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SYNTHESIS OF FERROCENOPHANES BY CYCLIZATION OF DINITRILES

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Summary

A method has been developed for synthesizing cyanenamine derivatives of [*m*]ferrocenophanes (m = 3,5,11,15) by cyclization of 1,1'-bis(ω-cyanoalkyl)-ferrocenes ($Fcd[(CH_2)_nCN]_2$, n = 1,2,5 or 7, $Fcd = C_5H_4FeC_5H_4$) using CH_3MgI and $C_6H_5N(CH_3)Na$ 1,1'-Bis(3-cyanopropyl)ferrocene cyclizes to give only low yields of cyclization products analogous to the minimal yields of alicyclic compounds containing 9 to 13 CH_2 groups prepared from aliphatic dinitriles by this same method When 1,1'-bis[*O*-(2-cyanoethyl)-1-hydroxyethyl]ferrocene is treated with $C_6H_5N(CH_3)Na$ decyanoethylation occurs to give 1,1' bis(1-hydroxyethyl)ferrocene A description is given of the preparation of the initial dinitriles, and of the identification of the compounds obtained by their IR, ^1H and ^{13}C NMR, and mass spectra The possible conformations of macrocylic ferrocenophanes are discussed

Introduction

As a continuation of the study of the synthesis and properties of ferrocenes [1-12], we employed the method of cyclization of 1,1'-bis(ω-cyanoalkyl)ferrocenes to synthesize ferrocenophanes

[*m*] Ferrocenophanes with relatively small heteroannular bridges (m = 2-5) have already been studied in adequate detail [1,13] and whilst only a few studies of ferrocenophanes with average-sized bridges (m = 6-10) have been published [14-17] the macrocyclic bridged ferrocenes ($m > 10$) have not been described until now

The only general method available for preparing ferrocenophanes of different bridge lengths, (acyloin condensation) has been used in the synthesis of bridged ferrocenes with short- and average-length bridges (m = 4,6,8,9 or 10) [14,15] but the acyloin ferrocenophanes produced in this way were not studied by chemical or physical methods. It should be noted that acyloin condensation is unsuitable for the synthesis of ferrocenophanes containing an odd number of methylene units since in such cases it would be necessary to use the asymmetric 1,1′ bis(ω-carbmethoxyalkyl)ferrocenes as starting compounds and these are not readily available

The aim of the present study was to develop a method of synthesizing ferrocenophanes with different bridge lengths but in particular those with long bridges ($m > 10$) The method we used was that of cyclization of dinitriles discovered by Thorpe and used by him for the preparation of 5 and 6-membered rings [18-20] This method has also been employed for the synthesis of macrocycles by Ziegler [21-25] The literature data (Fig 1) indicate that unlike acyloin condensation, dinitrile cyclization does not provide good yields of average-sized rings (n = 9 13) [26-28] The rather high yields of these rings in the acyloin condensation reaction may be explained by the fact that it is a heterophase reaction In the synthesis of short bridged rings dinitrile condensation gives better yields in comparison with acyloin condensation The yields of the larger cyclic compounds increase with increasing ring size [26-28]

Recently dinitrile cyclization has been used for the synthesis of derivatives of cyclopentane [29,30], cyclohexane [31], indol [32] and six-membered cycles containing nitrogen [33] and phosphorus [34] This method was also successfully used in the synthesis of catenanes [35,36] Ethylsodium in ethanol [18-20, 32], sodium tert-butoxide [30,34], magnesium tert-butylamide [30], naphthalenesodium [33], and *N*-methylanilinemagnesium bromide [31] were used as condensation agents Ziegler's sodium *N*-methylanilide was used in the synthesis of macrocycles [21-25]

The long bridged ferrocenophanes obtained in the present work are interesting from different aspects Noteworthy was the presence of a minimum in ferrocenophane yield versus bridge length, as in the case of alicyclic compounds [26-28], which must be linked with the conformational lability of the molecule The molecules of [*m*]ferrocenophanes with short bridges (m = 2,3,4) are strained and therefore possess limited lability For example it is known that in [2]ferrocenophane the dihedral angle between the rings is equal to 23° [37] while in [3]ferrocenophane-1-one it is 9° [38] In [4]ferrocenophane the rings are probably parallel, but the bridge is rather short which considerably restricts ring vibrations In [5]ferrocenophane the rings may vibrate about the axis passing through the cyclopentadienyl ring centers and iron atom In this case the angle of deviation of each ring carbon may be equal to or greater than $2\pi/5$ Such vibrations occur with bridge inversion and this was identified by us from changes in the ^{13}C NMR spectra [1,8] Temperature variation results in a change of conformer populations and in the variation of chemical shifts of the 2- and 3-bridge carbon atoms vibrating in the nonhomogeneous deshielding field of the ferrocene fragment

As can be seen from models one of the possible conformations of ferrocenophanes with $m \gtrsim 15$ is a structure with part of the bridge lying above the plane of one cyclopentadienyl ring In realizing such a conformation the introduction of a substituent X into one asymmetric position of the bridge would produce two topological conformers* e g structures A and B ($n > m$) More-

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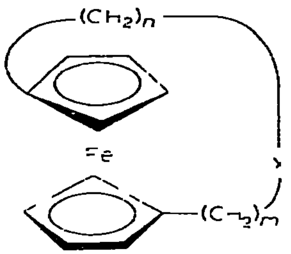
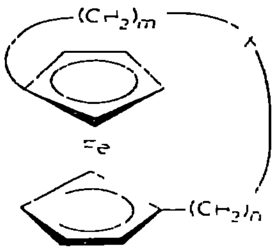
[*] The topological problems of chemistry have been reviewed by Prelog [39] and Sokolov [40]

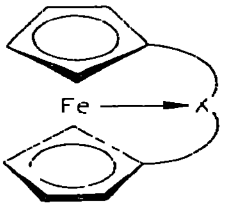


(A)



(B)

over in [*m*]ferrecenophanes with certain groups as substituent X a transannular effect may be expected [27,41,42] [i e the effect of the iron atom on group X (structure C)] The transannular effect should be most clearly pronounced in



(C)

ferrocenophanes with short bridges but its appearance may also be expected in average and long bridged ferrocenes An example of the iron effect could be a discovery of Fe OH coordination in hydroxyl ferrocenophanes such as has been found in non bridged ferrocenes [43,44] Certain Japanese authors have observed the effect of the iron atom in the carbene produced from [3]ferrocenophane-2-one [45] and stabilization of the cationic center at the β-position of the bridge with the iron atom in [4]ferrocenophane [46] In both cases the through space transannular iron effect may be pronounced

Results and discussion

1,1'-Disubstituted ferrocenes

The heteroannular bis(ω cyanoalkyl)ferrocenes we used for the synthesis of ferrocenophanes were hitherto unknown with the exception of 1,1'-bis(cyanomethyl)ferrocene (Ia) This was obtained by Sonoda and Montani [45] by the following scheme

$$\mathrm{Fcd(COCH_3)_2 \rightarrow Fcd(COOH)_2 \rightarrow Fcd(COOCH_3)_2 \rightarrow Fcd(CH_2OH)_2 \rightarrow}$$
$$\mathrm{Fcd(CH_2Cl)_2 \rightarrow Fcd(CH_2CN)_2 \quad (Fcd = C_5H_4FeC_5H_4)}$$

We used this same procedure for the synthesis of Ia

1,1'-Bis(2-cyanoethyl)ferrocene (Ib) had been isolated earlier by us in small quantities from cyanoethylation of ferrocene [2] and cyclopentadiene with

