenyl[5]ferrocenophane	2.62
1,1'-Dimethylferrocene	1.95
1,1'-Diethylferrocene	2.88

Ferrocenophanes (with $m \geq 3$) behave similarly to 1,1'-dialkylferrocenes in reactions with electrophilic agents. Rinehart et al.,[47] Rosenblum et al.,[54] and Watts and coworkers[161-163], who made a detailed study of the acetylation of [m]ferrocenophanes, found that the ratio of the acetyl[m]ferrocenophane isomers $\beta/\alpha > 1$ and increases with the length of the bridge[161], i.e. a behaviour similar to that of 1,1'-dialkylferrocenes is observed (Table 2). However, molecular orbital calculations[164] lead to the expectation that the α-isomer should predominate. For this reason, the preferential formation of the β-isomer in the acetylation of [m]ferrocenophanes and 1,1'-dialkylferrocenes is explained by the dominant influence of steric factors. With $m = 4$ and particularly with $m = 5$, the bridge methylene groups hinder markedly the α-positions in the cyclopentadiene rings.

Table 3. The ratio of the products of the acetylation of [m]ferrocenophan-1-ones[163] [for the significance of the symbols see the structure (LXXVIII)].

m	β/α	α'/α	$(\alpha+\beta)/\alpha'$
3	4.2	0.6	9.5
4	1.2	0.5	4.5
5	0.8	0.01	170

The acetylation of acetylferrocene results in the formation of a small amount of the 1,2-diacetyl derivative (the 1,3-isomer was not found) in addition to the main product 1,1'-diacetylferrocene. Derivatives containing the acetyl group in the β'-position of the ring bound to the carbonyl group were also not found among the products of the acetylation of [m]ferrocenophan-1-ones[163] (Table 3). On the other hand, the amount of the α-substituted products (particularly with $m = 3$ or 4) is fairly appreciable. This finding was accounted for in the following way. The aluminium chloride used in the acetylation reaction forms a complex with the carbonyl group of [m]ferrocenophanone, which results in the formation of the strongly polarised structure (LXXVIII). If the rate-determining stage is the formation of the σ-complex (LXXIX) or (LXXX), the addition of the acetylium ion to the α'-position should predominate despite the steric hindrance, since in this case [structure (LXXIX)] the sites with a reduced electron density are more remote from the carbonium centre formed from the carbonyl group than in the β'-addition [structure (LXXX)]:

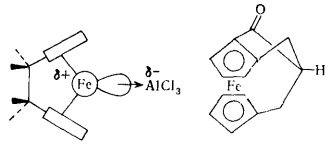


(LXXIX) (LXXVIII) (LXXX)

Thus the result is consistent with molecular orbital calculations and electronic factors presumably predominate in this case over steric factors. The sharp increase of the ratio β/α for $m = 3$ (cf. Table 2 and 3) was explained[163] on the basis of the *trans*-effect—the concept, which was adduced for the first time to account for the electronic effects in metallocenes. The diacetylation of [3]ferrocenophane has been described[61].

It is very remarkable that [2]ferrocenophane cannot be acetylated[14,16,161], whereas it is protonated at the iron atom significantly more readily than all other ferrocene derivatives[15,16]. This is shown by the disappearance of the 472 nm band ($\epsilon = 450$) from the [2]ferrocenophane spectrum after the addition of 0.1% sulphuric acid to the alcoholic solution[15,16]. The marked mutual inclination of the rings in this compound probably causes an electronic rearrangement in the molecule and withdrawal of electron density (of three filled non-bonding orbitals) from the side opposite to that of the bridge. This leads to a sharp increase of the basicity of the compound. The coordination of one of the electron pairs with $AlCl_3$ induces a flow of electron density from the rings to the iron atom, as a result of which the compound loses the capacity for electrophilic substitution [structure (LXXXI)][161].

A somewhat lower rate of solvolysis of 1-acetoxy[3]ferrocenophane compared with the corresponding non-bridged ferrocene derivatives has been observed, which has been attributed to some destabilisation of the α-carbonium centre in the ferrocenophane molecule, since in this case the cationic centre and the cyclopentadiene ring are non-coplanar[165].



