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BRIDGED FERROCENES—VI[1]

SYNTHESIS AND STEREOCHEMISTRY OF [1,1]FERROCENOPHANES

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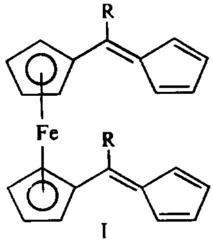
Abstract—Synthetic routes to compounds of the [1 1]ferrocenophane class have been devised making use of fulvene and acid chloride precursors and the parent compound has been prepared by direct synthesis. The bridged ferrocenes obtained by these different approaches have been chemically interrelated and their structure and stereochemistry have been investigated through study of their spectral properties. Sodamide promotes intramolecular cyclisation of 1,1'-bis(α-cyclopentadienylideneethyl)ferrocene to a [3]ferrocenophane derivative

INTRODUCTION

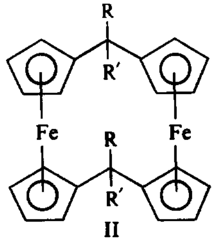
DERIVATIVES of ferrocene in which the cyclopentadienyl rings are connected by heteroannular bridges have attracted much research interest[2] and the study of the physical and chemical properties of these species has refined our understanding of the steric and electronic effects operative in the ferrocene molecule. In contrast, little attention has been paid to compounds of the type in which two ferrocene nuclei are linked in an annular fashion by bridging chains (*i.e.* [m.n]ferrocenophanes[3] and related compounds). At the outset of the work to be described in this paper,* the only authenticated examples of this class which had been reported were [4.4]ferrocenophane[5] and bis(*as*-indacenyliron)[6] although a few related compounds containing bridge heteroatoms had been prepared.[2] More recently, the simplest member, [0.0]ferrocenophane, has been obtained in two independent investigations.[7] We have synthesized a number of derivatives of the [1.1]ferrocenophane system and describe herein the methods of preparation and structure of these compounds.

SYNTHETIC ROUTES

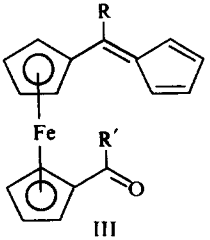
From fulvenes. The facile conversion of fulvenes into cyclopentadienide salts by reaction with hydride or carbanion reagents has provided a convenient means of synthesis of alkyl-substituted metallocenes.[8] In an analogous fashion, bisfulvenes of the type I can be converted into the corresponding [1.1]ferrocenophanes (II), albeit in low yield.



I



II



III

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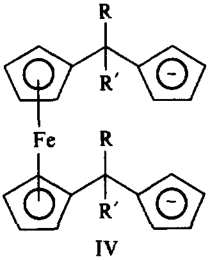
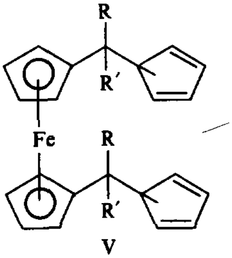
* Some preliminary results have been reported.[4]

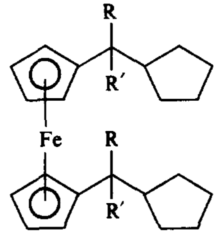
The precursors (I; R = Me[9] and Ph) were prepared by the reaction of cyclopentadiene with 1,1′-diacetyl- and 1,1′-dibenzoylferrocene respectively in the presence of sodium ethoxide. The IR spectrum of the deep red oil obtained from 1,1′-diformylferrocene* by a similar reaction was in accord with the expected structure (I; R = H). This product polymerized rapidly in solution or on standing, however, and this instability† prevented satisfactory characterization and precluded its use as an intermediate. Unless a large excess of cyclopentadiene was used in these base—catalysed condensations, the intermediate keto-fulvenes were isolated as the major products, e.g. III (R = R′ = Me) from 1,1′-diacetylferrocene. The greater reactivity of an acyl compared with an aroyl group in this fulvene synthesis was demonstrated by the conversion of 1-acetyl-1′-benzoylferrocene into the keto-fulvene (III; R = Me, R′ = Ph). The corresponding bisfulvene was not obtained pure by this approach.



IV

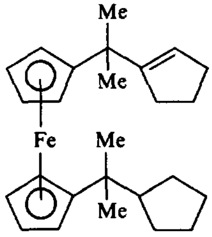


V

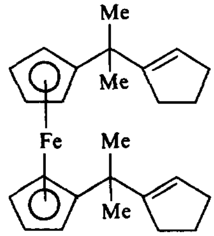


VI

Reduction of the bisfulvenes (I; R = Me and Ph) with LAH in THF gave yellow salts of the dianions (IV; R = Me and Ph respectively, R′ = H) which reacted with ferrous chloride to give low yields of the [1.1]ferrocenophanes (II; R = Me[4a] and Ph respectively, R′ = H). Similarly, the tetramethyl derivative (II; R = R′ = Me) was formed in 2·5% overall yield by treatment of the bisfulvene (I; R = Me) with MeLi followed by ferrous chloride. These bridged ferrocenes were separated chromatographically from polymeric material and mixtures of bis(cyclopentadiene) isomers (V), formed by protonation of the intermediate dianions (IV) during work-up procedure.