TABLE 1

PHYSICAL CONSTANTS AND ANALYSES OF FERROCENES $(C_5H_4R)_2Fe$ AND FERROCENOPHANES

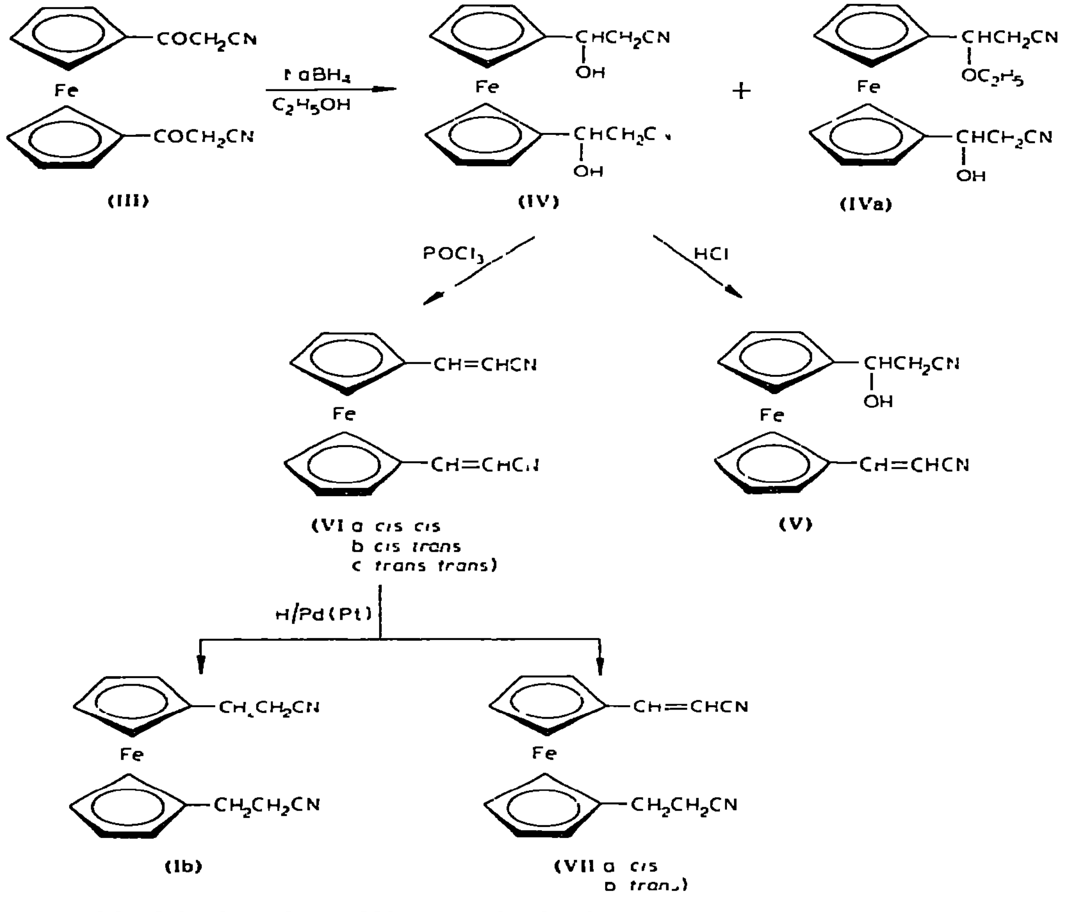
No	R or bridge	M p (dec) (°C)	Formula	Analysis found (calcd) (%)			
				C	H	N	Fe
Ib	—CH_2CH_2CN	69	$C_{16}H_{16}FeN_2$	65 87 (65 80)	5 53 (5 48)	9 44 (9 59)	19 61 (19 12)
Ic	—$(CH_2)_3CN$	43 5-44	$C_{18}H_{20}FeN_2$	67 21 (67 51)	6 32 (6 29)	8 70 (8 75)	
Id	—$(CH_2)_5CN$	50 51	$C_{22}H_{28}FeN_2$	70 63 (70 40)	7 43 (7 52)	7 37 (7 46)	
Ie	—$(CH_2)_7CN$	51 52	$C_{26}H_{36}FeN_2$	72 80 (72 22)	8 41 (8 39)	6 17 (6 47)	
IIa	—$C(CN)=C(NH_2)CH_2$—	(250)	$C_{14}H_{12}FeN_2$	62 93 (63 66)	4 77 (4 58)	10 21 (10 60)	
IIb	—$CH_2C(CN)=C(NH_2)CH_2CH_2$—	(218 220)	$C_{16}H_{16}FeN_2$	66 06 (65 80)	5 67 (5 48)	9 54 (9 59)	
IIc	Polymer	Oil	$(C_{18}H_{20}FeN_2)_n$	68 76 (67 51)	6 28 (6 29)	9 09 (8 75)	
IId	—$(CH_2)_4C(CN)=C(NH_2)(CH_2)_5$—	140-142	$C_{22}H_{28}FeN_2$			7 57 (7 46)	
IIe	—$(CH_2)_6C(CN)=C(NH_2)(CH_2)_5$—	108 112	$C_{26}H_{36}FeN_2$	72 76 (72 22)	8 41 (8 39)	6 44 (6 47)	
IV	—$CH(OH)CH_2CN$	122 124	$C_{16}H_{16}FeN_2O_2$	58 72 (59 28)	5 04 (4 98)	8 70 (8 64)	
IVa	—$CH(OH)CH_2CN$ —$CH(OC_2H_5)CH_2CN$	Oil	$C_{18}H_{20}FeN_2O_2$	61 95 (61 33)	5 52 (5 72)		
V	—$CH(OH)CH_2CN$ —$CH=CHCN$	Oil	$C_{16}H_{14}FeN_2O$	62 17 (62 76)	4 60 (4 61)	9 15 (9 15)	
VIa	—$CH=CHCN$(*cis cis*)	114	$C_{16}H_{12}FeN_2$	67 04 (66 69)	4 15 (4 20)	9 72 (9 72)	19 89 (19 38)
VIb	—$CH=CHCN$(*cis trans*)	78	$C_{16}H_{12}FeN_2$	66 80 (66 69)	4 25 (4 20)		19 28 (19 38)
VIc	—$CH=CHCN$(*trans trans*)	147 147 5	$C_{16}H_{12}FeN_2$	66 36 (66 69)	4 32 (4 20)		19 62 (19 38)
VII	—CH_2CH_2CN (*cis* and *trans* —$CH=CHCN$ mixture)		$C_{16}H_{14}FeN_2$	66 85 (66 23)	5 23 (4 86)	9 65 (9 65)	
X	—$(CH_2)_3CONH_2$	139 5 140 5	$C_{18}H_{24}FeN_2O_2$	60 59 (60 68)	6 45 (6 79)	7 79 (7 86)	
XI	—$CO(CH_2)_4Cl$	80	$C_{20}H_{24}Cl_2FeO_2$	56 80 (56 75)	5 95 (5 71)		
XII	—$CO(CH_2)_6Cl$	77	$C_{24}H_{32}Cl_2FeO_2$	60 56 (60 11)	6 81 (6 74)		
XIII	—$(CH_2)_5Cl$	Oil	$C_{20}H_{28}Cl_2Fe$	61 68 (60 77)	7 36 (7 13)		
XIV	—$(CH_2)_7Cl$	Oil	$C_{24}H_{36}Cl_2Fe$	65 44 (65 30)	8 05 (8 22)		13 03 (12 65)
XVI	—$CH(CH_3)OCH_2CH_2CN$	Oil	$C_{20}H_{24}FeN_2O_2$	62 75 (63 17)	6 34 (6 36)	6 62 (7 37)	
XVIII	—$(CH_2)_6CH(CN)CO(CH_2)_7$—	(73 77)	$C_{26}H_{35}FeNO$	72 50 (72 05)	8 17 (8 14)	3 22 (3 23)	
XIX	—$(CH_2)_5CO(CH_2)_5$—	81 83	$C_{21}H_{28}FeO$	71 56 (71 59)	8 03 (8 02)		
XX	—$(CH_2)_7CO(CH_2)_7$—	53 56	$C_{25}H_{36}FeO$	73 60 (73 53)	8 92 (8 88)		
XXI	—$(CH_2)_6CH(CN)(CH_2)_8$— mix	51 52	$C_{26}H_{37}FeN$	74 79	8 58	3 29	
XXII	—$(CH_2)_6C(CN)=CH(CH_2)_7$ ture?		$C_{26}H_{35}FeN$	(74 45) (74 81)	(8 89) (8 45)	(3 34) (3 40)	
	—$COC(CH_3)_2CN$	144 5-146	$C_{20}H_{20}FeN_2O_2$	63 94 (63 84)	5 58 (5 36)	7 36 (7 45)	
	—$CH=CHCOOC_2H_5$	98 5-99 5	$C_{20}H_{22}FeO_4$	63 19 (62 84)	5 83 (5 80)		14 63 (14 62)

subsequent treatment with FeCl$_3$ [3] These methods, however, are not preparative and thus we used another method for the synthesis of compound Ib

In the synthesis of 1,1'-bis(2-cyanoethyl)ferrocene we used heteroannular bis(cyanoacetyl)ferrocene (III) (Scheme 1) prepared by condensation [47] of dimethyl 1,1'-ferrocenedicarboxylate [45] with acetonitrile Compound III was reduced with sodium borohydride to the hydroxynitrile IV (physical constants and elemental analysis of all compounds obtained are shown in Table 1) A quantity of 1-(1-ethoxy-2-cyanoethyl) 1'-(1-hydroxy 2-cyanoethyl)ferrocene (IVa) was also isolated The structures of compounds IV and IVa were confirmed by the IR, PMR and mass spectra (see Experimental)

In the course of isolation from the reaction mixture compound IV underwent partial dehydration to give two isomers of 1-(1-hydroxy-2-cyanoethyl)-1'(2-cyanovinyl)ferrocene It is known that 1,1' bis(1 hydroxyalkyl)ferrocenes are readily dehydrated by HCl to give bridged oxygen-containing ferrocenes [1] The first step of dehydration is formation of the α-ferrocenyl carbocation Its cationic center then attacks the hydroxyl group intramolecularly If the

SCHEME 1



CH_2CN group is adjacent to the carbocation center then proton elimination from the β-position with respect to the ferrocenyl nucleus takes place with formation of a double bond. Thus, by shaking an ethereal solution of compound IV with dilute HCl 1-(1-hydroxy-2-cyanoethyl)-1′-(2-cyanovinyl)ferrocene is obtained as the *trans*-isomer. $POCl_3$ was used for complete dehydration of compound IV. Thus, a mixture of three isomers of bis(2-cyanovinyl)ferrocene (VI) was obtained.

It may be expected that the less electron-withdrawing carbethoxylic group in the β-position to the cationic center would lead to the formation of oxygen-containing ferrocenes by dehydration of the respective diols. However in this case dehydration occurs readily to give 1,1′ bis(2-carbethoxyvinyl)ferrocene. In the synthesis of diols IV and 1,1′-bis(1-hydroxy 2-carbethoxyethyl)ferrocene by reduction with $NaBH_4$ partial dehydration may be avoided if the reaction is conducted in a mixture of ethanol and ethyl bromide.

A sample of the mixture of isomers of VI was separated by TLC on alumina. The three isomers have the following order of decreasing solubility and R_f: VIa > VIb > VIc. Compounds VI were characterized by means of the ^1H and ^{13}C NMR, IR, electronic and mass spectra discussed elsewhere [4,12]. We note that 1,1′-bis(2-cyanovinyl)ferrocene has been obtained recently by palladium catalyzed ferrocenylation of acrylonitrile [48].

The mixture of isomers of 1,1′-bis(2-cyanovinyl)ferrocene (VI) was hydrogenated to 1,1′-bis(2-cyanoethyl)ferrocene. Hydrogenation of compound VI by hydrogen on platinum resulted in partial reduction of the nitrile groups with the formation of large quantities of amine products. The yield of Ib was rather low. Hydrogenation with tetraline on palladium black gave better results. Compound Ib was isolated from the reaction mixture by subsequent oxidation to the ferricinium cation and subsequent reduction. The quality of the palladium black affects the yield of 1,1′-bis(2-cyanoethyl)ferrocene in the hydrogenation with tetraline. If the palladium black is not freshly prepared only partial reduction occurs, together with formation of Ib and two isomers of 1-(2-cyanovinyl)-1′-(2-cyanoethyl)ferrocene (VII). The configurations of these compounds were established on the basis of ^1H NMR spectra [4].

In the IR spectrum of compound Ib the nitrile group vibration appears at 2251 cm^{-1}. The ^1H NMR spectrum of Ib is a typical AA′BB′ pattern for cyclopentadienyl ring protons centered at 4.09 ppm, the difference between H_α and H_β absorptions is quite small (2.2 Hz at 90 MHz). The protons of the cyanoethyl groups appear in the form of a typical A_2B_2 spectrum (J_{AB} 6.9 Hz).

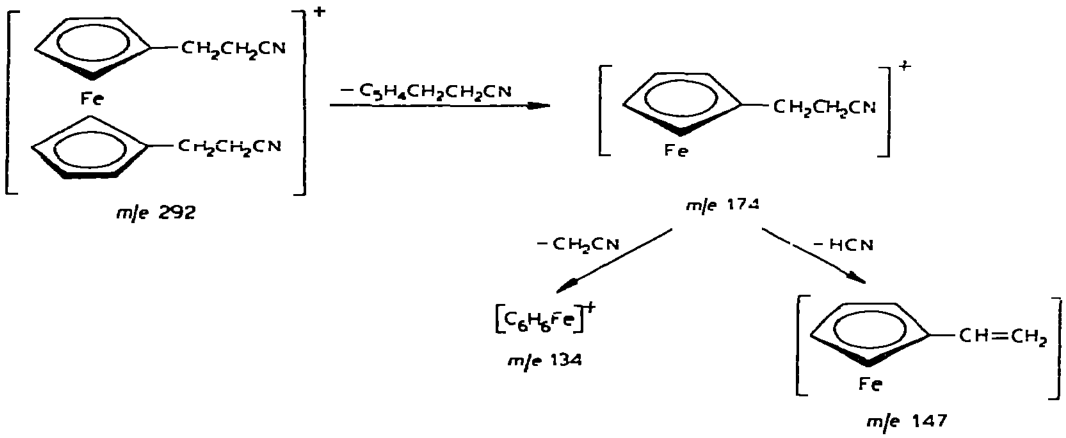
In the mass spectrum of compound Ib the most intense peak at *m/e* 174 corresponds to the $[FeC_5H_4CH_2CH_2CN]^+$ fragment. Decay of the molecular ion Ib is shown in Scheme 2. We note that generally the first step of the decay of heteroannular disubstituted nonbridged ferrocenes [49-51] involves elimination of the C_5H_4R fragment

$$[(C_5H_4R)_2Fe]^+ \xrightarrow{-C_5H_4R} [C_5H_4RFe]^+$$

1,1′ Bis(3-cyanopropyl)ferrocene (Ic) was obtained from 1,1′-bis(carboxypropyl)ferrocene (VIII) prepared from ferrocene by two steps [52]