(LXXXI) (LXXXII)

Several studies have been made on reactions involving the bridge, see for example Refs. 113, 116, 166, and 167. Some of these reactions were mentioned in the description of the methods of synthesis of ferrocenophanes. [3]Ferrocenophanes with a carbonyl group in the 1-position[168] or 2-position[169] were converted into tosylhydrazones from which the corresponding carbenes were generated. It was shown that the carbenes exist in the triplet state[169]. When the two tosylhydrazones were heated with sodium hydride, [3]ferrocenophan-1-ene was obtained. It is interesting that the reduction of ferrocenophane (LXXXII) gives rise only to the corresponding carbinol and the hydrocarbon could not be obtained[9,170].

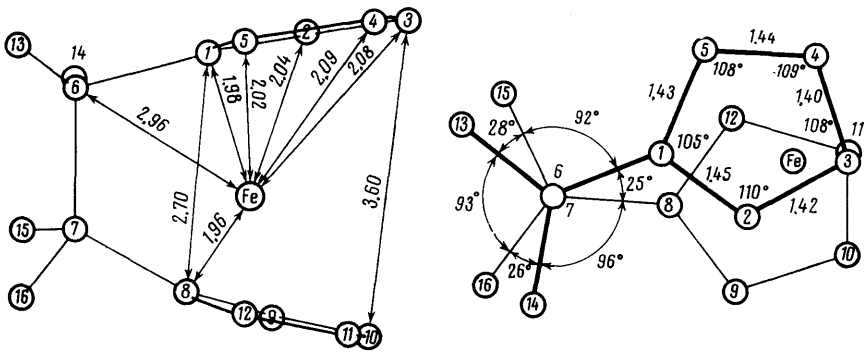


Figure 1.

IV. STUDIES BY PHYSICAL METHODS

A. Structural Studies

The structures and conformations of bridged ferrocenes were discussed theoretically in early investigations[171,172]. The determination of the crystal and molecular structures of 1,1,2,2-tetramethyl[2]ferrocenophane[173] showed that the two cyclopentadiene rings in this compound are inclined relative to one another at an angle of 23° and, in contrast to ferrocene, are staggered to the extent of only 9°. The strain in this system is shown by the fact that the dihedral angle in the bridge is only 26°. The bond lengths slightly exceed the normal values. The structure of this compound is illustrated in Fig. 1. We may note that, according to a calculation[174], the distortions in the structure accompanied by inclination of the rings by up to 45° should not be reflected in the metal–ring bond energy.

The mutual inclination of the cyclopentadiene rings in [3]ferrocenophan-1-one is naturally smaller than in the more strained [2]ferrocenophane, amounting to 8.8°.[175] Some of the experimental angles and bond lengths (Å) are indicated in Fig. 2. The second bridge in [3][3](1,3)ferrocenophane does not increase appreciably the mutual inclination of the rings (the angle is 9°).[176] The two cyclopentadiene rings in this molecule are in the eclipsed prismatic conformation. A virtually eclipsed conformation was also found in 1,2,3-trithia[3]ferrocenophane (the angle of ring inclination is 2.85°).[177] The crystal and molecular structures of [1,1,1]ferrocenophane[178] and the molecular structure of [1,1]ferrocenophane[179,180] have also been determined and the crystal lattice constants of the compounds (XLVI, R = thienyl)[181] and (LXXVII, E = As, R = CH_3, and M = NiI_2CO)[182] have been published.

X-Ray diffraction analysis of "bis-(π-azulene) iron" showed that this compound is a ferrocenophane in which the two seven-membered rings are non-planar and are linked via the *ortho*- and *para*-positions with formation of a two-membered bridge[29,30]. A similar structure was recently found for bis(pentalenyl)iron[28]. This compound exists in the form of two enantiomers (XVa and XVb).