VII



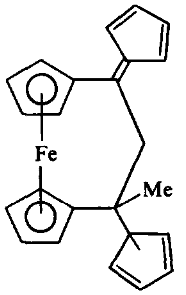
VIII

The unsaturated compounds (V) were unstable and were characterized by reduction to the corresponding cyclopentyl derivatives (VI). Thus, catalytic hydrogenation of V (R = Me, R′ = H) gave the saturated product VI (R = Me, R′ = H) which was identical with that prepared by a similar reduction of the bisfulvene (I; R = Me).

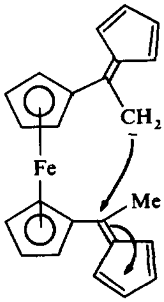
* This dialdehyde was prepared in 77% yield by oxidation of 1,1′-bis(hydroxymethyl)ferrocene in refluxing benzene solution with active manganese dioxide (*cf.* ref. 10).

† The corresponding monofulvene is also unstable.[10]

The partially reduced compounds (VII and VIII) were also isolated from incomplete hydrogenation of V(R = R′ = Me) and their structures were established from their PMR spectra which, in particular, revealed the presence of one and two vinyl protons respectively. Both olefins were converted into the saturated product VI (R = R′ = Me) upon further hydrogenation.



IX



X

Sodamide abstracts a proton from 6-alkylfulvenes yielding alkenylcyclopentadienide salts which have been used to prepare unsaturated ferrocene derivatives.[8a] An attempt to prepare the bridged diene (II; R,R′ = CH_2) by this approach was unsuccessful. Treatment of the bisfulvene (I; R = Me) with sodamide in THF or liquid ammonia led instead to the formation of a product to which the [3]ferrocenophane structure (IX; mixture of double bond isomers) is assigned on PMR and mass spectral evidence (Experimental). This compound presumably arises from intramolecular cyclization of an intermediate carbanion (X) as shown, a process which bears close analogy to the ring closure postulated by Hauser *et al.* as an intermediate step in the sodamide-catalysed condensation of 1,1′-diacetylferrocene with esters[11] or with benzyl chloride.[12]

The stereochemical constraints imposed upon the interannular bridge in the derivative (IX) hinder the attainment of coplanarity by the fulvene group and the attached cyclopentadienyl ring. The resulting reduction in conjugative interaction between these groups is reflected in the hypsochromic shift and reduced intensity of the long wavelength band* (450 nm; $\varepsilon = 960$) in the electronic spectrum of this compound compared with those of non-bridged analogues. e.g. 6-ferrocenyl-6-methylfulvene[14] (484 nm; $\varepsilon = 2340$), where full conjugation is conformationally possible.

Friedel–Crafts cyclization.[4b] The presence of a CO group attached directly to a cyclopentadienyl ring in ferrocene deactivates that ring towards electrophilic substitution.[15] With this in mind, the reaction between ferrocene and 1,1′-bis(chlorocarbonyl)ferrocene under Friedel–Crafts conditions was investigated as a potential route to [1.1]ferrocenophane-1,12-dione (XI). This reaction was carried out in dilute chloroform solution using aluminium chloride as catalyst. The benzene-insoluble portion of the reaction product consisted of polymeric material and the diketone (XI), which could be extracted with hot chloroform. The compound crystallized from this solvent in fine maroon needles, m.p. >350°, and its structure was established from its chemical reactions (*vide infra*) and from mass spectral data from which a molecular formula of $C_{22}H_{16}Fe_2O_2$ was calculated.

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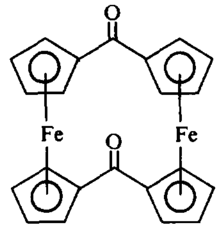
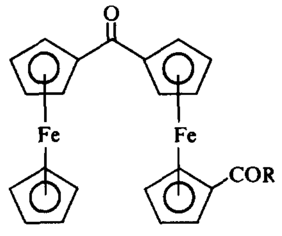
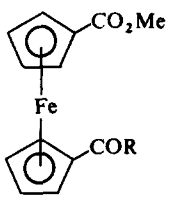
* The sensitivity of this band to conjugation effects has been demonstrated.[13]


XI

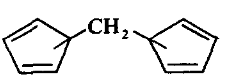

XII

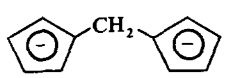

XIII

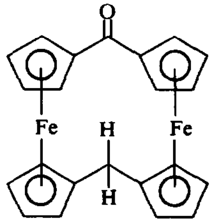
The benzene-soluble material from the above reaction was separated chromatographically into 1,1′-bis(carboethoxy)ferrocene, 1-carboethoxy-1′-ferrocenoylferrocene (XII; R = OEt), and 1,1′-diferrocenoylferrocene (XII; R = Fc). The structure of the last compound was proved by mixed hydride reduction[16] to the known 1,1′-bis(ferrocenylmethyl)ferrocene.[17] The above ethyl esters must arise from the presence of ethanol in the chloroform solvent since they were not formed when methylene chloride was used in its place.