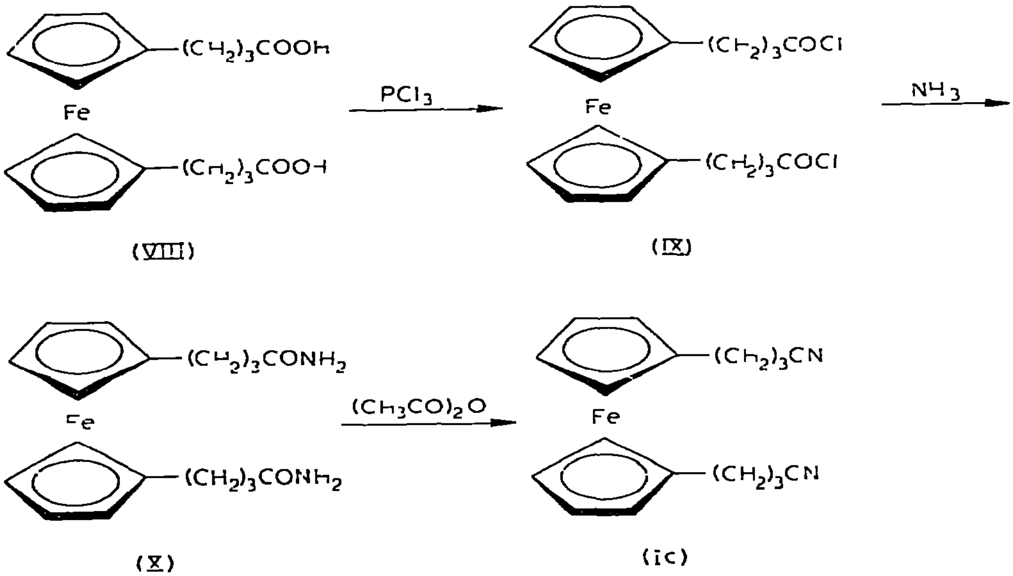
$$FcdH_2 \rightarrow Fcd(COCH_2CH_2COOH)_2 \rightarrow Fcd(CH_2CH_2CH_2COOH)_2$$

SCHEME 2



By the action of PCl_3 on the dicarboxylic acid (VIII) the dichloride IX was obtained, this compound was treated with ammonia without being isolated The diamide X thus produced then afforded 1,1′-bis(3-cyanopropyl)ferrocene (Ic) on heating to 130° in acetic anhydride (Scheme 3) The IR spectrum of X shows an intense band at 1655 cm^{-1} (C=O) and further broad, intense bands

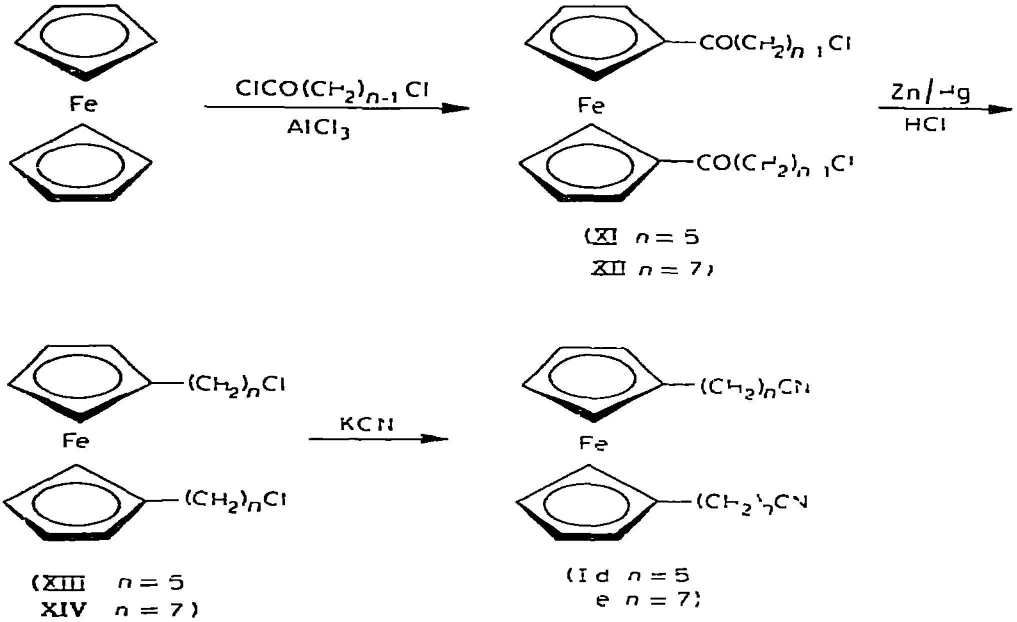
SCHEME 3



at 3180 and 3385 cm^{-1} (NH_2) The IR spectrum of compound Ic exhibits an intense band at 2246 cm^{-1} (CN)

1,1′-Bis(5-cyanopentyl)ferrocene (Id) and 1,1′-bis(7-cyanoheptyl)ferrocene (Ie) were synthesized by the same method (Scheme 4) In the preparation ferrocene was acylated with the respective (ω-chloroalkyl)carbonyl chloride to give compounds XI and XII, these were then subjected to Clemmensen's reduction to give the bis(ω-chloroalkyl)ferrocenes XIII and XIV The reaction of XIII and XIV with KCN in ethanol or dimethyl sulfoxide gave the respective nitriles Id and Ie

SCHEME 4



Compounds XI, XII, Id and Ie are crystalline solids while compounds XIII and XIV are orange colored oils The IR spectrum of XI showed a ketone group absorption at 1669 cm^{-1} (in KBr) In the spectrum of XII the ketone group band is split if taken as KBr pellets (1661 and 1674 cm^{-1}), however, in solution in CCl_4 only one band, at 1678 cm^{-1}, appeared The nitrile groups in compounds Ie and Id appeared as several broadened bands at 2255 and 2249 cm^{-1} respectively The ^{1}H NMR spectra of these compounds are summarized in Table 2

We also prepared the heteroannular ferrocene dinitrile derivatives with oxygen atoms in the chain Compound XVI (Scheme 5) was obtained by cyanoethylation of diol (obtained by reduction of diacetylferrocene) with acrylonitrile in the presence of KOH in dioxane The IR spectrum of this compound showed an intense band at 2252 cm^{-1} (CN). Its structure was confirmed by its ^{1}H NMR spectrum (Table 2)

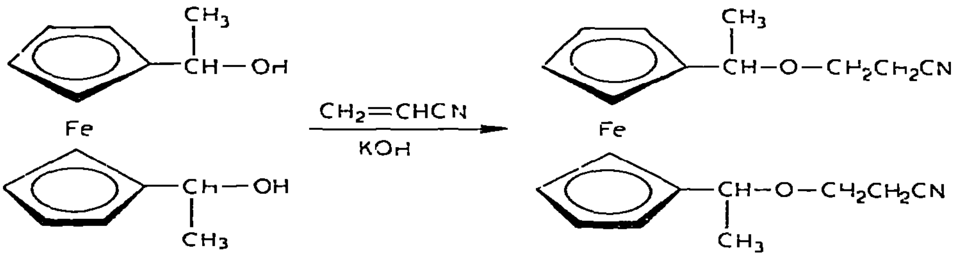
TABLE 2

^{1}H NMR SPECTRA OF FERROCENES $(C_5H_4R)_2Fe$ AND FERROCENOPHANES (δ ppm)^a

No	R or bridge	Solvent	Cyclopentadienyl rings signals H_α H_β	Other signals
Ib	$-CH_2^aCH_2^bCN$	$CHCl_3$	4 09m	2 30 2 80m(H^a and H^b) (J_{ab} 6 9 Hz)
Ie	$-(CH_2)_7CN$	CS_2	3 83s	2 03 2 45m(8H) 1 19 1 63m(20H, CH_2)
IIb	$-CH_2(CN)=C(NH_2)CH_2CH_2-$	$CDCl_3$	4 05s	2 55s 3 05s (CH_2)
IId	$-(CH_2)_4(CN)=C(NH_2)(CH_2)_5-$	$CHCl_3$	4 03s	1 40 1 87m(CH_2)
IVa	$-CH(OH)CH_2CN$ $-CH(OC_2H_5)CH_2CN$	$CHCl_3$	4 19	1 32t(C_2H_5) 2 93($CHCH_2$)
V	$-CH^a=CH^bCN$ $-CH(OH)CH_2CN$	Acetone	4 77 4 62 4 31	7 50d(H^a) (J_{ab} 15 7 Hz)
VIa	$-CH^a=CH^bCN-$ *cis cis*	C_6F_6	4 77t 4 54t	6 87(H^a) 5 31d(H^b) (J_{ab} 11 2 Hz)
VIc	$-CH^a=CH^bCN$ *trans trans*	Acetone	4 66t 4 53t	7 30d(H^a) 5 73d(H^b) (J_{ab} 16 4 Hz)
VIIa	$-CH_2CH_2CN$ $-CH^a=CH^bCN$-*cis*	C_6F_6	4 28s 4 82t 4 59t	2 50 2 90m(CH_2CH_2) 7 09d(H^a) 5 33d(H^b) (J_{ab} 12 6 Hz)
XI	$-CO(CH_2)_4Cl$	$CHCl_3$	4 80t 4 53t	3 47 3 67m($ClCH_2$ 4H) 2 51 2 93 m(CH_2 4H) 1 67 2 05m(CH_2 8H)
XII	$-CO(CH_2)_6Cl$	$CHCl_3$	5 02t 4 72t	3 88t ($ClCH_2$ 4H) 2 57 2 92m(CH_2 4H), 1 23 2 05m(CH_2 16H)
XIII	$-(CH_2)_5Cl$	CS_2	3 84s	3 39t($ClCH_2$ 4H) 2 05-2 41m(CH_2 4H) 1 17 1 92m(CH_2 12H)
XIV	$-(CH_2)_7Cl$	CS_2	3 80s	3 45t($ClCH_2$ 4H) 2 09 2 45m(CH_2 4H) 1 11 1 97m(CH_2 20H)
XVI	$-CH^a(CH_3^b)OCH_2^cCH_2^dCN$	$CHCl_3$	4 08s	4 30q(H^a) 1 42d(H^b) 2 42m(H^c), 3 50m(H^d)
XVIII	$-(CH_2)_6CH(CN)CO(CH_2)_7-$	CS	3 86m	1 20 2 93(CH_2)
XIX	$-(CH_2)_5CO(CH_2)_5-$	CS_2	3 89m	1 12 1 99m(12H) 1 99 2 61m(8H CH_2)
XX	$-(CH_2)_7CO(CH_2)_7$	CS_2	3 83m	1 13 1 89m(20H) 2 09 2 49m(8H CH_2)
XXI XXII	$-(CH_2)_6CH(CN)(CH_2)_8-$ $-(CH_2)_6C(CN)=CH(CH_2)_7-$	CS_2	3 88	2 04 2 48m(6H) 1 13 1 84(22H CH_2)
	$-COC(CH_3)_2CN$	$CHCl_3$	5 21t 4 86t	1 67(CH_3)
	$-CH^a=CH^bCOOC_2H_5$	CCl_4	4 42t 4 34t	7 33d(H^a) 5 89(H^b) (J_{ab} 16 0 Hz) 1 29t 4 17q(C_2H_5)