B. The Study of Conformational Mobility

The cyclopentadiene rings in the ferrocene molecule are parallel and the barrier to their mutual rotation about the axis passing through the iron atom and the centre of the ring is very small (0.9 kcal mole^{-1} compared with 3.0 kcal mole^{-1} for rotation about the C–C axis in ethane)[183]. The introduction of a bridge into the ferrocene molecule precludes such rotation, but the mutual rotational oscillations of the rings persist and their amplitude should diminish with decrease of the length of the bridge. X-Ray diffraction analysis (see above) established that the cyclopentadiene rings are mutually inclined in [*m*]ferrocenophane molecules with fairly short bridges (*m* = 2 or 3).

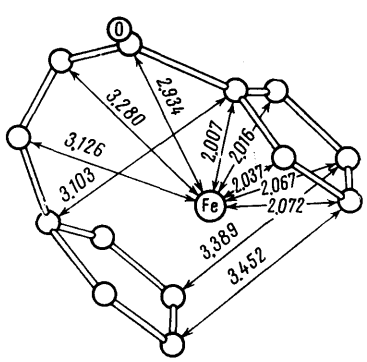


Figure 2.

Models have shown that with longer bridges the rings are parallel. The decrease of conformational mobility following the introduction of a bridge and particularly the mutual inclination of the rings are reflected in the spectroscopic characteristics of ferrocenophanes. Thus the sharp deformation of the [2]ferrocenophane molecule is reflected by the marked bathochromic shift of the "440 nm" band, associated‡ with the $A_{2g}(e_{2g} \rightarrow e_{2g}^*)$ transition[184], to 472 nm (Table 4). Its intensity increases at the same time. On the other hand, the displacement from conjugation of the carbonyl groups in the α-positions of the bridge

‡ Other assignments have also been made (see the paper of Barr and Watts[185] and the reference quoted therein).

leads to a hypsochromic shift of the above band. This effect has been observed in electronic spectra on passing from 1-acetyl-1′-methylferrocene to its bridged analogues—[3]- and [4]-ferrocenophan-1-ones[54]. The absorption maximum in the spectrum of the bridged [5]ferrocenophane-1,5-dione occurs at a lower wavelength (452 nm) than in the spectrum of the uncyclised and unstrained 1,1′-diacetylferrocene (460 nm).[186] Comparison of the electronic spectra of [3]ferrocenophane and [3]ferrocenophan-1-ene shows that there is virtually no conjugation of the double bond with the ferrocenyl fragment[168].

Table 4. Electronic spectroscopic data[15,185] [λmax (nm) and ϵ].

Compound	λ, nm	ϵ
Ferrocene	440	90
1,1′-Dimethylferrocene	437	100
1,1′-Di-(t-butyl)ferrocene	442	105
[2]Ferrocenophane	472	450
[3]Ferrocenophane	442	185
[4]Ferrocenophane	433	100
[5]Ferrocenophane	448	110
1,1′-Di(methoxymethyl)ferrocene	434	110
2-Oxa[3]ferrocenophane	443	220

Table 5 shows that an increase of the strain in the molecule and the displacement of the carbonyl group from conjugation with the cyclopentadiene ring as the length of the bridge is reduced are reflected in the infrared spectra [a shift of ν(C=O) towards higher frequencies].

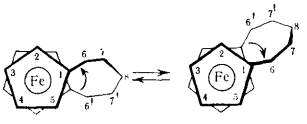
Table 5. The stretching vibration wave-numbers of the carbonyl group[54,113].

Compound	ν, cm^{-1}
[5]Ferrocenophan-1-one	1642
[5]Ferrocenophane-1,5-dione	1658
[4]Ferrocenophan-1-one	1647
[4]Ferrocenophan-2-one	1681
[3]Ferrocenophan-1-one	

The protons of the cyclopentadiene rings are shown in the ^{1}H NMR spectra of [m]ferrocenophanes[54,183,186] by multiplets, characteristic of an AA′BB′ system, resembling the corresponding signals in the spectra of 1,1′-disubstituted ferrocenes with electron-donating substituents[101]. Whereas in the spectrum of [4]ferrocenophane whose cyclopentadiene rings are parallel the signal of the above protons constitutes a fairly narrow singlet (40 MHz in C_6D_6), in the spectra of [3]- and particularly [2]-ferrocenophane, whose cyclopentadiene rings are inclined, the above signal splits into two triplets corresponding to the α- and β-protons. In the spectrum of the latter the spacing between the triplets reaches 0.54 p.p.m. The anomalous spectra of [2]- and [3]-ferrocenophanes were explained by the fact[183] that, owing to the mutual inclination of the rings, the orbitals of the lone electron pairs of the metal are rehybridised. The resulting asymmetric distribution of electron density in the space between the cyclopentadiene rings leads to different degrees of shielding of the α- and β-protons [structure (LXXXI)].