The diketone (XI) was also isolated in low yield from the self-condensation of chlorocarbonylferrocene under similar conditions although a greater proportion of polymeric material was formed.* Since the yields of diketone (XI) isolated from these reactions were poor, a more efficient synthesis of the probable intermediate (XII; R = Cl) was sought. Partial hydrolysis of 1,1′-bis(carbomethoxy)ferrocene (XIII; R = OMe) gave[19] the half-ester (XIII; R = OH) which, on treatment with phosphorus trichloride, was converted into the acid chloride (XIII; R = Cl). This, in turn, reacted with ferrocene in the presence of aluminium chloride to give the keto-ester (XII; R = OMe) which, on hydrolysis, gave the same keto-acid (XII; R = OH) as that similarly obtained from the previously prepared ethyl ester (XII; R = OEt). The acid chloride (XII; R = Cl) derived from this acid underwent intramolecular Friedel–Crafts cyclization to the diketone (XI), identical with the compound previously prepared. The efficiency of this reaction was poor and the disappointing yield of XI must reflect the low probability of attainment by the intermediate (XII; R = $AlCl_4$) of a conformation in which intramolecular electrophilic attack by the acylium carbon upon the unsubstituted cyclopentadienyl ring can occur.

Direct synthesis. Schaltegger *et al.* have shown[20] that bis(cyclopentadienyl)methane (XIV) can be readily synthesized by the reaction of sodium cyclopentadienide with methylene dihalides. We have used this hydrocarbon to prepare the parent [1.1]-ferrocenophane (II; R = R′ = H) by the reaction of the derived dianion (XV) with ferrous chloride in THF. During the course of this work, an investigation of the same


XIV


XV


XVI

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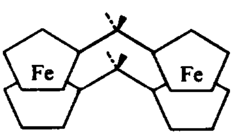
* In sulpholane solution, using boron trifluoride etherate catalyst, poly(ferrocenylketones) have been isolated from these reactions.[18]

reaction was reported[21] by Katz *et al.* who also isolated a range of oligomeric ferrocenophanes in addition to the simplest member (II; R = R′ = H).

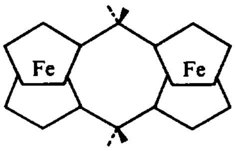
Depending upon the reaction conditions, [1.1]ferrocenophane (II; R = R′ = H) can be selectively oxidized by manganese dioxide either to the monoketone (XVI) or the diketone (XI), the latter identical with the compound prepared by the Friedel–Crafts route (*vide supra*). Mixed hydride reduction[16] of the diketone (XI) gave [1.1]-ferrocenophane (II; R = R′ = H) in high yield. Treatment of XI with MeMgI gave an unstable diol (II; R = Me, R′ = OH) which, on reduction with mixed hydride,[16] gave a high yield of a product, identical in all respects (m.p., IR, PMR, R_f) with the compound prepared from the bisfulvene (I; R = Me) to which the structure II (R = Me, R′ = H) was assigned (*vide supra*). The structural interrelationship of the [1.1]ferrocenophanes prepared by the various synthetic routes (fulvene, Friedel–Crafts, direct sythesis) was this firmly established by this set of reactions.

STRUCTURE AND STEREOCHEMISTRY

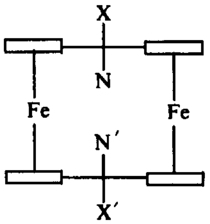
The [1.1]ferrocenophane system is particularly interesting from a stereochemical viewpoint.* In principle, such compounds are capable of existence in different steric modifications in which the hydrocarbon ligands are formally eclipsed (XVIIA) or gauche (XVIIB). Further, a substituent attached to a bridging carbon may occupy either an *exo* (X,X′) or an *endo* (N,N′) configuration (see XVIIC) with respect to the Fe atoms.



XVIIA



XVIIB



XVIIC

Inspection of molecular models† reveals that the eclipsed structure (XVIIA) is much more flexible than the gauche modification (XVIIB) and indicates that interconversion of these structures can occur only at the expense of gross deformation of preferred bond angles and distances. Further, in the essentially rigid gauche structure (XVIIB), the cyclopentadienyl rings of each ligand are constrained to a coplanar geometry. Assuming normal values for bond angles and distances, such an arrangement would lead to an impossibly severe steric interaction between the protons of each H_α pair (see XVIII). Relief of these nonbonded interactions by mutual twisting of the ring planes is resisted in the gauche structure but can occur easily in the eclipsed ligand arrangement.

