

BRIDGED FERROCENES—VII¹

THE PREPARATION AND PROPERTIES OF [2]FERROCENOPHANES[†]

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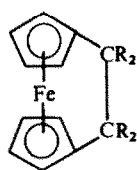
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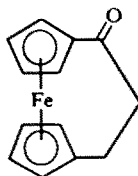
Abstract—The preparation of [2]ferrocenophane and its tetramethyl derivative has been effected by direct synthesis from 1,2-dicyclopentadienylalkane dianions and ferrous chloride. The chemical and spectroscopic properties of these ring-tilted compounds have been investigated and found to be different from those of related [m]ferrocenophanes of longer bridge length.

INTRODUCTION

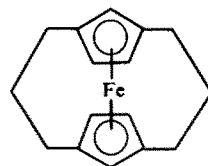
THE INTER-RING separation in ferrocene (*ca.* 3.3Å) cannot be spanned by bridging chains of fewer than four carbon atoms without incurring ring-tilt distortion of the molecule. For example, crystal structure analyses of the (2)- (1; R = Me),² (3)- (2),³ and [3][3]-ferrocenophane (3)⁴ have established that the cyclopentadienyl rings are displaced by *ca.* 23°, 9°, and 9° respectively from the parallel-plane arrangement adopted by ferrocene and its simple non-bridged derivatives.⁵ The chemical properties of bridged ferrocenes whose rings are only slightly tilted, e.g. [3]ferrocenophanes, have been found to be little different from those of analogous non-bridged 1,1'-dialkylferrocenes.⁶ At the outset of this work the chemistry of the grossly distorted [2]ferrocenophane system (1) was unexplored, in part due to the experimental difficulties associated with the synthesis of compounds of this type. Since it appeared possible that these molecules might possess unusual electronic properties⁸ and in connection with a general interest in the properties of [m]ferrocenophanes (see previous papers of this series), we have investigated the properties of the parent compound and its tetramethyl derivative (1; R = H and Me respectively). Some preliminary results have been reported.⁷



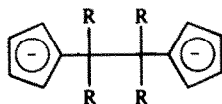
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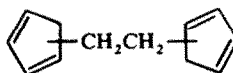
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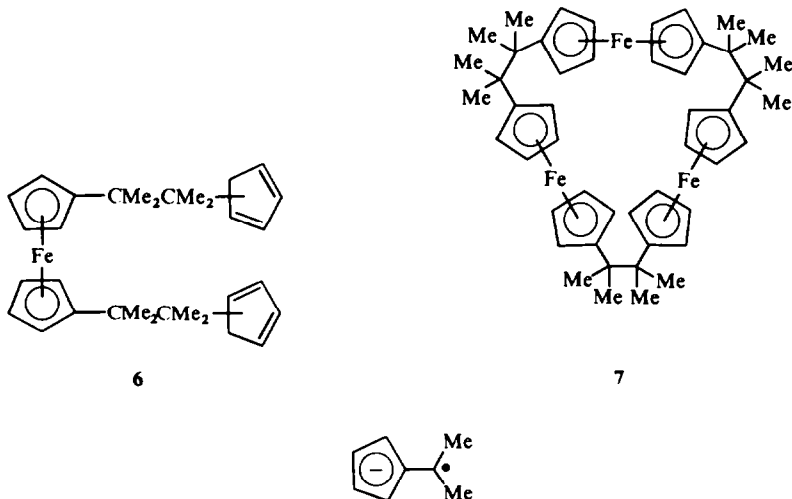
[†] Abstracted in part from the Ph.D. thesis of H.L.L., University of Strathclyde (1970)