Detailed studies of the temperature variation of the ^{1}H NMR spectra of ferrocenophanes to investigate the conformational mobility of the molecules have not been made. It is only known that the methylene singlet in the spectrum of the [3]ferrocenophane is slightly broadened at −55°C[183] and the multiplet due to the cyclopentadiene protons of [5]ferrocenophane loses its fine structure at −110°C and at the same time shifts towards a high field[186]. The changes in the spectra of 1,2,3-trithia[3]ferrocenophane with increase of temperature indicate the mobility of this molecule[88].

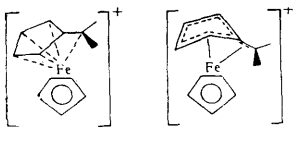
The ^{13}C NMR spectrum of [5]ferrocenophane was investigated recently[186]. The carbon atoms of the cyclopentadiene rings give rise to three signals with δ = 68.4 and 66.9 p.p.m. ($C_{2,5}$ and $C_{3,4}$) and 89.2 p.p.m. (C_1) relative to tetramethylsilane (in CH_2Cl_2 at +15°C). The bridge methylene groups give rise to three signals in the range δ = 22–26 p.p.m. Whereas one of these signals, probably associated with $C'_{6,6}$, does not change its position when the temperature is altered (in the range between −70° and +70°C), the other two signals shift appreciably to a lower field with increase of temperature. This change in the spectrum may be caused by the conformational transitions (LXXXIIIa) ⇌ (LXXXIIIb) due to the mutual rotation of the cyclopentadiene rings and the inversion of the bridge. The change in the contributions of the conformational populations as the temperature is altered leads to a significant change in the average anisotropic screening of the C_7 and C_8 nuclei in the inhomogeneous magnetic field[187] due to the ferrocene rings. The ^{13}C NMR spectrum of [5]ferrocenophane-1,5-dione may indicate a lower conformational mobility of the molecule[186].



(LXXXIIIa) (LXXXIIIb)

C. Application of Ferrocenophanes in the Study of α-Ferrocenylcarbonium and Ferricenium Ions

The problem of the structure of α-ferrocenylcarbonium ions has been solved with the aid of ferrocenophanes. To account for the unusual stability of α-ferrocenylcarbonium ions, two fundamental alternative structures, (LXXXIV) and (LXXXV), were proposed. In the first the cyclopentadiene ring with the α-carbonium centre assumes a fulvenoid configuration and is displaced relative to the iron atom, while in the second the cyclopentadiene ring is deformed and the carbonium centre approaches the iron atom.

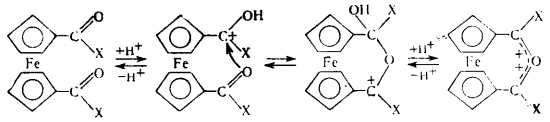


(LXXXIV) (LXXXV)

If structure (LXXXIV) is correct, the introduction of a bridge in the α- or β-position with respect to the carbonium ion centre should prevent the displacement of the

cyclopentadiene ligand, whereas a bridge of this kind cannot interfere with the deformation of the ring. [3]- and [4]-Ferrocenophanes with the $-\overset{+}{C}H_2$, $-CH\overset{+}{C}H_3$, or $-\overset{+}{C}(CH_3)_2$ cationic centre in the α- or β-positions with respect to the bridge have been obtained[188-192]. It was found that these compounds are no less stable than the cations without a bridge and that the ^{1}H NMR spectra of ferrocenophanes with a carbonium ion centre resemble those of the corresponding 1,1′-dialkylferrocenes with a cationic centre in the α- or β-position with respect to the alkyl substituent. On this basis, preference was given to structure (LXXXV). Japanese workers investigated the ^{1}H NMR spectra[3] of [3]- and [4]-ferrocenophane carbonium ions[191] in which the positive charge arises at the α- or β-carbon atom of the bridge. The authors believe that the spectra reflect the molecular deformations arising in consequence of the interaction of the positive charge both with the π electrons of the cyclopentadiene rings and with the iron atom.