A crystal structure determination of the major isomer (*vide infra*) (II; R = Me, R′ = H) obtained by the fulvene route has been carried out[24] and has shown that

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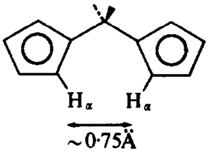
* Some features of the stereochemistry of this class of compound have been discussed by Struchkov.[22] The structures of the compounds of this type referred to in this review, however, are incorrect (see Ref. 23).

† Dreiding ferrocene stereomodels supplied by W. Büchi Glasapparatefabrik, Flawil, Switzerland were used.



XVIII

the molecule is in the eclipsed configuration (XVIIA) with both Me groups in an *exo* environment (XVIIC; X = X′ = Me, N = N′ = H). The planar cyclopentadienyl rings of each ferrocene nucleus are staggered by 22° (*cf.* 36° in crystalline ferrocene[25]) and mutually tilted by 3°. The planes of the rings linked through the bridges are twisted by 31° to each other, thereby relieving the aforementioned H_α—H_α interaction.

Further information regarding the structure and stereochemistry of the bridged ferrocenes prepared in this study was gained from their spectral properties, particularly mass and PMR spectra, which are discussed below. The IR spectra conformed to those expected of heteroannularly disubstituted ferrocene derivatives and, except for the absence of bands at 9 and 10 μ,[26] were broadly similar in feature to those of non-cyclic analogues (i.e. Fc_2CRR', Fc_2CO, etc.).

Mass spectra. In common with the behaviour of most ferrocene derivatives,* the mass spectra of the [1.1]ferrocenophanes are characterized by the presence of an intense group of molecular ions, the base peaks of the spectra. The presence of two Fe atoms in each molecule was established from the relative intensities of these parent ions which arise from the four naturally occurring iron isotopes (atomic mass: 54, 56, 57, and 58). Accurate mass measurement of the $^{56}Fe_2$ molecular ion established for each compound a molecular formula in agreement with the assigned structure. The spectra also contained relatively intense groups of doubly charged molecular ions, probably diferrocenium species, formed by the loss of an electron from each Fe atom.

In general, fragmentation of the molecular ions is limited and occurs either by loss of bridge substituents or by expulsion of a fulvene moiety. For example, the parent ion of the 1,12-dimethyl derivative (II; R = Me, R′ = H) eliminates either a C_7H_8 fragment (methylfulvene?) or two Me groups in succession. The primary cracking pattern of this compound, which is typical of alkylbridged [1.1]ferrocenophanes, has been given more fully elsewhere.[27a] The main fragmentation pathways for the ketones (XI and XVI), on the other hand, involve loss of carbon monoxide or elimination of a C_6H_4O fragment (cyclopentadienylidene ketene?). Each of the transitions described above was confirmed by the presence of the appropriate metastable peak.

PMR spectra. The PMR spectra of the ferrocenophanes and related non-cyclic compounds are summarized in Table 1. In the case of diferrocenylalkanes (Fc_2CRR'), very little distinction in chemical shift is shown between ring protons located α- or β- to the alkyl linkage. In contrast, the ring proton patterns of the [1.1]ferrocenophanes are more complex, appearing as two well-separated triplets (A_2B_2 pattern) of equal intensity in the spectra of the parent compound (II; R = R′ = H), the tetramethyl

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* The mass spectra of organo-transition metal compounds, including ferrocene derivatives, have been discussed in recent reviews.[27]

TABLE 1. PMR SPECTRA[a, b]

Compound[c]	Cyclopentadienyl protons (τ)	Bridge protons (τ)
Non-cyclic compounds		
Diferrocenylmethane[17a]	5·92, 5·95 (2s; 18H)	6·60 (s; 2H)
1,1-Diferrocenylethane[37]	5·95, 5·99 (2s; 18H)	6·50 (q; 1H); 8·38 (d; 3H)
2,2-Diferrocenylpropane[d]	5·92 (s; 18H)	8·40 (s; 6H)
Ferrocenoylferrocene[38]	5·01 (t; 4H); 5·50 (t; 4H); 5·81 (s; 10H)	
[1.1]*Ferrocenophanes*		
II (R = R′ = H)	5·61 (t; 8H); 5·82 (t; 8H)	6·45 (s; 4H)
II (R = Me, R′ = H)[e]	5·3–5·5 (m; 4H); 5·6–5·9 (m; 12H)	6·22 (q; 2H); 8·84 (d; 6H)
II (R = R′ = Me)	5·66 (t; 8H); 5·80 (t; 8H)	8·62 (s; 12H)
II (R = Me, R′ = OH)	5·50 (t; 8H); 5·75 (t; 8H)	4·92 (bs; 2H); 8·60 (s; 6H)
II (R = Ph, R′ = H)	5·05–5·25 (m; 4H); 5·7–6·0 (m; 12H)	2·96 (s; 10H); 4·97 (s; 2H)
XVI	4·97 (t; 4H); 5·43 (t; 4H) 5·5–5·7 (m; 4H); 5·83 (t; 4H)	6·96 (bs; 2H)

[a] In $CDCl_3$ soln against TMS as internal reference.