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Synthetic methods

From cyclopentadienes. The *in situ* reaction of substituted cyclopentadienide salts with FeCl_2 has been used extensively for the preparation of substituted ferrocene derivatives.⁹ These salts are conveniently generated either by proton abstraction from substituted cyclopentadienes¹⁰ or 6-alkylfulvenes^{11, 12} or by addition of nucleophiles to fulvenes^{12, 13} or fulvene-like molecules^{12, 14} and their conversion to 1,1'-disubstituted ferrocenes usually proceeds efficiently (> 50% yield). The reaction of α,ω -dicyclopentadienylalkane dianions $[\text{C}_5\text{H}_4(\text{CH}_2)_n\text{C}_5\text{H}_4]^{2-}$ ($n = 3, 4$ and 5), however, produces mainly oligomeric ferrocene derivatives.¹⁵ Presumably the hydrocarbon chain adopts a preferred linear conformation in which the negatively charged termini are distant from each other. Accordingly, very poor yields (< 3%) of intramolecularly coupled products, *i.e.* [m]ferrocenophanes ($m = 3, 4$ and 5), are isolated from these reactions.¹⁵ Somewhat improved but still disappointing yields have similarly been encountered in the direct synthesis of [1.1]ferrocenophanes from dicyclopentadienylmethane dianion^{1, 16} or from ferrocene derivatives bearing heteroannular fulvene substituents.¹

In contrast, the relatively high yield (*ca.* 50%) of [2]ferrocenophane (**1**; $\text{R} = \text{H}$) which we have obtained from the reaction of the dianion (**4**; $\text{R} = \text{H}$) with FeCl_2 probably reflects the close proximity in which the cyclopentadienyl rings are held such that intramolecular cyclisation is favoured. This synthetic route to ring-tilted ferrocenes is rendered less attractive, however, by the difficulties associated with the preparation of workable quantities of the hydrocarbon (**5**) from which the dianion (**4**; $\text{R} = \text{H}$) is derived by proton abstraction with BuLi . Following the method used successfully by Schaltegger *et al.* for the synthesis of dicyclopentadienylmethane,¹⁷ this unstable (polymerization) hydrocarbon (**5**) is formed only in low yield from the reaction of 1,2-dibromoethane with sodium cyclopentadienide in THF and can be separated from spiro[2.4]hepta-4,6-diene, the principal product of the reaction,^{18, 19} by fractional distillation.



From fulvenes. The conversion of alkylfulvenes to [2]ferrocenophanes (**1**) was originally reported in patent literature by Pruett and Morehouse.²⁰ The method involves reductive coupling of the fulvene with Na²¹ and reaction of the dicyclopentadienylalkane dianions (of the type **4**) thus formed with FeCl₂. We have reinvestigated the synthesis of the tetramethyl derivative (**1**; R = Me) from 6,6-dimethylfulvene by this method but were unable to reproduce the reported yield of product (70%) although a variety of experimental conditions were employed (Experimental). In our hands, small amounts of the desired ferrocenophane were isolated but the main products of the reaction were 1,1'-diisopropylferrocene and the unstable bis(cyclopentadiene) derivative (**6**). The formation of minor amounts of other compounds containing both isopropyl and cyclopentadiene groups was indicated by ¹H NMR spectroscopy and the reaction also afforded a pale yellow solid of molecular formula C₄₈H₆₀Fe₃ (mass spectrum) to which the trimeric structure **7** is tentatively assigned on the basis of analytical and spectroscopic evidence.

The reductive coupling of 6,6-dimethylfulvene probably involves initial electron transfer from Na to the fulvene giving the radical anion (**8**). This species may then dimerise and the reaction of the resulting dianion (**4**; R = Me) with FeCl₂ accounts for the formation of the products **1** (R = Me), **6** by protonation during the work-up procedure, and **7**. The formation of isopropylated compounds,²² however, indicates that the radical anion (**8**) may alternatively abstract a hydrogen atom, probably from the ether reaction solvent, giving the isopropylcyclopentadienyl anion and thence isopropyl-substituted ferrocenes.