^{a} s singlet t triplet q quartet m multiplet

SCHEME 5

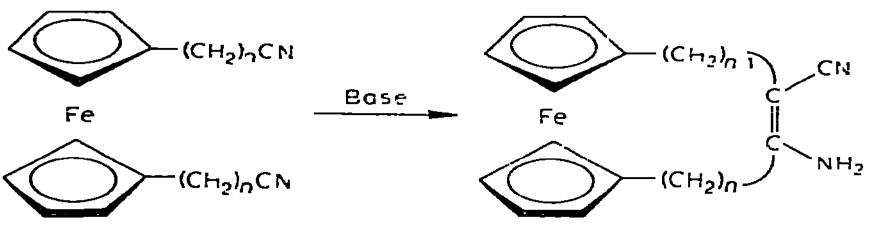


(XV) (XVI)

Ferrocenophanes

We found that under the action of a base, 1,1'-bis(ω-cyanoalkyl)ferrocenes cyclize to the bridged derivatives II Condensing agents used were methylmagnesium iodide [for cyclization of 1,1'-bis(cyanomethyl)ferrocene] and sodium *N*-methylanilide (for cyclization of other nitriles) In both cases the reaction was carried out in ether (Scheme 6)

SCHEME 6



(I a $n = 1$
b $n = 2$
d $n = 5$
e $n = 7$)

(II a $n = 1$, $m = 3$,
b $n = 2$ $m = 5$,
c $n = 5$, $m = 11$,
e $n = 7$, $m = 15$)

In the case of dinitriles Ia and Ib the cyclization occurs without much diluting The Ruggli-Ziegler rule [22-25] of diluting should be applied in the cyclization of dinitriles Id and Ie In these latter two cases the cyclization reaction was carried out in a special vessel The cyclization was performed by refluxing the reaction mixture with the ethereal dinitrile solution being added slowly dropwise to the solvent condensate However, even upon considerable dilution the nitriles Id and Ie gave appreciable amounts of polymeric products

The dinitrile Ic (n = 3) afforded traces of cyclization products Generally this was the starting compound Ic with some quantity of polymer The low yield of the dinitrile Ic cyclization product may be explained by the fact that 1,1'-bis(3-cyanopropyl)ferrocene has a chain length corresponding to the aliphatic dinitriles which produce average sized cycles (Fig 1) in low yields

We also failed to cyclize 1,1' bis[*O*-(2-cyanoethyl) 1-hydroxyethyl]ferrocene (XVI) Heating an ethereal solution of XVI with sodium *N*-methylanilide gave only a decyanoethylation product XV, together with XVI Action of the base led to formation of the carbanion XVIa which unlike the cases already mentioned decomposed with acrylonitrile elimination

Dinitrile cyclization involves the intermediate formation of carbanion R—$^-$CH—CN In 1,1'-bis(cyanomethyl)ferrocene the anionic center is adjacent to the ferrocenyl fragment In spite of the fact that the ferrocenyl nucleus considerably stabilizes the α-carbocationic center an example of α,α-ferrocenyl

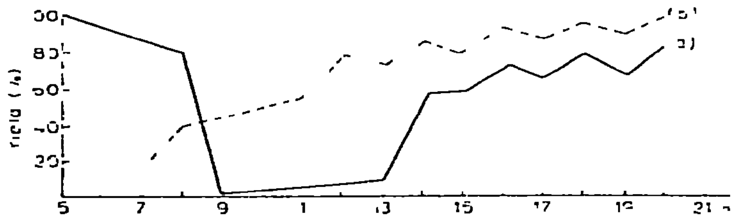
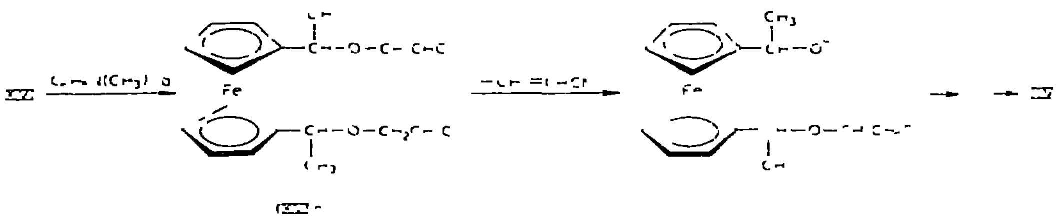


Fig 1 Yield of cyclic compound vs cycle dimensions (a) dinitrile cyclization (b) acyloin condensation

SCHEME 7



dicarbanion formation (by treatment of ferrocenylacetonitrile with butyllithium) has been reported [53,54] Treatment of ferrocenylacetonitrile with methylmagnesium chloride is also known to afford a carbanion which then attacks the second ferrocenylacetonitrile molecule at the nitrile group giving rise to a noncyclic cyanenamine 3 amino-2,4-diferrocenylcrotonitrile [55,56]

Cyclization of compounds I yielded the respective cyanenamines (II) The light yellow, highly fusible, crystalline solids formed possess rather low solubilities in ether and are almost insoluble in hexane Solubility increases with increasing bridge length in the series IIa < IIb < IId < IIe, melting points decrease on going from IIa to IIe

The samples of compound II for analysis and spectral measurements were isolated by TLC on alumina and purified by crystallization The poor solubility of compound IIa made chromatography unnecessary

As has been noted already the dependence of [*m*] ferrocenophane yield on bridge length in the cyclization of dinitriles is at a minimum at $m = 7$ This minimum corresponds to the low yields of alicyclic compounds with $n = 9$-13 in the Thorpe-Ziegler reaction (Fig 1)

For steric reasons the CN and NH_2 groups in 2-amino-1-cyano[3]ferrocenophane should occupy *cis*-positions with respect to the double bond The *cis*-configuration may also be assumed to be retained in the highest analogs

All cyanenamine derivatives II show a band at 2180 2190 cm^{-1} in the IR spectrum due to the nitrile group vibration (Table 3) Such a low frequency (in the primary and secondary aliphatic nitriles this band is observed at 2240 2260 cm^{-1} [57]) may be explained by mutual conjugation of the nitrile group with the double bond and the amino group

TABLE 3

IR DATA FOR FRAGMENT $-C(CN)=C(NH)_2-$ OF [*m*]FERROCENOPHANES (ν cm^{-1} KBr)

No	*m*	C=C	C≡N	NH_2			
				Stretch	Other		
IIa	3	1576	2180	1651	3416	3348	3249
IIb	5	1592	2185	1655	3430	3345	3250
IId	11	1600	2188	1646	3467	3340	3249 3229
IIe	15	1596	2181	1645	3460	3345	3248 3228

The stretching mode of the amino group appears as three intense bands at 3200-3500 cm^{-1} (KBr pellets) In the case of [11]- and [15]ferrocenophanes the band at 3250 cm^{-1} is split into two lines 3-Amino-2,4-diferrocenylcrotonitrile [55] showed four bands in KBr, but in CCl_4 only two peaks were observed [56] The presence of four bands in KBr may be explained by the existence of hydrogen bonds in the solid form We note that the spectra of 2-aminoanthraquinone and β-naphthylamine also had three bands in the 3200-3500 cm^{-1} region which may be due to hydrogen bond formation between NH_2 groups [58].

The spectra of all ferrocenophanes II showed two strong bands of nearly equal intensity at 1600-1650 cm^{-1} Hammer and Hines [29] observed these bands at 1605 and 1645 cm^{-1} in the IR spectrum of 1-amino 2-cyanocyclopentene-1 obtained from adiponitrile They assigned the first of these bands to the double bond vibration and the second to the NH_2 bending However, Pauson and Toma [56] have assigned the band at 1635 cm^{-1} in the IR spectrum of 3-amino-2,4-diferrocenylcrotonitrile to the bending mode of the double bond

Compound IId was deuterated by shaking its ether solution with a solution of NaOD in D_2O The IR spectrum of deuterated compound II showed new bands at 2400-2600 cm^{-1} (Fig 2) due to the N—D vibrations, but the bands at 3450 and 1495 cm^{-1} appear as well Attention is drawn to the change in relative intensities of the bands at 1600 and 1646 cm^{-1} On deuteration the intensity of the second band decreases somewhat which is in agreement with its assignment to the NH bending mode

The low value of the C=C bending frequency in the spectrum of compound Ia is worthy of note In general the value of ν(C=C) increases with increasing bridge length (Table 3) This may be explained by the decreasing strain in ferrocenophanes in the order (m=) 3 > 5 > 11 > 15 In the case of cycloalka-

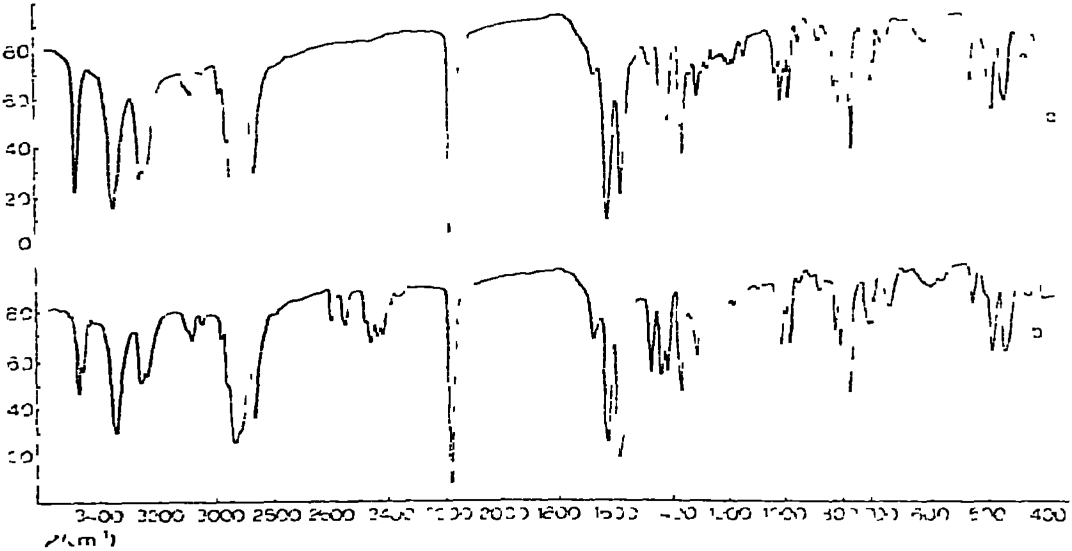


Fig. 2 IR spectra (KBr) (a) compound IId (b) deuterated IId

nes ν(C=C) also increases with decreasing strain in the series cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene (1570, 1615, 1654, 1650 and 1664 cm^{-1} respectively) [59] Cyclopropene is an exception in this series (1641 cm^{-1}) It may be expected that a decrease of double bond conjugation with the ferrocenyl fragment in [3]ferrocenophane-1-ene should enhance ν(C=C) analogously to the case of aromatic compounds [60] but on going from vinylferrocene to [3]ferrocenophane-1-ene the value of ν(C=C) increases (1635 [61,62] and 1641 [45] cm^{-1} respectively) Probably in this case a decrease in conjugation [and thus an increase in ν(C=C) is dominant over the increase of strain [and thus a decrease in ν(C=C)] Since the double bond in 2 amino-1-cyano[3]ferrocenophane-1-ene (IIa) is close to the iron atom, a direct interaction between the iron atom and the double bond can not be excluded and this shows itself in the lower ν(C=C) for this compound We also note a decrease in the absorption frequency of the antisymmetric NH_2 stretching modes from 3416 for IIa to 3467 and 3460 cm^{-1} for IId and IIe respectively This indicates hydrogen bond enhancement