[b] Diketone (XI) was too insoluble to permit determination of spectrum.

[c] Formulae in text.

[d] Synthesis is given in Experimental section.

[e] Major isomer (see text).

derivative (II; R = R′ = Me), and the diol (II; R = Me, R′ = OH), and as two groups of multiplets in the intensity ratio 1:3 for the dimethyl and diphenyl derivatives (II; R = Me and Ph respectively, R′ = H).

It is well established that the volume between the rings in ferrocene is deshielding in character,[28] and a differentiation in chemical shift would have been expected for the protons of a substituent attached to a [1.1]ferrocenophane bridge in an *exo* compared with an *endo* configuration.* The bridge protons of the compounds (II; R = R′ = H or Me) appear in each case as a sharp singlet, however, suggesting the occurrence of a conformational exchange process which renders equivalent on time-average the *exo* and *endo* substituents. An equilibration process of this nature has been suggested for [1.1]ferrocenophane itself[4b] and its PMR spectrum interpreted accordingly. A full analysis of the conformational mobility of compounds of this type, however, is deferred to a future paper.[30]

The PMR spectrum of the unpurified ferrocenophane product (II; R = Me, R′ = H) obtained either by the fulvene route or from the diketone (XI) *via* the diol (II; R = Me, R′ = OH) contained two separate Me doublets of relative intensity ca. 1:6 centered at τ 8·72 and 8·84 respectively ($J \sim 7·5$ Hz). After one recrystallization from ligroin, the major isomer was obtained pure (PMR, crystal structure[24]) but attempts to separate the minor component were unsuccessful. Since the ring proton resonance patterns for the product before and after recrystallization were identical and for reasons to be detailed elsewhere,[30] the minor component is tentatively assigned an eclipsed structure (XVIIA) with *exo–endo* Me groups (XVIIC; X = N′ = Me, X′ = N = H).

Finally, since the [1.1]ferrocenophanes prepared by the various synthetic routes have been chemically interconverted (*vide supra*), it may be inferred from the stereo-

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* Illustrative examples have been provided by Rosenblum.[29]

chemistry established by crystal structure studies[24] that the hydrocarbon ligands in the structures of these compounds have an eclipsed geometry (XVIIA).

EXPERIMENTAL

For general remarks, see Part I.[31] PMR spectra were recorded in $CDCl_3$ solns, electronic spectra in abs EtOH solns, and IR spectra as KBr discs unless indicated otherwise. Mol. wts were determined by accurate mass measurements of the 56Fe molecular ion in the high resolution mass spectrum. Active MnO_2 and anhyd $FeCl_2$ were prepared by the reported methods.[32, 33] BuLi in hexane was supplied by Alfa Inorganics, Inc., and the chlorocarbonylferrocenes were obtained from Research Organic Chemicals, Inc. Chromatographies were carried out using Spence Grade H alumina, partially deactivated by exposure to the atmosphere. Ligroin refers to light petroleum, b.p. 40–60°.

1,1'-Bis(α-cyclopentadienylideneethyl)ferrocene (I: R = Me)

Freshly distilled cyclopentadiene (33 g; 0·5 mole) was added slowly to a soln of NaOEt (from 23 g Na; 1 g at) in EtOH (750 ml). After 15 min, a soln of 1,1'-diacetylferrocene (13·6 g; 0·05 mole) in EtOH (350 ml) was added. The mixture was stirred for 30 min at room temp and then for 2 hr under reflux. The mixture was cooled to 0° and filtered, affording I (R = Me) (12·3 g) as a red-brown solid. The filtrate was diluted with H_2O (500 ml) and extracted thoroughly with CH_2Cl_2. The total extract was washed (H_2O), dried (Na_2SO_4), and concentrated, yielding a further amount (1·7 g) of product (total yield 77%). The compound crystallized from EtOHaq as red needles, m.p. 133–134° (lit.[9] 134°). PMR τ 3·47 (s; 8H; vinyl protons), 5·36, 5·57 (2 t; 8H; Cp protons), 7·57 (s; 6H; Me protons).

1-Acetyl-1'-(α-cyclopentadienylideneethyl)ferrocene (II; R = R' = Me)

The reaction between 1,1'-diacetylferrocene (13·6 g; 0·05 mole) and cyclopentadiene (8·0 g; 0·12 mole) in the presence of NaOEt (0·25 mole) was carried out as in the preceding experiment and the product was chromatographed. Ligroin–benzene (2:1) eluted the bisfulvene (I: R.=.Me) (1·5 g; 9·5%), identical with the compound described above. Ligroin–benzene (1:1) eluted the ketone (III: R = R' = Me) (6·3 g; 46%), which was obtained as a red oil which could not be crystallized. Due to the instability of this compound, satisfactory analytical data were not obtained. PMR τ 3·44 (s; 4H; vinyl protons), 5·2–5·6 (m; 8H; Cp protons), 7·49 (s; 3H; allylic Me protons), 7·72 (s; 3H; COMe protons). Benzene eluted unchanged 1,1'-diacetylferrocene (1·75 g; 13% recovery).