In a study of ^{1}H NMR spectra the formation of the bridged dications (LXXXVII) in solutions of 1,1′-diacylferrocenes (LXXXVI) in strong acids was postulated[193]. When [5]ferrocenophane-1,5-dione is dissolved in concentrated sulphuric acid, a carbonium ion is formed, which is reflected[194] in the ^{13}C NMR spectrum. Comparison of the ^{13}C NMR spectra of mono- and 1,1′-di-acylferrocenes in protic acids[194] also indicates the possible formation of the bridged ion (LXXXVII).



(LXXXVI) (LXXXVII)

Bitterwolf and Ling[195] showed that in a strongly acid medium ($BF_3.H_2O$) biferrocenyl, diferrocenylmethane, and 1,2-diferrocenylethane are readily protonated as both iron atoms, which is reflected in the ^{1}H NMR spectra. However, in contrast to ferrocene, the solute is then oxidised, the rate of oxidation increasing with decrease in the length of the chain joining the two ferrocene fragments. The oxidation of [1,1]ferrocenophane is very rapid and is accompanied by the liberation of one mole of hydrogen. The hydrogen atoms in the specific conformation of the diprotonated [1,1]ferrocenophane (Fig. 3) probably approach one another and a chemical bond is formed between them, which leads to the elimination of hydrogen. The iron atoms are then oxidised.

[0,0]Ferrocenophane can be oxidised at one of the iron atoms with formation of ferricenium picrate or fluoroborate. An intense absorption, consisting of a double band at 1550 nm (ϵ = 2100) and 1140 nm, was observed in the electronic spectrum of this compound[22,196]. The position of this band and its molar extinction coefficient are independent of the solvent and concentration, which enabled the authors to assign this absorption to an intramolecular electron transfer between the two iron atoms. [1,1]Ferrocenophane gives rise to a picrate which absorbs at 780 nm[22]. In both cases the band undergoes a sharp hypsochromic shift relative to its position in the spectrum of ferrocenylferricenium picrate (1900 nm, ϵ = 551).[197]

D. Other Studies

It has been established that the two bands in the region of 1000 and 1100 cm^{-1}, characteristic of the vibrations of the unsubstituted cyclopentadiene rings, are absent from the infrared spectra of ferrocenophanes, but almost always occur in the spectra of mono- or homopoly-substituted ferrocenes. This feature can be used to establish whether the intramolecular cyclisation reaction is homoannular or heteroannular (see Scheme 4).

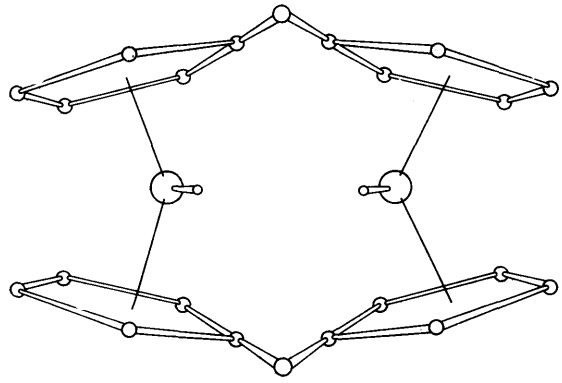


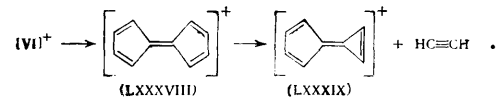
Figure 3.