Chemical reactivity

The chemical properties of the [m]ferrocenophanes (m = 3, 4, and 5) have been investigated previously and found to parallel those of non-bridged 1,1'-dialkylferrocenes.⁶ The presence of a flexible interannular bridge in these compounds has little effect on the overall reactivity of the ferrocene residue compared with non-bridged analogues although differences in the steric and conformational constraints imposed by the bridges serve to modify the relative reactivities of the α- and β-ring positions through the series.²³

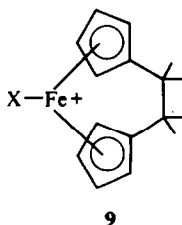
[2]Ferrocenophanes, on the other hand, have been found to exhibit properties quite different from those of their homologues of longer bridge length. Thus, repeated attempts to carry out Friedel–Crafts acetylation of these compounds (**1**; R = H and Me) were unsuccessful although the other [m]ferrocenophanes undergo facile substitution.²³ Even under very mild conditions (AcCl—AlCl₃ Perrier complex in CH₂Cl₂ at 0°), extensive decomposition of the substrates was observed and only minute traces of unidentified products were isolated. A similar lack of success in the attempted acetylation of the tetramethyl derivative (**1**; R = Me) has been indicated in a patent.²⁰ Similarly, although alkylferrocenes are readily lithiated on treatment with BuLi,²⁴ we were unable to effect a similar reaction with [2]ferrocenophane (**1**; R = H). The relative intensities of the signals in the ¹H NMR spectrum of the compound before and after treatment with BuLi followed by D₂O were unchanged and no evidence for the incorporation of deuterium at ring positions was obtained from mass spectroscopy. We were also unable to introduce a functional group in the bridge. Under conditions which effect smooth oxidation of the other [m]ferrocenophanes to the corresponding [m]ferrocenophan-1-ones (e.g. **2**),⁶ [2]ferrocenophane (**1**; R = H) underwent a rapid reaction with active MnO₂ to give a

very complex mixture of products (TLC) which were present in insufficient amounts for further investigation.

The reaction of [2]ferrocenophanes with protic acids has been studied by electronic spectroscopy (*vide infra*) which indicated the formation of a metal-protonated cation. Repeated attempts to identify or isolate the species present were unsuccessful although protonated ferrocene has been characterized by IR²⁵ and ¹H NMR spectroscopy²⁶ and isolated as a tetrachloroaluminate salt.^{25, 27} Thus, using the vacuum technique developed by Levenberg²⁸ for the identification of protonated ferrocene, no metal-hydride resonance could be discerned by ¹H NMR spectroscopy and attempts to precipitate salts from acidified solutions of [2]ferrocenophane with bulky anions (e.g. BF₄) under a variety of conditions met with failure.

It seems reasonable to suppose that the unique behaviour of the [2]ferrocenophanes is related to the distortion imposed by the short two-carbon bridge upon the geometry of the ferrocene system. As mentioned previously, the cyclopentadienyl rings in the tetramethyl compound are displaced by *ca.* 23° from parallel planes in the crystal² and it is unlikely that the geometry of the ferrocene residue in the parent compound (1; R = H) would differ appreciably. Gross distortion of this nature is not imposed upon the other [m]ferrocenophanes although the rings in the [3]-compound may be slightly tilted (*cf.* ref. 3).

Clearly, the electronic distribution in ring-tilted ferrocenes will differ from that found for undistorted compounds. Ballhausen and Dahl have devised a bonding scheme for ring-tilted metallocenes and the results of their calculations⁸ suggest that the metal-ring bond strength is only slightly weakened as the molecule is distorted by up to 30° from a regular sandwich geometry. In the case of ferrocene, however, the six electrons which are accommodated in essentially non-bonding a_{1g} (3d_{z²}) and e_{2g} (3d_{xy}, x²-y²) orbitals in the undistorted molecule are relocated in three new hybrid orbitals oriented in the equatorial plane in the direction of the sandwich opening of the ring-tilted form. Ballhausen and Dahl further speculated that, in protonated ferrocene, the proton is attached to the metal atom in a ring-tilted structure through coordination with the electrons in the central metal hybrid orbital.⁸