1,1'-Bis(α-cyclopentadienylidenebenzyl)ferrocene (I: R = Ph)

The reaction between 1,1'-dibenzoylferrocene (4·5 g; 0·01 mole) and cyclopentadiene (26·4 g; 0·4 mole) in the presence of NaOEt (0·8 mole) was carried out as in the preceding experiments. The product I (R = Ph; 3·8 g; 78%) crystallized from EtOH as a black solid, m.p. 145–146°. (Found: C, 83·2; H, 5·5. $C_{34}H_{26}Fe$ requires: C, 83·3; H, 5·3%). PMR τ 2·73 (s; 10H; Ph protons), 3·0–4·4 (m; 8H; vinyl protons), 5·60 (s; 8H; Cp protons).

1-Benzoyl-1'-(α-cyclopentadienylideneethyl)ferrocene (III: R = Me, R' = Ph)

The reaction between 1-acetyl-1'-benzoylferrocene[34] (3·3 g; 0·01 mole) and cyclopentadiene (4·4 g; 0·07 mole) in the presence of NaOEt (0·14 mole) was carried out as described in preceding experiments and the product was chromatographed. Ligroin eluted a red band which afforded a dark red gum (possibly the bisfulvene) which could not be crystallized and was not obtained pure. Ligroin–ether (5:1) eluted III (R = Me, R' = Ph; 1·6 g; 44%), which crystallized from ligroin–ether as a red solid, m.p. 81–82°. (Found: C, 75·9; H, 5·3. $C_{24}H_{20}FeO$ requires: C, 75·7; H, 5·3%); PMR τ 2·0–2·8 (m; 5H; Ph protons), 3·50 (s; 4H; vinyl protons), 5·10, 5·3–5·6 (t and m; 8H; Cp protons), 7·52 (s; 3H; Me protons).

1,1'-Diformylferrocene

A mixture of active MnO_2 (50 g) and 1,1'-bis (hydroxymethyl)ferrocene[35] (5·0 g; 0·02 mole) in dry benzene (100 ml) was heated under reflux with stirring for 4 hr. The mixture was cooled and filtered and the filtrate evaporated giving 1,1'-diformylferrocene (3·84 g; 77%) as a red solid, m.p. 185–186° (lit.[10] 183–184°); PMR τ 0·08 (s; 2H; CHO protons), 5·08, 5·27 (2 t; 8H; Cp protons).

Attempted preparation of the bisfulvene (I: R = H)

The reaction between 1,1'-diformylferrocene (3·07 g; 12·7 mmole) and cyclopentadiene (9·9 g; 0·15 mole) in the presence of NaOEt (0·30 mole) was carried out as described previously and the product was chromatographed. Ligroin eluted a deep red band which afforded a deep red oil. This product, which contained cyclopentadiene dimer, polymerized rapidly and could not be characterized. The IR spectrum lacked CO absorption and was compatible with the structure I (R = H).

1,12-*Dimethyl*[1.1]*ferrocenophane* (II: R = Me, R′ = H)

A soln of I (R = Me; 3·66 g; 0·01 mole) in THF (50 ml) was added to a suspension of LAH (1·0 g; 0·025 mole) in THF (150 ml) and the mixture was stirred for 20 hr. A yellow slurry was formed. The mixture was diluted with THF (500 ml) and $FeCl_2$ (1·3 g; 0·01 mole) was added. The mixture was stirred for 16 hr and then poured carefully into ice-water (1000 ml). The soln was extracted thoroughly with $CHCl_3$ and the combined extracts were washed (H_2O), dried (Na_2SO_4), and evaporated. The residue was dissolved in ligroin and chromatographed Ligroin eluted the bis(cyclopentadiene) mixture (V; R = Me, R′ = H; 0·59 g; 16%), an unstable orange-yellow oil, which was immediately hydrogenated (*vide infra*) Ligroin eluted II (R = Me, R′ = H; 1·14 g; 27%), which crystallized from ligroin as orange-yellow rods, m.p. 185–186° (lit.[4a] 182–184°). (Found: C, 68·1; H, 6·1; *M*, 424. $C_{24}H_{24}Fe_2$ requires: C, 68·0; H, 5·7%; *M*, 424). PMR see Table; λ_{max} 320 (shoulder) (ε = 210), 440 nm (ε = 205). Ligroin–ether mixtures eluted intractable gums which were not examined further.