The dipole moments of [m]ferrocenophanes have been measured[198] and have been found to decrease in the following sequence: Me_4[2]§ > [3] > [4] > [5] (1.00, 0.85, 0.81, and 0.76 D respectively), owing to the increase of the mobility of the molecule with increase in the length of the bridge. It is interesting that the dipole moments of β-acetyl[m]ferrocenophanes (m = 3, 4, or 5) are equal to the sums of the dipole moments of acetylferrocene and the corresponding [m]ferrocenophane. This finding was explained by the hyperconjugation between the methylene and carbonyl groups in the $CH_3CO-C_5H_3-CH_2-$system. The polarographic behaviour of various ferrocenophanes has been studied[199,200] and their magnetic susceptibilities have been measured[200]. It was found that [m]ferrocenophanes are oxidised electrochemically more readily than ferrocene and are comparable in this respect to 1,1′-dialkylferrocenes[199]. Under these conditions, [2]ferrocenophane decomposes, since the ferricenium cation formed is unstable. The magnetic anisotropy of the carbonyl group in 2-acetyl[3]ferrocenophane has been discussed[201].

Unfortunately systematic and detailed mass-spectrometric studies on ferrocenophanes have not been made[202,203]. The spectra of [5]ferrocenophanes, like those of the majority of the ferrocene derivatives, are characterised by an intense molecular ion peak. The fragmentation of this ion for the simplest [5]ferrocenophane is accompanied by the loss of CH_3, C_2H_5, C_3H_5, and C_4H_7. When the bridge contains an α-carbonyl group, CO is the first to be eliminated[113]. Very intense M^+ and M^{2+} peaks were observed in the spectrum of [3][3](1,3)ferrocenophane. The fragmentation of the molecular ion involves the loss of methyl, acetylene, ethylene, and propene with subsequent decomposition of the ions formed[204]. The mass spectra of [1,1]-ferrocenophanes have been described[21,202,205]. Apart from the most intense M^+, M^{2+}, and Fe^+ peaks,

§ 1,1,2,2-Tetramethyl[2]ferrocenophane.

the [0,0]ferrocenophane spectrum shows small peaks with m/e 128 and 102, which may be due to the (LXXXVIII) and (LXXXIX) ions respectively[90]. The spectra of [2,2]ferrocenophane-1,13-diyne[92] and 1-hydroxy[3]ferrocenophane[206] have been published. The formation of an ion corresponding to the ferrocenophane (LXX) was noted in the fragmentation of the dicarbinols (LIII)[206]:

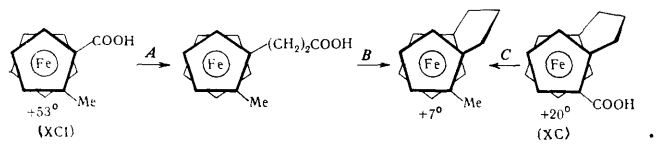


V. THE STEREOCHEMISTRY OF FERROCENOPHANES

The configurational and conformational studies on metallocenes, particularly on [3]ferrocenophanes, have been reviewed by Schlögl[207,208].

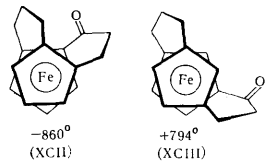
Monosubstituted [m]ferrocenophanes, as well as homoannular disubstituted ferrocenes, should exist in the form of two optical isomers. Detailed stereochemical studies have so far been made only on [3]ferrocenophanes. The key compound for the determination of the absolute configurations of these derivatives is [3]ferrocenophane-α'-carboxylic acid (XC), the absolute configuration of which was established by a correlation with methylferrocene-α-carboxylic acid (XCI), as shown in Scheme 12. The transformations were carried out as follows: Stage A involves the transformations COOH → CHO → CH = CHCOOH → CH_2CH_2COOH, stage B involves cyclisation with the aid of $(CF_3CO)_2O$ and reduction by a mixture of $LiAlH_4$ and $AlCl_3$, and stage C involves reduction by the same mixture. The absolute configuration of the acid (XCI) had been established previously[209]. Similar studies have been made also for ferrocenophanes containing substituents in the β-position[210]. Apart from chemical correlations, the Horeau method of kinetic resolution was used to establish the configuration of [3]ferrocenocarboxylic acids by the interaction of their anhydrides with (-)-α-phenylethylamine[210].