It appears plausible that electronic reorganization of this nature would lead to an increase in the Lewis basicity of the metal atom and the facile reaction of [2]ferrocenophanes with protic acids can be accounted for in these terms.⁷ Similarly, it can be envisaged that these molecules would react with the AcCl-AlCl₃ Perrier complex to give a species in which a pair of metal electrons is coordinated either with the AlCl₃ (9; X = Cl₃Al⁻) or with the acetylum ion (9; X = MeCO). The inability to reverse the protonation process with added base (*vide infra*) and the decomposition observed in

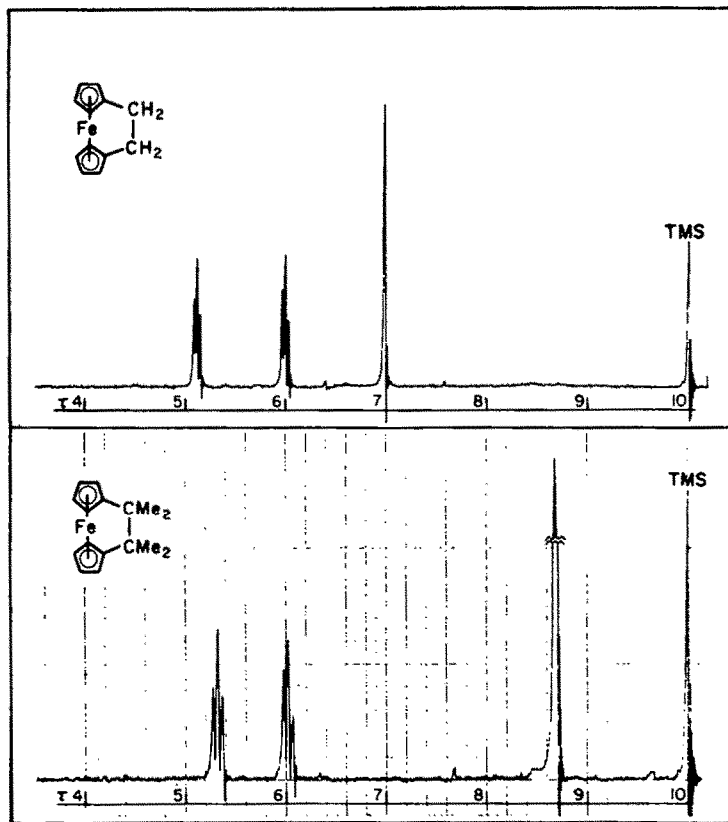


FIG. 1. ^1H NMR spectra of [2]ferrocenophanes (CDCl_3 solutions)

TABLE CHEMICAL SHIFTS OF ALKYL SUBSTITUENTS IN ^1H NMR SPECTRA OF FERROCENE DERIVATIVES^a

Compound	CH_2 resonance ^b τ	CMe_2 resonance ^b τ
1,1'-Diethylferrocene	7.66 (q)	—
1,1'-Diisopropylferrocene	—	8.86 (d)
1,1'-Di- <i>t</i> -butylferrocene	—	8.80 (s)
[2]Ferrocenophane	6.99 (s)	—
1,1,2,2-Tetramethyl[2]ferrocenophane	—	8.68 (s)
[3]Ferrocenophane ^c	8.05 (s)	—
2,2-Dimethyl[3]ferrocenophane ^d	8.25 (s)	8.75 (s)
[4]Ferrocenophane ^d	7.3–8.4 (m)	—
[5]Ferrocenophane ^e	7.4–8.4 (m)	—

^a In CDCl_3 solution against TMS as internal standard

^b Signal multiplicity indicated in brackets; (s) singlet, (d) doublet, (q) quartet

^c Ref. 31

^d Ref. 36

^e Ref. 35

attempted acetylation, however, indicate that cations of the type **9** ($X = \text{H}, \text{MeCO}, \text{or } \text{Cl}_3\text{Al}^-$), if formed, are thermodynamically unstable and decompose under the reaction conditions by ring-metal fission. In support of this conclusion, force-constant measurements²⁵ have shown that protonation of the Fe atom in ferrocene itself is accompanied by a significant weakening of the ring-metal bonds.