1,1′-*Bis*(α-*cyclopentylethyl*)*ferrocene* (VI: R = Me, R′ = H)

(a) The bis(cyclopentadiene) mixture (V · R = Me, R′ = H; 0·59 g; 1·6 mmole) described in the preceding experiment was dissolved in benzene (50 ml) and hydrogenated over Pt. When uptake of H_2 had ceased, the soln was filtered and the filtrate evaporated. The residue was dissolved in ligroin and chromatographed. Ligroin eluted VI (R = Me, R′ = H; 0·57 g; 94%), an orange-yellow oil, b.p. 200° (bath)/0·01 mm. (Found: C, 76·1; H, 9·2. $C_{24}H_{34}Fe$ requires: C, 76·2; H, 9·0%); PMR (CS_2) τ 6·12 (s; 8H; Cp protons), 8·74 (d; 6H; Me protons), 8·2–8·9 (m; 20H; remaining protons).

(b) A soln of I (R = Me; 1·6 g; 4·4 mmole) in ether–EtOH (1:1) was hydrogenated over Pt in the presence of a trace of HOAc. The soln was filtered, washed ($NaHCO_3$aq and then H_2O), dried (Na_2SO_4), and evaporated. Chromatography afforded VI (R = Me, R′ = H; 1·54 g; 95%), identical with the compound described under (a).

1,12-*Diphenyl*[1.1]*ferrocenophane* (II: R = Ph, R′ = H)

The reaction between I (R = Ph; 3·22 g; 6·9 mmole), LAH (2·0 g; 50 mmole), and $FeCl_2$ (2·6 g; 20 mmole) in THF (750 ml) was carried out as described in a previous experiment. The ligroin-soluble portion of the product afforded V (R = Ph, R′ = H; 0·11 g; 3%) which was not characterized. The ligroin-insoluble residue was extracted thoroughly with ether and the extract was evaporated giving II (R = Ph, R′ = H; 0·32 g; 9%), which crystallized from ligroin–ether as a yellow solid, m.p. 279–282°. (Found: C, 74·4; H, 5·3 *M*, 548 $C_{34}H_{28}Fe_2$ requires: C, 74·5; H, 5·1%; *M*, 548); PMR—see Table 1 The ether-insoluble product (2·05 g) was polymeric.

1,1,12,12-*Tetramethyl*[1.1]*ferrocenophane* (II; R = R′ = Me)

A soln of I (R = Me; 5·5 g; 15 mmole) in ether (70 ml) was added to a soln of MeLi (ca. 80 mmole) in ether (120 ml). The mixture was heated under reflux for 2 hr and then stirred at room temp for 16 hr. The yellow slurry was diluted with THF (250 ml), $FeCl_2$ (3·0 g; 75 mmole) was added, and the mixture was stirred at 40° for 6 hr. The mixture was poured carefully into ice-water (1000 ml) and the product was isolated as described in previous experiments. The product was extracted with ether leaving a polymeric residue (2·95 g) which was not examined. The ether extract was concentrated and chromatographed. Ligroin eluted V (R = R′ = Me; 0·6 g; 11%), a yellow oil, which was immediately hydrogenated (*vide infra*). Ligroin–ether (5:1) eluted II (R = R′ = Me; 0·17 g; 2·5%), which crystallized from ligroin–ether as a red solid, m.p. 141–142°. (Found: C, 68·8; H, 6·3; *M*, 452. $C_{26}H_{28}Fe_2$ requires: C, 69·0; H, 6·2%; *M*, 452); PMR see Table 1; λ_{max} 325 (shoulder) (ε = 215), 464 nm (ε = 285). Ligroin–ether mixtures eluted further products, probably oligomeric, which were not examined.

Hydrogenation of the bis(*cyclopentadiene*) *mixture* (V: R = R′ = Me)

The mixture (0·6 g) from the preceding experiment was hydrogenated in benzene soln over Pt and the product was isolated as described previously and chromatographed. Ligroin eluted 3 yellow bands which were not cleanly separated A pure sample of each of the 3 products was obtained by preparative TLC (on Al_2O_3) which separated (in order of elution) the following compounds: VI (R = R′ = Me), which crystallized from ligroin as an orange solid, m.p. 73–75°. (Found: C, 76·5; H, 9·4. $C_{26}H_{38}Fe$ requires: C, 76·8; H, 9·3%); PMR (CS_2) τ 6·12 (s; 8H; Cp protons), 8·70 (bs; 18H; cyclopentyl protons), 8·78 (s; 12H; Me protons); VII, which crystallized from ligroin as an orange solid, m.p. 79–81°. (Found: C, 76·6; H, 9·0. $C_{26}H_{36}Fe$ requires: C, 77·2; H, 8·9%); PMR (CS_2) τ 4·95 (m; 1H; vinyl proton), 6·11 (s; 8H; Cp protons), 8·62 (s; 6H; $Me_2CC{=}C$ protons), 8·78 (s; 6H; Me protons), 7·7–8·8 (m; 15H; remaining protons); VIII, which crystallized from ligroin as an orange solid, m.p. 103–105°. (Found: C, 76·9; H, 8·6. $C_{26}H_{34}Fe$ requires: C, 77·6; H, 8·5%); PMR (CS_2) τ 4·95 (m; 2H; vinyl protons), 6·09 (bs; 8H; Cp protons), 7·5–8·3 (m; 12H; CH_2 protons), 8·60 (s; 12H; Me protons).