The IR spectra of ferrocenophanes obtained by cyclization of 1,1'-bis(ω-cyanoalkyl)ferrocenes are thus in better agreement with the cyanenamine structure II [—C(CN)=C(NH_2)—] than with the imine structure [—CH(CN)C(=NH)—] assumed earlier for similar compounds [18-20]

The mass spectra of ferrocenophanes II confirm a monomeric structure and the most intense peaks are due to the molecular ion All other peaks are less than 10% of the intensity of M^+ in the spectra of IId and IIe but it is interesting that the spectrum of IIa exhibits a rather strong peak at *m/e* 237 (14% of M^+) corresponding to $[M - HCN]^+$ In the spectrum of IIb the ion $[M - HCN]^+$ has a much lower intensity (4% of M^+) while in the spectra of IId and IIe the corresponding intensities are weak IIb shows a fairly intense peak at *m/e* 277 (M^+ — NH) It may be assumed that in ferrocenophanes with short bridges (IIa and IIb) the iron atom exerts influence over the functional groups in the bridge and this alters the fragmentation pattern on going from IIa and IIb to IId and IIe The mass spectra of ferrocenophanes II are described in the Experimental section The ^{1}H NMR spectra of ferrocenophanes IIb and IId are described in Table 2

Ferrocenophanes IId and IIe are converted to XVII and XVIII on being shaken with dilute H_2SO_4 (Scheme 8) Compounds XVII and XVIII could not be purified by chromatography on alumina because of the presence of the acidic hydrogen atom in —CO—CH(CN)— Similar labile hydrogen atoms in cyanoketone III may be substituted by methyl groups upon refluxing an alkaline solution of III in alcohol with CH_3I This affords the fully methylated 1,1'-bis(dimethylcyanoacetyl)ferrocene

Cyanoketones XVII and XVIII afford ketones XIX and XX on refluxing with concentrated HCl/CH_3COOH Heating IIc with 50% H_2SO_4 (analogously to the synthesis of alicyclic ketones in the preparation of catenanes [35]) completely destroys the ferrocene nucleus Refluxing IIc in a HCl/CH_3COOH mixture gave large quantities of decomposition products Ketones XIX and XX were isolated by TLC on alumina

The ketone carbonyl absorptions in the IR spectra of ketones XIX and XX are shown in Table 4 As a comparison Table 4 also shows the ν(CO) values

SCHEME 8

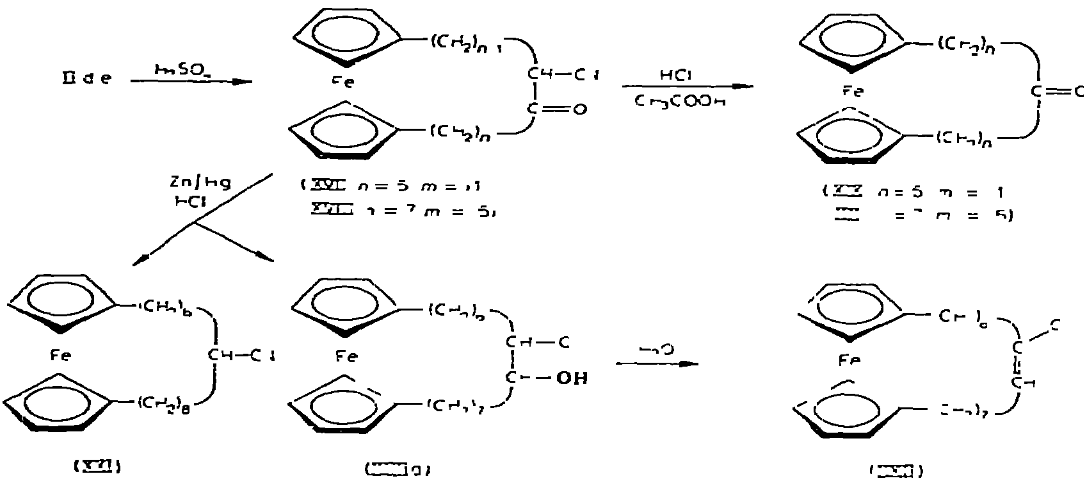


TABLE 4

IR DATA FOR SOME KETONES

Compound	Solvent	ν(C=O) cm^{-1}	Ref
Cyclobutanone	Liquid	1775	64
Cyclopentanone	Liquid	1740	64
	CCl_4	1751	65
Cyclohexanone	Liquid	1710	64
	CCl_4	1718	65
Cycloheptanone	Liquid	1699	66
	CCl_4	1706	65
Cyclooctanone	Liquid	1692	26
	CCl_4	1704	65
Cyclononanone	Liquid	1698	26
	CCl_4	1703	65
Cyclodecanone	Liquid	1694	26
	CCl_4	1705	65
Cycloundecanone	Liquid	1700	26
Cyclododecanone	Liquid	1697	26
	CCl_4	1713	65
Cyclotridecanone	Liquid	1707	26
	CCl_4	1713	65
Cyclotetradecanone	CCl_4	1714	65
Cyclopentadecanone	CCl_4	1715	65
Didecylketone	CCl_4	1718	67
Acetone	CCl_4	1724	67
[3]Ferrocenophane-2-one	Nujol	1690	45
	CCl_4	1703	63
[4]Ferrocenophan-2-one		1706	68
[5]Ferrocenophan 3-one	Nujol	1698	69
[11]Ferrocenophan-6-one	KBr	1712	a
[15]Ferrocenophan-8-one	KBr	1710	a
	CCl_4	1712	a

[a] This work

for alicyclic ketones and the other ferrocenophanones Attention may be drawn to the low values in the cases of [3]ferrocenophan-2-one, [4]ferrocenophan-2-one and [5]ferrocenophan-3-one A similar decrease of ν(CO) in the spectra of cyclic ketones with ring sizes of between 7 and 12 units has been explained by transannular interaction of each C=O group with the opposite alicyclic methylene group [41,42] The strained bridge in [3]ferrocenophan-2-one should enhance ν(CO) (analogously to the value 1775 for cyclobutanone, as against 1715 cm^{-1} in cyclopentadecanone), however, the CO group in the IR spectrum of this compound appears only at 1690 cm^{-1} The possibility that this is a result of the iron *d* electron interaction with carbonyl π-electrons [63] has not been eliminated The carbonyl absorption in macrocyclic ferrocenophanes XIX and XX appears in the region specific to open-chain and macrocyclic ketones (1710-1712 cm^{-1})

In the ^{1}H NMR spectra of ferrocenophanes XIX and XX the cyclopentadienyl ring protons appear in the form of close multiplets at 3 8-3 9 ppm (Fig 3) typical of an AA'BB' system and resembling the one observed in the

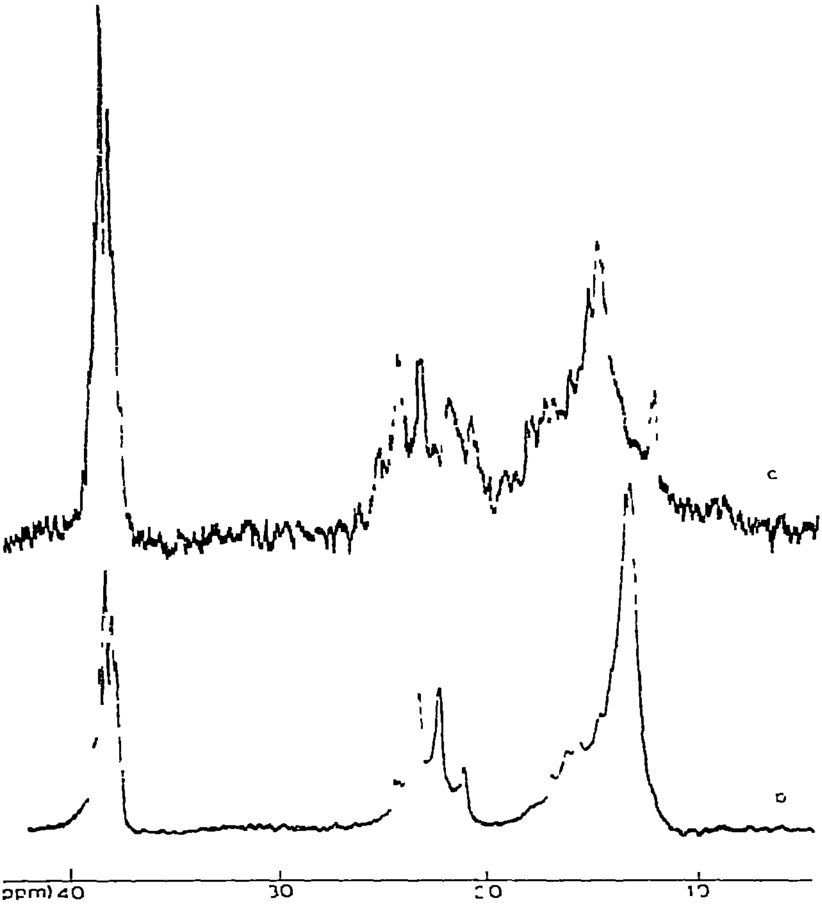


Fig 3 The ^{1}H NMR spectra of (a) compounds XIX and (b) compound XX

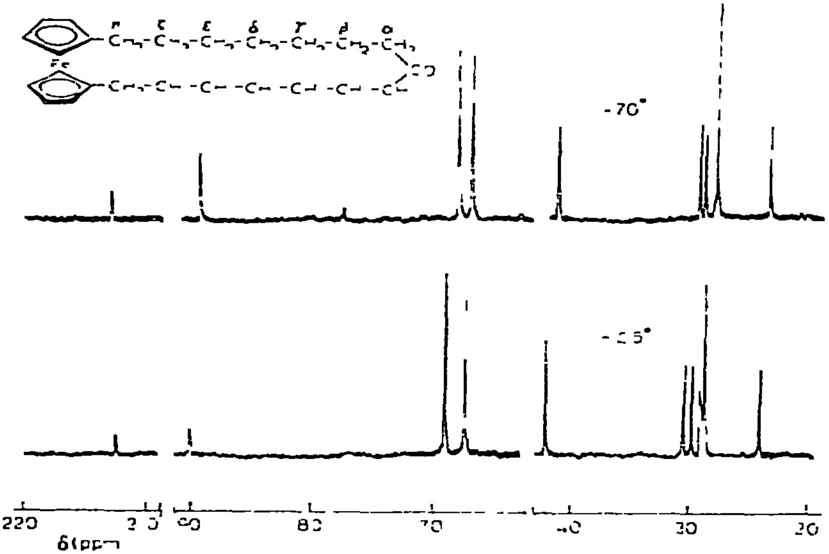


Fig 4 The ^{13}C NMR spectra of compound XX (in CH_2Cl_2)

spectrum of [5]ferrocenophane [8] In the spectra of 1,1'-dialkyl derivatives Ie, XIII and XIV these protons give rise to singlets The methylene protons in XIX and XX appear as complex multiplets at 1 1-2 0 and 2 0-2 5 ppm The relative area of the downfield multiplet is equivalent to 8 protons It probably includes the methylene protons adjacent to the carbonyl group and the cyclopentadienyl ring in the ferrocene fragment [70] We note the difference in multiplet patterns of the CH_2 groups in the spectra of XIX and XX