Spectroscopic properties

¹H NMR spectra. The ¹H NMR spectra of the [2]ferrocenophanes (**1**; R = H and Me) are reproduced in Fig. 1. The cyclopentadienyl protons give rise to an A₂B₂ pattern comprising two unsymmetrical triplets separated by 0.88 ppm (**1**; R = H) and 0.70 ppm (**1**; R = Me). The spectrum of the tetramethyl compound was originally discussed by Rinehart *et al.*¹¹ The large chemical-shift difference between the α - and β -protons was attributed to the ring-tilted structure[†] which, it was argued, would cause the α -protons to be located closer to the metal atom and thereby preferentially shielded. In an earlier paper of this series,³¹ however, this interpretation was questioned in light of the close similarity found for the Fe-ring C distances in the crystal.²

Alternatively, it was suggested that a differential shielding of the ring protons could arise as an outcome of the unsymmetrical distribution of electron density about the Fe-ring centroid (*vide supra*) in accord with the Ballhausen-Dahl bonding scheme.⁸ The assignment¹¹ of the high-field triplet to the resonance of the α -protons, therefore, rests on tenuous evidence. Unfortunately, we have so far been unable to prepare ring-substituted [2]ferrocenophane derivatives whose spectra might allow unambiguous interpretation of the ring-proton patterns.

The bridge protons of the [2]ferrocenophanes give rise to sharp singlet resonances (Fig. 1). Comparison of the chemical shift values for the CH₂ and CMe₂ protons of these compounds with those for the same groups in undistorted analogues (see Table) shows clearly that the interannular bridges of these ring-tilted ferrocenes are located in a deshielding region associated with the structure.

Electronic spectra. The electronic spectra of ferrocene and its alkyl derivatives contain two broad relatively weak absorptions around 325 and 440 nm. and there is general agreement³³ that these bands represent symmetry-forbidden transitions of electrons from nonbonding e_{2g} and a_{1g} levels respectively to the antibonding e_{1g}* level. Right-tilt induced reordering of the nonbonding levels produces corresponding changes in absorption characteristics and we earlier showed that the 440 nm. band is particularly sensitive to molecular distortion of this nature.³⁴ Thus, in the spectra of the [2]ferrocenophanes (**1**; R = H and Me), the intensity of this band ($\epsilon \approx 450$) is increased over fourfold compared with that found for non-bridged analogues e.g. 1,1'-diethylferrocene ($\lambda_{\text{max}} = 438 \text{ nm.}; \epsilon = 105$). Further, the absorption maximum is bathochromically shifted by ca. 30 nm., accounting for the characteristic red colour of these ferrocenophanes.

The spectrum of [2]ferrocenophane (Fig. 2), in EtOH is immediately and dramatically changed upon addition to the solution of H₂SO₄ in low concentration (< 0.1%

[†] Very little difference in chemical shift is found between the resonances of the α - and β -protons of undistorted 1,1'-dialkylferrocenes.²⁹ Large chemical-shift differences have been found for sulphonamide-bridged analogues of [2]ferrocenophanes.³⁰ In view of the electronic nature of the ring substituents in these compounds, however, it is difficult to assess the contribution of ring-tilting to the separation of the proton resonances.

v/v). Under similar conditions, the spectra of ferrocene and its simple alkyl derivatives, including the [m]ferrocenophanes ($m = 3, 4$ and 5), are not significantly altered by the presence of acid at much greater concentration (> 100 times). The disappearance of the 472 nm band upon acidification of the [2]ferrocenophane solution is strongly suggestive of the occurrence of a metal-protonation process [e.g. to give **9**; $X = H$]. However, upon basification of the solution with NaOH, the original spectrum was not reproduced and substrate decomposition was apparent. Reversible metal protonation, therefore, does not occur under these conditions.