Scheme 12



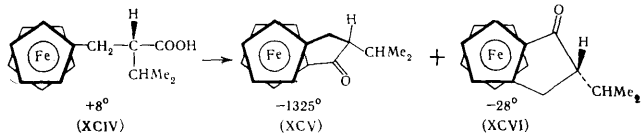
The doubly bridged ketone (XCII) was synthesised by a series of consecutive transformations from the acid (XC) obtained by the resolution of the racemate with (-)-α-phenylethylamine. The β-derivative (CXIII) was obtained similarly[210].

The intramolecular cyclisation of 1-(β-carboxypropyl)-1′-methylferrocene yielded the corresponding α- and β-methyl[3]ferrocenophanones with the oxo-group in the bridge. Each ketone was resolved into its optical isomers by the formation of methylhydrazones[210].

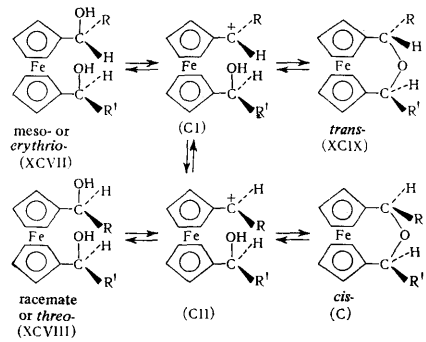


The study of the circular dichroism (CD) of optically active homo-disubstituted ferrocenes and [3]ferrocenophane substituted in the α-position of the ring led to conclusions concerning the preferred conformations of the substituents or the bridge[208,211]. The study of the dipole moments and the temperature variation of the circular dichroism of α- and β-substituted (in the cyclopentadiene ring relative to the bridge) [3]ferrocenophanes showed that the activation energy for the inversion of the bridge is significantly higher for the α-derivative, as was to be expected, and this results in the existence of a preferred bridge conformation[211]. Moreover, on passing from [3]ferrocenophanes α-substituted in the cyclopentadiene ring to the β-substituted derivatives, a decrease of the amplitude of the Cotton effect may be noted and in certain cases the sign of the curves is reversed[212].

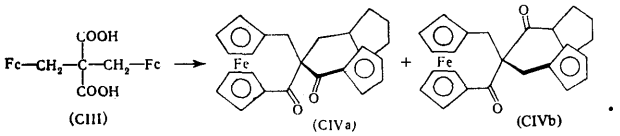
The chirality of the ferrocenophane molecule may be caused by the introduction of a substituent not only in one of the rings, as in the above discussion, but can arise also when an asymmetric centre is introduced into the bridge. The cyclisation of the optically active acids $FcCH_2CHRCOOH$, leading to ketones with hetero- and homo-bridges, which also exhibit optical activity [for example compounds (XCV) and (XCVI)], has been described[48,49].



A careful study of the stereochemistry of the 1,1′-diol⇌2-oxa[3]ferrocenophane interconversions was made by Yamakawa and Hisatome[213]. 1,1′-Di-(α-hydroxyalkyl)ferrocenes can exist in the *meso*-form (*erythro*- if R ≠ R′) (XCVII) and as the racemate of two optical isomers (*threo*- when R ≠ R′) (XCVIII). The resolution into the *meso*-form and the racemate was achieved by 7–8 recrystallisation of the product obtained by the reduction of the corresponding diacylferrocene. On treatment with dilute HCl, the mixture of compounds (XCVII) and (XCVIII) is converted into a mixture of the *cis*- and *trans*-isomers of the ferrocenophane, (C) and (XCIX) respectively, which can be separated chromatographically. The ferrocenophanes (XCIX) and (C) are converted reversibly into the diols (XCVII) and (XCVIII) on treatment with acid alumina. It is significant that the interconversions are stereospecific. The relative amounts of the products in the (XCVII) ⇌ (XCIX) and (XCVIII) ⇌ (C) interconversions have been determined but small amounts of another isomer are also obtained in these processes owing to the equilibrium (CI) ⇌ (CII) between the two forms of the intermediate carbonium ion.