The spectra of 1,1'-dialkylferrocenes containing functional groups (XIII and XIV) also contain multiplets at 2 0-2 5 ppm The area of this signal in the nitrile derivative is equivalent to 8 protons which could be assigned to the four methylene groups adjacent to the ferrocene nucleus and the nitrile groups In the spectra of the ω-chloroalkyl derivatives of XIII and XIV the CH_2Cl protons are still downfield (3 4 ppm)

We recorded the ^{13}C NMR spectrum of [15] ferrocenophan-8-one (XX) at —70 and +25° (Fig 4) It can be seen from Table 5 that such temperature changes may considerably alter the spectrum of XX, the molecules of which exhibit certain conformational flexibility At high temperatures the C(2,5) and C(3,4) signals shift downfield, the shift being greater in the case of the C(2,5) signal This may serve as evidence that the bridge methylene groups are closer to the α-carbons of ferrocene cyclopentadienyls The bridge α-carbon signals occur at 41-42 ppm (with respect to the carbonyl group) which is in good agreement with the data on cycloalkanes (Table 5) At the higher temperature the 212 ppm carbonyl is shifted upfield The bridge methylene C(β)—C(η) signals appear at 23-30 ppm, the upfield singlet at 23 ppm being due to carbons adjacent to the ferrocene moiety C(η) Other C(β)—C(ξ) signals occur in the narrow range of 27-30 ppm This range is shifted downfield of the cycloalkanone methylene signals (23-25 ppm) which should confirm that all methylene groups

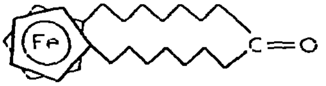
TABLE 5

^{13}C NMR SPECTRA (δ ppm TMS INTERNAL REFERENCE)[a]

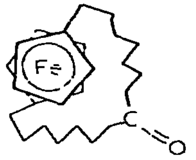
Compound	Temp (°C)	Substituent								Cyclopentadienyl rings		
		C=O	C_α	Other signals						C(1)	C(2 5)	C(3 4)
[15] Ferrocenophan 8 one	−70	212 6	41 0	29 0	28 7	27 4	27 4	27 4	22 9	89 0	67 3	66 3
	+25	211 8	42 0	30 0	29 3	28 6	28 4	28 4	23 9	89 8	68 8	67 0
Cyclooctane	R t[b]		26 1	26 1								
Cyclooctanone[c]	R t	215 9	41 2	26 8	25 1 (C_β and C_γ) 24 3 (C_ω)							
Cyclodecane	R t		25 3	25 3								
Cyclodecanone	R t	212 4	41 3	24 6	24 5	22 9 (C_β C_γ C_δ) 24 7 (C_ω)						
Cyclododecane	R t		23 5	23 5								
Cyclododecanone	R t	207 7	39 8	22 2	24 4	24 3	23 8 (C_β C_ω)					

[a] Solvent for [15] ferrocenophan 8-one CH_2Cl_2 solvent for other ketones CS_2 [b] R t room temperature [c] Data for alicyclic ketones are from ref 77

are located quite close to the iron atom and within the deshielded area of the ferrocenyl moiety Two alternative conformations are possible for compound XX In structure XXa some of the bridge methylene groups are located away



(XXa)



(XXb)

from the ferrocene moiety Structure XXb is more probable with the bridge coiled about the ferrocene fragment In this form all methylene groups are fairly close to the iron atom and essentially deshielded by the ferrocenyl fragment In such a case an iron—carbonyl interaction may be assumed Temperature increase enhances the cyclopentadienyl ring vibrations This brings the methylene groups nearer the iron atom and they are thus further deshielded by the ferrocenyl group [8] At the same time, the change of temperature should affect the iron—carbonyl interaction and the carbonyl orientation in the ferrocene magnetic field The actual conformation of compound XX may be an intermediate between XXa and XXb

The mass spectrum of [15] ferrocenophan-8 one has its most intense molecular ion fragment at m/e 408 In the spectra of aliphatic ketones, however, the M^+ ion is not the most intense signal [71,72] In compound XX peaks at m/e 406 ($M^+ - H_2$), 380 ($M^+ - CO$), 378 ($M^+ - CO - H_2$) are also present although they are less intense than the M^+ peak

Clemmensen reduction of ketonitrile XVIII yielded a yellow crystalline solid (after TLC on alumina) having two strong ion fragments at m/e 419 and 417 It may be assumed that a mixture of nitriles XXI and XXII has formed, XXI being the carbonyl to-methylene reduction product, and compound XXII being the dehydration product of carbonyl XXIIa We failed to separate XXI and XXII by TLC on alumina

The ^{13}C NMR spectrum* of the carbonyl reduction product of XVIII recorded at 24 8-33 1 ppm showed 21 signals due to bridge carbon atoms with several superimposed lines Four signals appear at 66 6 68 5 ppm which may be due to the cyclopentadienyl ferrocene carbon atoms [6-12, 73-75] Probably the signals at 68 5 and 66 8 ppm are due to the cyclopentadienyl α and β carbon atoms respectively of one compound, whereas the lines at 68 3 and 66 6 ppm result from the second compound The signals at 124 1 and 134 8 ppm may be assigned to the double bond carbon atoms The same region shows two less intense signals at 120 6 and 122 3 ppm which could be due to the nitrile carbon atoms We note that new signals appear at 120-135 ppm at −80° in CH$_2$Cl$_2$ However the IR spectrum of the XVIII reduction product exhibited only the band at 2239 cm^{-1} (CN), probably being an overlap of two nitrile modes in XXI and XXII

Experimental

IR spectra were taken on a UR-20 instrument ^{1}H NMR spectra were recorded on Perkin—Elmer R-12 and R-20 (60 MHz) and Bruker HX-90 (90 MHz) spectrometers ^{13}C NMR spectra were taken on a Bruker HX 90 (22 635 MHz) instrument Mass spectra were recorded on an MX-1303 spectrometer and electronic spectra were registered on an Hitachi EPS 3T spectrometer

1,1'-Bis(1-hydroxy-2-cyanoethyl)ferrocene (IV)

2 0 g of NaBH$_4$ was gradually added to a solution of 2 0 g (0 0063 mole) of bis(cyanoacetyl)ferrocene (III) [47] in 100 ml of 95% ethanol and 50 ml of ethyl bromide, at 40° The mixture was stirred at 40° under argon for 1 h The solvent was then removed in vacuo and the residue treated with dilute HCl and extracted with CH$_2$Cl$_2$ The organic part was washed with water and dried over Na$_2$SO$_4$ The solvent was removed in vacuo 1 7 g (82%) of compound IV, yellow crystals, was obtained (from chloroform) IR spectrum 495 s, 518 s, 830 s, 850 s, 1033 s, 1075 s, 1418 s, 1600 1800 m, 2262 s, 2940 m, 3100 m, 3400 s (br) cm^{-1}

1,1'-Bis(2-cyanovinyl)ferrocene (VI)

1 9 g (0 05 mole) of NaBH$_4$ was added very gradually to a solution of 2 0 g (0 0063 mole) of 1,1'-bis(cyanoacetyl)ferrocene (III) in 200 ml of 95% ethanol The mixture was stirred at 50° under argon for 1 5 h and the solvent removed in vacuo The residue was treated with dilute HCl and extracted with CH$_2$Cl$_2$ The organic part was washed with water and dried over Na$_2$SO$_4$ The solvent was evaporated in vacuo and the residue chromatographed on an alumina column (chloroform hexane (1/1) as eluting agent) An orange oil (1 4 g) of compounds IV and IVa (pure samples were obtained by TLC on deactivated alumina) and the partial dehydration products of IV were obtained

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* ^{13}C NMR spectroscopy has been used already in the study of macrocycles [76 78]

1-(1-Ethoxy-2-cyanoethyl) 1'-(1-hydroxy 2-cyanoethyl)ferrocene (IVa) was obtained as a yellow oil IR spectrum 498 m, 540 m, 670 w, 765 s, 841 m, 900 w, 950 w, 1030 m, 1090 s, 1249 m, 1290 w, 1333 m, 1420 m, 1600-1800 m, 2261 m, 2900 m, 2938 m, 2983 s, 3100 w, 3450 m (br) cm^{-1} Mass spectrum, *m/e* (*I*%) 353 (15), 352 (48)M^+, 350 (9), 334 (9)$M^+ - H_2O$, 312 (21), 311 (55)$M^+ - CH_3CN$, 306 (9)$M^+ - C_2H_5OH$, 294 (9)$M^+ - CH(OH)CN$, 288 (9)$M^+ - H_2O - C_2H_5OH$, 271 (24), 266 (30), 265 (24), 243 (24), 202 (55), 195 (48), 191 (21), 173 (100), 159 (24), 149 (36), 122 (24), 121 (27), 120 (58), 107 (36)

A solution of 4 5 g of the orange oil obtained above and 0 5 ml of $POCl_3$ in 175 ml of CH_2Cl_2 was refluxed for 2 h The mixture was washed with water, Na_2CO_3 solution, water, and dried over Na_2SO_4 The solvent was evaporated in vacuo Chromatography of the residue on an alumina column (benzene acetone 20/1) gave compound VI as three isomers (3 5 g of orange oil) The isomers were separated by TLC (benzene acetone 20/1)

1-(1 Hydroxy 2-cyanoethyl) 1'-(trans 2 cyanovinyl)ferrocene (V)

A solution of 0 3 g of IV in 100 ml of ether was shaken for 15 min with 25 ml of 15% HCl $SnCl_2$ was added to the aqueous layer and the latter extracted with ether The ethereal layer was washed with water, Na_2CO_3 solution, water and dried over Na_2SO_4 The ether was evaporated in vacuo The mixture of compounds VIa, VIb, VIc and V was separated on an alumina column The isomers of VI were eluted with benzene acetone (20/1) Compound V, an orange red oil (0 15 g, 53%), was eluted with ether IR spectrum 475 s, 510 s, 752 m, 830 s, 900 w, 960 m, 1029 s, 1055 s, 1067 s, 1189 w, 1200 w, 1258 m, 1275 m, 1295 m, 1335 w, 1355 m, 1375 m, 1390 m, 1410 m, 1461 m, 1612 s, 2215 s, 2252 m, 2930 w, 3090 m, 3440 s (br) cm^{-1}

1,1'-Bis(2-cyanoethyl)ferrocene (Ib)