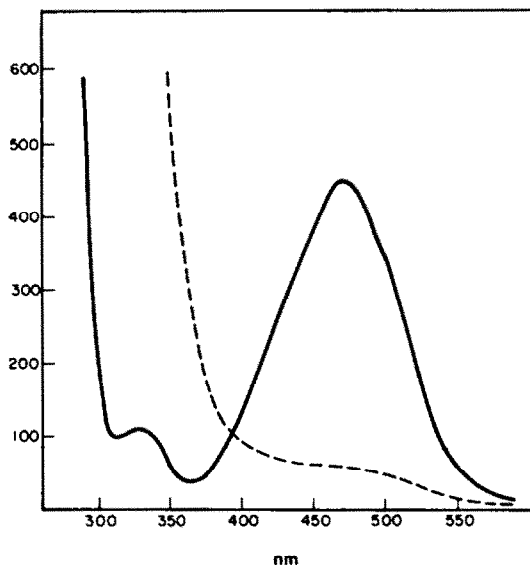


FIG. 2. Electronic spectra of [2]ferrocenophane (**1**; $R = H$) in absolute EtOH (unbroken curve) and in absolute EtOH containing ca. 0.5 ml H_2SO_4 /litre (broken curve)

CONCLUSION

The unique behaviour of the two carbon-bridged member of the [m]ferrocenophane series may be attributed to an electronic reorganization of the ferrocene system occasioned by ring-tilt distortion of the molecule.

EXPERIMENTAL

For general remarks, see Part I.³⁵

1,2-Dicyclopentadienylethane (5). Freshly distilled cyclopentadiene (28.8 g; 0.44 mole) was added slowly to Na wire (9.2 g; 0.4 g at) in dry THF (300 ml) at 0° . When the Na had been consumed, 1,2-dibromoethane (39.5 g; 0.21 mole) was added dropwise to the stirred solution of sodium cyclopentadienide, keeping at 0° . The mixture was stirred and allowed to reach room temp. overnight. Sufficient ice was added to dissolve all the NaBr which had pptd and the aqueous solution extracted with ether, dried (Na_2SO_4) and evaporated at low temp. The residual yellow oil was distilled using a Vigreux column. The first fraction consisted mainly of spiro [2.4] hepta-4,6-diene (lit.¹⁹ b.p. $45-47^\circ/93$ mm) and the crude product (**5**) was obtained as pale yellow oil (1.0 g; 3%), b.p. $41-45^\circ/0.1$ mm; n_D^{20} 1.5250; IR (liq) 3060, 2900, 1360, 900, 675 cm^{-1} . The compound polymerized on standing or in solution. Due to the small quantity available, further purification was not carried out and analytical data were not obtained.

[2]Ferrocenophane (1; R=H). BuLi (2.2 g; 0.034 mole) in hexane (10 ml) was added to a stirred solution of freshly prepared 1,2-dicyclopentadienylethane (1.0 g; 6.4 mmole) in dry THF (1000 ml) at 0°. The mixture was stirred for 1 hr, and then freshly prepared FeCl₂ (1.0 g; 8.0 mmole) was added. The mixture was stirred and allowed to reach room temp. overnight. MeOH was added to destroy excess BuLi and the mixture filtered through kieselguhr, evaporated to dryness and the residue extracted with ligroin. The ligroin extract was evaporated to dryness and the residue sublimed affording [2]ferrocenophane (0.68 g; 50%), a red solid, m.p. 104–107°. (Found: C, 67.56; H, 5.70; M.W. 212.0286. C₁₂H₁₂Fe requires C, 67.95; H, 5.71%; M.W. 212.0288); PMR (CDCl₃) τ 5.12, 6.00 (2t; 4H and 4H; ring protons), τ 6.99 (s; 4H; bridge protons); λ_{max} (EtOH) 328 (ϵ = 100), 472 m μ (ϵ = 450).