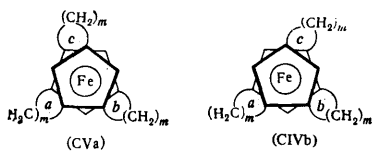


When the acid (CIII) was treated with $(CF_3CO)_2O$, a mixture of stereoisomeric spiranes (CIV) was obtained[214] and was resolved by chromatography on partly acetylated cellulose[215].



(CIII) (CIVa) (CIVb)

Optical isomerism of a new type may be expected for the ferrocenophanes (CV, $m = 4$ or 5) with three bridges, which have not yet been synthesised. Models show that such ferrocenophanes with fairly long bridges can exist in the antiprismatic configuration. The introduction of two bridges (a and b) restricts the mutual rotational oscillations of the rings, while the third bridge (c), which has rotated to the left or to the right, should result in the formation of two enantiomers—(CVa) and (CVb) respectively.



(CVa) (CIVb)

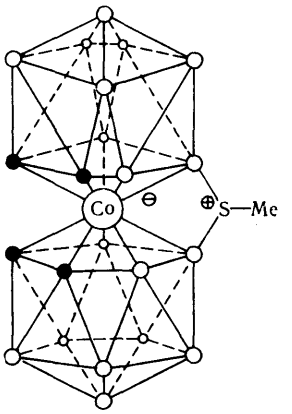
VI. APPLICATIONS

The use of ferrocenophane models for the solution of certain theoretical problems and the synthesis of polymers containing ferrocenophane fragments was mentioned above.

It has been suggested that [2]ferrocenophanes (Table 1, Nos. 1–5) be used as additives to epoxy-resins and silicones[14]. It was found recently that [3]ferrocenophanes with silicon and oxygen atoms in the bridge are effective inhibitors of the oxidation of polyorganosiloxanes[216,217]. Bridged cyclic ethers[218–221] and thioethers[218] exhibit biological activity and can be used in the treatment of diseases associated with iron deficiency in the organism. Derivatives of [3]ferrocenophan-1-one[167,222] and also 1-aza[4]ferrocenophane[149] exhibit a similar activity. These compounds have proved useful also as additives to fuel. It has been suggested that 2-aza[3]ferrocenophane be used in macromolecular chemistry. The dicarbinol formed on reduction of 3-phenyl[5]ferrocenophane-1,5-dione was converted into a bridged ether and thioether, which can be used as pesticides, dyes, fuel additives, and medicinal preparations for the treatment of iron-deficiency diseases[223]. Like titanocene dichloride, 1,1′-methylenetitanocene dichloride can be used for the fixation of molecular nitrogen and also as a cocatalyst in the polymerisation of olefins[19].

ADDENDUM

Japanese workers described recently the synthesis of bridged bicyclic ferrocenes with two nitrogen atoms in the bridge by the reaction of the 1,1′-diacetylferrocene–$AlCl_3$ complex with o-phenylenediamine[224]. French chemists continued the study of the stereochemistry of substituted [3]ferrocenophanes[225]. Plešek et al.[226] synthesised the interesting bridged carborane derivative (CVI).



(CVI)

Turbitt and Watts made special use of ferrocenophane models in a detailed study of α-ferrocenylcarbonium ions[227]. Continuing the investigation of ferrocenophanes by ^{13}C NMR, Nesmeyanov et al.[228] obtained the spectra of certain [3]ferrocenophanes and the carbonium ion formed when [3]ferrocenophan-1-one is dissolved in CF_3COOH. The introduction of the phenyl substituent in the 3-position of the bridge of [5]ferrocenophane results in the non-equivalence of all five carbon atoms of the cyclopentadiene ring owing to the diastereotopy (and the anisochronic properties) of the nuclei within each of the two pair $C_{(2)} - C_{(5)}$ and $C_{(3)} - C_{(4)}$ arising following the introduction of the substituent[228]. This effect was observed previously for non-bridged mono-substituted ferrocenes containing a chiral centre in the substituent[229–231].

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