(*a*) Platinum dioxide (obtained by heating a mixture of 0 5 g of H_2PtCl_6, 5 g of $NaNO_3$ and 2 ml of water) was added to a solution of 3 0 g (0 01 mole) of the mixture of isomers VI in 200 ml of absolute ethanol The mixture was shaken under hydrogen for 7 h The solution was filtered from platinum and the solvent removed in vacuo The residue was dissolved in benzene Quinone was added to the solution and the mixture extracted with dilute HCl The aqueous extracts were combined and washed with benzene $SnCl_2$ was added to the aqueous layer and the mixture extracted with benzene The benzene layer was extracted with water, $NaHCO_3$ solution, water and dried over Na_2SO_4 The benzene solvent was evaporated in vacuo and the residue chromatographed on an alumina column Compound Ib was eluted with ether, 0 2 g (7%) of yellow crystals being obtained (hexane ether 3/1) IR spectrum 479 m, 493 s, 506 s, 722 w, 768 w, 830 s, 848 m, 892 w, 921 w, 945 w, 1030 m, 1048 s, 1159 w, 1235 m, 1340 s, 1430 m, 1450 m, 1478 w, 1600-1800 m, 2251 s, 2870 w, 2935 m, 3090 w cm^{-1}

(*b*) Palladium black was prepared by the method described in ref 79 The preparation of tetraline and catalyst activation are described in ref 80

Palladium black (from 0 5 g of $PdCl_2$) was added to a solution of 0 5 g (0 002 mole) of VI (isomer mixture) in 15 ml of tetraline The solution was refluxed under argon for 4 h The mixture was cooled to room temperature and the palladium filtered off After addition of quinone the soltuion was extracted with 10% HCl The aqueous phase was washed with benzene, treated with SnCl$_2$ and extracted with benzene The benzene solution was washed with water, NaHCO$_3$ solution, water, and dried over Na$_2$SO$_4$ The solution was concentrated in vacuo and placed on an alumina column 0 11 g (22%) of Ib was eluted with ether

If the palladium black used was not freshly prepared, compound VI is partially reduced to a mixture of isomers VII which may be separated by TLC on alumina

IR spectrum of the *cis* isomer of 1-(2-cyanovinyl) 1' (2 cyanoethyl)ferrocene (VIIa) 485 s, 495 s, 512 s, 580 w, 750 w, 770 w, 816 m, 837 s, 976 m 1037 s, 1056 s, 1240 w, 1252 w, 1266 w, 1295 w, 1343 w, 1380 w, 1400 w, 1430 m, 1450 m, 1466 m, 1619 s, 1600-1800 m, 2221 s, 2255 m, 2865 m, 2930 m, 3110 w cm^{-1}

IR spectrum of the *trans* isomer of 1 (2 cyanovinyl)-1'-(2-cyanoethyl)-ferrocene (VIIb) 482 s, 493 s, 512 s, 582 m, 750 m, 770 m, 816 m, 836 s, 846 s, 925 m, 938 m, 1035 s, 1055 s, 1240 w, 1255 m, 1270 w, 1280 m, 1295 w, 1341 m, 1378 m, 1400 m, 1429 m, 1449 s, 1462 m, 1618 s, 1630-1820 w, 2219 s, 2254 m, 2865 w, 2930 m, 3100 m cm^{-1}

1,1' Bis(3-carboxypropyl)ferrocene diamide (X)

A mixture of 2 15 g (0 006 mole) of 1,1'-bis(3 carboxypropyl)ferrocene [52], 1 05 ml (0 012 mole) of PCl$_3$ and 100 ml of absolute benzene was heated at 60° for 2 5 h The solvent was evaporated in vacuo The residue was dissolved in 100 ml of absolute ether and the resulting solution was added dropwise to 100 ml of liquid ammonia The ammonia was then evaporated and the residue which was insoluble in ether was washed repeatedly with water and dried 1 5 g of X (70%) was obtained and was purified by crystallization from dioxane IR spectrum 484 m, 502 m, 517 m, 607 m, 692 m, 800 m, 812 s, 841 m, 863 w, 892 w, 928 w, 990 w, 1018 m, 1032 m, 1043 m, 1112 m, 1148 m, 1189 m, 1195 m, 1230 m, 1283 m, 1303 m, 1347 m, 1360 m, 1414 s, 1438 s, 1655 s, 2852 m, 2870 m, 2930 m, 2947 m, 3175 s, 3355 s, 3384 s cm^{-1}

1,1' Bis(3-cyanopropyl)ferrocene (Ic)

A mixture of 0 8 g (0 0022 mole) of compound X and 16 ml of acetic anhydride was heated at 130° for 1 5 h The excess acetic anhydride was evaporated in vacuo and the residue dissolved in CH$_2$Cl$_2$ and chromatographed on alumina (petroleum ether acetone 4/1) 0 41 g (55%) of Ic was isolated Recrystallization from hexane gave yellow crystals IR spectrum 487 s, 493 s, 502 m, 682 w, 739 m, 794 m, 822 s, 840 s, 860 m, 907 m, 936 m, 1019 s, 1033 m, 1052 s, 1228 m, 1317 s, 1364 m, 1395 m, 1417 m, 1437 m, 1462 m, 2246 s, 2850 m, 2818 s, 2838 s, 2956 m, 3084 m cm^{-1}

1,1'-Bis(5-chlorovaleryl)ferrocene (XI)

26 6 g of AlCl$_3$ was added dropwise to a solution of 31 g of 5-chlorovaleryl chloride [81,82] in 200 ml of dichloroethane A solution of 18 6 g (0 1 mole) of ferrocene in 150 ml of dichloroethane was then added to the mixture at 0° during 5 min The reaction mixture was stirred under argon at 20°

for 8 h and left standing overnight The resulting mixture was poured into 300 ml of a water-ice mixture The aqueous layer was extracted with dichloroethane The organic extracts were combined, washed with water, $NaHCO_3$ solution, water, and dried over Na_2SO_4 The solvent was evaporated in vacuo and the residue was crystallized from CH_2Cl_2-hexane (1/2) 21 g (52%) of crude XI was obtained Recrystallization from hexane gave yellow crystals IR spectrum 482 w, 500 m, 520 w, 535 w, 550 m, 645 m, 710 w, 730 w, 753 w, 765 w, 790 w, 835 m, 889 m, 973 w, 1025 w, 1050 w, 1070 w, 1088 m, 1230 s, 1255 m, 1280 w, 1300 w, 1340 w, 1380 m, 1405 m, 1452 s, 1670 s, 2870 w, 2890 w, 2950 m, 3120 w cm^{-1}

1,1 -Bis(5-chloropentyl)ferrocene (XIII)

A mixture of 4 0 g (0 0095 mole) of compound XI, 40 ml of concentrated HCl, 20 ml of water and 10 ml of dioxane was refluxed for 6 h with 15 g of Zn/Hg The solution was cooled and extracted with benzene and the organic phase was washed with water and dried over Na_2SO_4 Benzene was evaporated in vacuo and the residue was chromatographed on an alumina column Compound XIII a yellow orange oil (1 5 g, 37%), was eluted with petroleum ether The sample was purified by TLC IR spectrum 490 m, 520 m, 535 w, 650 m, 725 m, 805 m, 821 s, 850 w, 900 w, 1040 s, 1222 w, 1255 w, 1300 m, 1341 w, 1365 w, 1392 w, 1440 s, 1460 s, 1600-1800 w, 2855 s, 2830 s, 3085 m cm^{-1}

1,1' Bis(5-cyanopentyl)ferrocene (Id)

A solution of 1 0 g (0 0025 mole) of XIII and 1 0 g of KCN in 120 ml of 95% ethanol was refluxed for 40 h The solvent was evacuated, the residue dissolved in benzene and the benzene layer washed with water and dried over Na SO_4 Benzene was removed in vacuo and the residue was chromatographed on an alumina column (petroleum ether acetone 4/1) The order of elution was as follows initial XIII (0 1 g), 1-(5 chloropentyl)-1'-(5 cyanopentyl)ferrocene (0 2 g) and compound Id (0 4 g, 42%) (yellow crystals obtained from hexane) IR spectrum 500 m, 820 s, 920 m, 1020 m, 1470 s, 1600-1800 w, 2255 m, 2860 s, 2915 s, 2935 s cm^{-1}

1 1' Bis(7 chloroheptanoyl)ferrocene (XII)

26 6 g of AlCl was gradually added to 36 6 g of 7-chloroheptanoyl chloride [83] in 200 ml of dichloroethane A solution of 18 6 g (0 1 mole) of ferrocene in 200 ml of dichloroethane was added to the mixture during 10 min The resulting mixture was stirred under argon at 20° for 10 h and left to stand overnight The mixture was then poured into 300 ml of icy water and the aqueous layer was extracted with dichloroethane The organic extracts were combined, washed with water, $NaHCO_3$ solution, water, and dried over Na_2SO_4 The solvent was evaporated in vacuo and the residue crystallized from a mixture of dichloroethane and heptane (1/2) 30 g (62%) of compound XII (red-brown powder) was obtained Recrystallization from heptane gave red-brown crystals IR spectrum 500 m, 535 w, 550 w, 645 m, 715 m, 720 m, 740 m, 755 m, 815 w, 828 m, 840 m, 890 m, 925 w, 975 m, 1030 m, 1062 s, 1095 m, 1211 w, 1230 s, 1262 s, 1292 m, 1349 m, 1380 s, 1395 m, 1450 s,

1466 s, 1660 s, 1674 s, 2860 m, 2890 w, 2930 s, 3090 w, 3120 w cm^{-1} IR spectrum in CCl_4 1679 cm^{-1}

1,1' Bis(7-chloroheptyl)ferrocene (XIV)

A mixture of 9 6 g (0 02 mole) of compound XII, 50 ml of concentrated HCl, 20 ml of water and 40 ml of CH_3COOH was refluxed with 30 g Zn/Hg for 20 h The resulting mixture was extracted with benzene The benzene layer washed with water, dried over Na_2SO_4 and evaporated in vacuo The residue was chromatographed on an alumina column Compound XIV (red liquid) was eluted with petroleum ether (8 3 g, 94%) The product was purified by crystallization from pentane at −78° IR spectrum 490 s, 650 s, 722 s, 805 s, 820 s, 920 w, 1020 s, 1038 s, 1100 w, 1225 m, 1300 m, 1340 w, 1360 w, 1440 s, 1460 s, 1600-1800 w, 2855 s, 2930 s, 3090 m cm^{-1}

1 1'-Bis(7-cyanoheptyl)ferrocene (Ie)

A mixture of 8 0 g (0 018 mole) of compound XIV, 4 0 g of KCN and 130 ml of dimethyl sulfoxide was refluxed under argon for 3 h After cooling, the resulting mixture was poured into 500 ml of water and the aqueous layer was extracted with chloroform The chloroform layer was washed with water, dried over Na_2SO_4 and the solvent evaporated in vacuo The residue was chromatographed on an alumina column (petroleum ether acetone 4/1) The order of eluting was compound XIV, 1 (7-chloroheptyl) 1' (7-cyanoheptyl) ferrocene and finally compound Ie (2 5 g, 34%) as yellow crystals obtained from hexane IR spectrum 465 s, 505 m, 720 m, 820 s, 1020 m, 1040 m, 1420 m, 1465 s, 1600-1800 w, 2260 m, 2855 s, 2920 s cm^{-1}

1,1'-Bis[O (2 cyanoethyl) 1 hydroxyethyl] ferrocene (XVI)