1,1,2,2-Tetramethyl[2]ferrocenophane (1; R=Me). A solution of 6,6-dimethylfulvene (10.6 g; 0.1 mole) in dry THF (50 ml) was added over 30 min to a vigorously stirred suspension of finely dispersed Na (2.5 g; 0.11 g at) in THF (950 ml), below 10°. The mixture was stirred until most of the Na had been consumed (ca. 2 hr) and then freshly prepared FeCl₂ (ca. 12 g) added. The mixture was stirred overnight and filtered through kieselguhr, reduced to low bulk and chromatographed on alumina. The following compounds were eluted by ligroin in the order given; unchanged 6,6-dimethylfulvene (0.53 g; 5%); 1,1'-diisopropylferrocene (0.54 g; 4%), b.p. 100° (bath)/0.7 mm, identical with an authentic sample;¹⁰ the bis(cyclopentadiene) derivative (6) (5.20 g; 43%), an unstable dark yellow liquid which decomposed upon distillation. (Found: C, 79.64; H, 9.25. C₃₂H₄₄Fe requires C, 79.32; H, 9.15%); the PMR spectrum contained vinyl, cyclopentadienyl, and Me resonances but the patterns were too complex to permit analysis; the [2]ferrocenophane (1; R=Me) (0.44 g; 3%), which crystallized from ligroin at 0° in flaky orange-red leaflets, m.p. 138–143° (lit.²⁰ m.p. 137–145°); PMR (CDCl₃) τ 5.34, 6.04 (2t; 4H and 4H; ring protons), τ 8.68 (s; 12H; Me protons); λ_{max} (EtOH) 326 (ϵ = 105), 466 m μ (ϵ = 460). In addition to the above compounds, ligroin also eluted fractions whose PMR spectra indicated the presence of vinyl (cyclopentadiene) and isopropyl groups. These compounds were present in too small amounts to permit further examination. Finally, ligroin/ether (1:1) eluted a pale yellow compound (0.23 g) which crystallized from ligroin in small leaflets, m.p. 179–180°. (Found: C, 71.75; H, 7.50; M.W. 804.6. C₄₈H₆₀Fe₂ requires C, 71.65; H, 7.52%; M.W. 804.56); the PMR spectrum lacked vinyl resonances and contained only cyclopentadienyl and Me resonances in the intensity ratio 2:3 respectively. This compound is tentatively assigned the structure 7.

Repetition of the reaction using different ether solvents (e.g. 1,2-dimethoxyethane), different molar ratios of reactants, and different time and dilution factors did not result in an improvement of the yield of the [2]ferrocenophane (1; R=Me).

Attempted acetylation of [2]ferrocenophanes. A Perrier complex of AcCl was prepared by stirring a solution of the chloride in CH₂Cl₂ with an excess of finely ground AlCl₃ in a flask protected from atmosphere for 2 hr and then filtering to give a clear yellow-brown solution. A quantity of this solution (containing 0.32 g AcCl; 4.0 mmole) was added slowly with stirring to an ice-cold solution of either ferrocenophane (1; R=H or Me; 4.0 mmole) in CH₂Cl₂ (100 ml). The solution was stirred for 30 min., washed with water, dried (Na₂SO₄), and evaporated to dryness. The brown residue appeared to consist mainly of polymeric material together with traces of unchanged starting material and other coloured compounds (TLC) which were present in insufficient quantities to permit characterization.

Repeated attempts to affect acetylation using a variety of experimental methods were similarly unsuccessful.

Attempted lithiation/deuteration of [2]ferrocenophane. [2]Ferrocenophane was allowed to react with an equimolar amount of BuLi in dry ether for six hr and the reaction quenched by addition of D₂O. The product was isolated as described in a previous experiment. The relative intensities of the signals in the ¹H NMR spectra of the product and the starting material were identical. No evidence for the presence of deuteriated compounds was obtained from the mass spectrum of the product which was very similar to that of the starting material.

Attempted oxidation of [2]ferrocenophane. A solution of [2]ferrocenophane in dry C₆H₆ was refluxed with active MnO₂ for three hr. The mixture was filtered and the filtrate evaporated to dryness. The residue consisted mainly of decomposition (polymeric?) material. TLC analysis of the ether-soluble product showed the presence of a large number of coloured compounds, formed only in trace amounts.

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