2 1 g (0 04 mole) of acrylonitrile was added dropwise to a mixture of 1 1 g (0 004 mole) of 1,1' bis(1 hydroxyethyl)ferrocene, 0 11 g of KOH and 50 ml of dioxane The mixture was stirred for 4 h and then the solvent was evaporated in vacuo The residue was washed with water, dissolved in benzene and dried over Na_2SO_4 Benzene was removed in vacuo 1 2 g (78%) of XVI, an orange red oil, was obtained and purified by freezing at −78° from hexane

2-Amino 1 cyano[3]ferrocenophan 1-ene (IIa)

A solution of CH_3MgI (prepared by dissolving 0 05 g of Mg and 0 12 ml of CH_3I in 10 ml of ether) was added during 2 h to a refluxed solution of 0 53 g (0 002 mole) of compound Ia in 50 ml of ether The mixture was refluxed for 0 5 h and 25 ml of water and 20 ml of dilute HCl were then added The solid which precipitated was washed with ether and recrystallized from hexane-CH_2Cl_2 (1/1) 0 1 g of IIa (yellow crystals) was obtained Mass spectrum *m/e (I%)* 265 (24), 264 (100), 262 (10), 237 (14), M^+—HCN, 224 (10), 222 (24) 204 (20), 202 (90), 201 (28), 200 (78), 199 (52), 198 (36), 134 (24), 131 (78), 130 (24), 118 (24), 117 (60), 106 (28), 105 (40), 92 (72), 91 (60), 57 (30), 56 (18), 55 (14)

3-Amino 2-cyano[5]ferrocenophan 2-ene (IIb)

Sodium (0 04 g, 0 002 mole) was dispersed in decaline and the solvent then replaced by absolute ether (10 ml) A solution of 0 1 ml of styrene and 0 3 ml of *N* methylaniline in 40 ml of ether was added to the suspension and the resultant solution was stirred for 0 5 h A solution of 0 2 g (0 001 mole) of Ib in 60 ml of ether was added at 40° to the mixture during 2 h The mixture was refluxed for 5 h After cooling, 100 ml of water was added and the aqueous layer was extracted with CH_2Cl_2 The extracts were combined with the ethereal layer, dried over Na_2SO_4 and the solvent evaporated in vacuo The residue was chromatographed on alumina plates (benzene acetone 20/1) 0 1 g of unreacted Ib and 0 05 g of IIb (25%) were obtained Crystallization from CH_2Cl_2-hexane (1/2) gave compound IIb (as light yellow leaves) Mass, *m/e* (*I*%) spectrum 293 (25), 292 (100), 290 (11), 277 (15) *M* −NH, 265 (4)*M* −HCN, 214 (19), 213 (9), 212 (13) 187 (34), 185 (10), 146 (13) 134 (19), 131 (16) 93 (20), 77 (32), 57 (26), 56 (16), 55 (16)

[11]Ferrocenophan 6 one (XIX)

A solution of 2 3 g (0 006 mole) of compound Id in 400 ml of ether was added in 21 h to a solution of sodium *N* methylanilide (obtained from 0 8 g of sodium, and excess *N*-methylaniline and styrene in 600 ml of absolute ether) and refluxed in ether under argon Compound Id was added to the reflux via a condenser The mixture was then refluxed for a further 5 h 200 ml of water acidified with HCl was added to the mixture The ethereal layer was washed with water, dried over Na_2SO_4 and the solvent evaporated in vacuo

A sample of the residue obtained was purified by TLC on alumina (heptane acetone 3/1) Compound IId was isolated as yellow crystals (from CH_2Cl_2 hexane 1/2) Mass spectrum *m/e*, *I*(%) 377 (30), 376 (100), 374 (9), 297 (3), 216 (10), 201 (14), 135 (13), 134 (13), 121 (14), 93 (67), 57 (12), 56 (12), 55 (12)

The remainder of the residue after ether evaporation was dissolved in 100 ml of benzene This solution was shaken with 700 ml of 40% H_2SO_4 for 2 h $SnCl_2$ was added to the solution and the aqueous layer was extracted with benzene The organic phase was washed with water, dried over Na_2SO_4, and the benzene evaporated 1 4 g (61%) of crude XVII was obtained

Compound XVII was heated at 70° with 50 ml of CH_3COOH, 50 ml of HCl and 2 g of $SnCl_2$ for 2 h The mixture was poured onto ice and the aqueous layer was extracted with chloroform The organic phase was washed with water, $NaHCO_3$ solution, water, and dried over Na_2SO_4 The chloroform was evaporated and the residue purified by TLC on alumina (heptane acetone 5/1) Compound XIX was isolated as yellow orange crystals (0 4 g) IR spectrum 475 s, 505 m, 808 s, 833 w, 922 w, 1020 m, 1057 s, 1110 w, 1130 w, 1160 w, 1230 w, 1285 w, 1365 m, 1440 m, 1462 s, 1600 1800 w, 1712 s 2860 s, 2932 s, 3090 w cm^{-1}

0 07 g of compound IId was deuterated by dissolving in 30 ml of ether and shaking the solution with 50 ml of 0 05 g of sodium in D_2O for 3 h The ethereal layer was separated, dried over Na_2SO_4, and the solvent evaporated The deuterated IId was obtained by crystallization from CH_2Cl_2-hexane (1/2)

7 Cyano[15]ferrocenophan-8-one (XVIII)

A solution of 2 4 g of Ie in 300 ml of ether was added under ether refluxing for 18 h in argon to the solution of sodium *N*-methylanilide (prepared from 0 8 g of sodium and excess *N*-methylaniline and styrene in 500 ml of absolute ether) The resultant mixture was refluxed for 3 h 200 ml of water acidified with HCl was added The ethereal layer was washed with water, dried over Na_2SO_4 and the ether evaporated in vacuo

A sample of the residue was purified by TLC on alumina (heptane-acetone 3/1) Crystallization from the mixture of CH_2Cl_2 hexane (1/3) gave IIe as yellow crystals Mass spectrum, *m/e* (*I*%) 433 (37), 432 (100), 430 (10), 419 (5), 417 (5), 353 (5)

The rest of the residue after ether evaporation was dissolved in 100 ml of benzene and shaken with 200 ml of 50% H_2SO_4 for 2 h $SnCl_2$ was added to the solution and the aqueous layer was extracted with benzene The organic phase was washed with water, $NaHCO_3$ solution, water and dried over Na_2SO_4 After benzene evaporation 1 4 g (59%) of compound XVIII was obtained (yellow crystals, from hexane) IR spectrum 485 s, 810 s, 840 m, 1022 m, 1040 m, 1052 w, 1370 m, 1400 m, 1438 m, 1468 s, 1720 s, 2255 w, 2855 s, 2920 s, 3090 w cm^{-1}

[15]Ferrocenophan-8-one (XX)

A mixture of 0 5 g of compound XVIII, 20 ml of CH_3COOH and 30 ml of HCl was refluxed for 2 h After cooling, the mixture was poured into 100 ml of water. $SnCl_2$ was added and the aqueous layer was extracted with chloroform The chloroform solution was washed with water, $NaHCO_3$ solution, water and dried over Na_2SO_4 The solvent was evaporated in vacuo The residue was purified by TLC on alumina (heptane-acetone 5/1) 0 3 g of XX was obtained (yellow-orange crystals from hexane) IR spectrum 482 s, 520 m, 710 w, 721 w, 810 s, 841 m, 921 w, 1010 w, 1020 w, 1029 m, 1038 s, 1058 w, 1130 m, 1225 w, 1257 m, 1320 w, 1370 m, 1415 s, 1437 m, 1467 s, 1600 1800 w, 1710 s, 2855 s, 2920 s, 3075 w, 3100 w cm^{-1} Mass spectrum, *m/e* (*I*%) 409 (32), 408 (100), 406 (11), 380 (2), 378 (1), 350 (2), 329 (3), 327 (2), 296 (4), 253 (3), 251 (2), 239 (5), 226 (5), 216 (5), 213 (5), 212 (5), 211 (5), 200 (6)

Reduction of 7 cyano[15]ferrocenophan-8-one

A mixture of 1 0 g of compound XVIII, 50 ml of CH_3COOH and 50 ml of HCl was refluxed with 25 g of Zn/Hg for 5 h The reaction mixture was poured into 300 of water, $SnCl_2$ was added and the aqueous layer extracted with chloroform The chloroform solution was washed with water, $NaHCO_3$ solution, water and dried over Na_2SO_4 The chloroform was evaporated in vacuo, the residue purified by TLC on alumina (petroleum ether acetone 5/1) Crystallization from pentane at —78° gave an oil which slowly crystallized, it was probably a mixture of XXI and XXII

1,1'-Bis(2-carboethoxyvinyl)ferrocene

Dry HCl gas was passed for 3 h through a suspension of 3 7 g (0 01 mole) of 1,1'-bis(cyanoacetyl)ferrocene in 100 ml of absolute ethanol The resultant mixture was poured into 200 ml of water and the solution obtained was extracted with CH_2Cl_2 The organic phase was washed with water, $NaHCO_3$ solution, water and dried over Na_2SO_4 After evaporating the solvent 3 6 g of crude 1,1'-bis(carboethoxyacetyl)ferrocene was obtained This was reduced to the diol without purification 1 0 g of $NaBH_4$ was added dropwise to a solution of the 1,1'-bis(carboethoxyacetyl)ferrocene obtained in 50 ml of 95% ethanol The mixture was stirred at 50° for 1 h The ethanol was evaporated in vacuo and the residue treated with dilute HCl and dissolved in CH_2Cl_2 (500 ml) 0 5 ml of $POCl_3$ was added to the resultant solution The mixture was refluxed for 0 5 h The solution was washed with water, $NaHCO_3$ solution, water and dried over Na_2SO_4 The solvent was evaporated in vacuo 0 55 g (46%) of crude 1,1'-bis(2-carboethoxyvinyl)ferrocene was obtained (brown crystals from hexane) IR spectrum 497 s, 566 m, 639 w, 730 m, 765 m, 822 m, 848 m, 874 m, 963 s, 1035 s, 1043 s, 1164 s, 1194 s, 1245 s, 1302 s, 1365 s, 1397 m, 1478 m, 1637 s, 1721 s, 2901 m, 2933 m, 3078 m, 3088 m cm^{-1}

1,1' Bis(dimethylcyanoacetyl)ferrocene

A solution of 0 12 g of sodium in 70 ml of ethanol was added during 0 5 h to a solution of 0 8 g (0 0025 mole) of 1,1' bis(cyanoacetyl)ferrocene in 200 ml of ethanol The mixture was refluxed for 1 h 20 ml of CH_3I in 30 ml of ethanol was added during 1 h to the resultant solution at 30° and the mixture was refluxed for 2 h After evaporating the solvent the residue was crystallized from hexane chloroform (5/1) 0 72 g (81%) of 1,1' bis(dimethylcyanoacetyl)ferrocene was obtained (red crystals) IR spectrum 488 s, 504 m, 514 m, 766 m, 800 w, 840 s, 853 m, 880 s, 900 w, 990 m, 1040 m, 1070 s, 1088 w, 1190 w, 1215 w, 1280 s, 1375 m, 1380 s, 1390 m, 1409 w, 1450 s, 1465 s, 1673 s, 2241 m, 2880 w, 2948 m, 2983 m, 3009 w, 3114 m, 3129 m cm^{-1}

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