Further hydrogenation of either VII or VIII in benzene containing a trace of HOAc over Pt afforded VI (R = R′ = Me) in quantitative yield.

1-*Methyl*-1-*cyclopentadienyl*-3-*cyclopentadienylidene*[3]*ferrocenophane* (IX)

(a) A soln of I (R = Me; 3·0 g; 8·2 mmole) in THF (25 ml) was added slowly to a suspension of $NaNH_2$ (3·0 g; 77 mmole) in THF (200 ml). The mixture was stirred for 16 hr at room temp and then for 5 hr under reflux. THF (300 ml) followed by $FeCl_2$ (1·0 g; 25 mmole) was added and the mixture was stirred for 15 hr and then poured into ice-water (1000 ml). The mixture was filtered through kieselguhr and the filtrate was extracted thoroughly with CH_2Cl_2. The extract was washed (H_2O), dried (Na_2SO_4), and evaporated, and the residue was chromatographed. Ligroin eluted IX (1·89 g; 63%), which crystallized from ligroin as an orange solid, m.p. 134–135°. (Found: C, 78·6; H, 6·2; *M*, 366. $C_{24}H_{22}Fe$ requires: C, 78·9; H, 6·0%; *M*, 366); PMR τ 3·50 (bs; 4H; fulvene protons), 3·65 (m; 3H; vinyl protons), 5·3–6·1 (m; 8H; Cp protons), 6·55 (s; 2H; bridge CH_2 protons), 7·09 (bs; 2H; cyclopentadiene CH_2 protons), 8·63 (s; 3H; Me protons); λ_{max} 380 (ε = 1455), 450 nm (ε = 960). Ether eluted a yellow-brown polymer which was not examined.

(b) The reaction was repeated using liquid NH_3–THF as solvent. IX (9%) was isolated together with a complex mixture of products whose separation was not attempted

[1.1]*Ferrocenophane*-1,12-*dione* (XI)

(a) A soln of ferrocene (14·0 g; 0·075 mole) in CH_2Cl_2 (100 ml) was added to a slurry of $AlCl_3$ (52·0 g; 0·39 mole) in CH_2Cl_2 (600 ml) at 0° and then a soln of 1,1′-bis(chlorocarbonyl)ferrocene (20·0 g; 0·064 mole) in CH_2Cl_2 (100 ml) was added slowly with stirring. The blue mixture was stirred overnight and then poured carefully into crushed ice (1000 ml). The organic layer was separated and combined with several $CHCl_3$ extracts of the aqueous layer. The total extract was washed with 5% NaOH aq and then with H_2O, dried (Na_2SO_4), concentrated, and chromatographed. Ligroin eluted unchanged ferrocene (3·0 g; 21% recovery). Ether–CH_2Cl_2 mixtures eluted several minor orange or red bands which were not examined. CH_2Cl_2–$MeCO_2Et$ (9:1) eluted a purple band which afforded XI (0·93 g; 3·5%). The compound crystallized from hot $CHCl_3$ on slow cooling in fine maroon needles, m.p. >350°. (Found: C, 62·6; H, 3·9; *M*, 424. $C_{22}H_{16}Fe_2O_2$ requires: C, 62·3; H, 3·8%; *M*, 424); IR 6·20 μ.

(b) The reaction between chlorocarbonylferrocene (9·4 g; 0·037 mole) and $AlCl_3$ (7·0 g; 0·052 mole) in CH_2Cl_2 (400 ml) was carried out as in the preceding experiment. Much insoluble polymeric material was formed and XI was obtained as before in 1·2% yield.

(c) The reaction between 1,1′-bis(chlorocarbonyl)ferrocene (11·9 g; 0·038 mole), ferrocene (7·0 g; 0·035 mole), and $AlCl_3$ (26·7 g; 0·2 mole) in technical grade $CHCl_3$ (400 ml) was carried out as described under (a). The deep red product was extracted with benzene (*vide infra*) leaving a maroon solid (2·0 g) This was extracted with hot $CHCl_3$ and, on slow cooling, XI (1.1 g: 7%) crystallized from the concentrated extract. extract.

The above benzene-soluble material was chromatographed. Benzene eluted unchanged ferrocene (0·7 g; 10% recovery). Benzene–ether (9:1) eluted 1,1′-bis(carboethoxy)ferrocene (3·3 g; 26%), which crystallized from ligroin as an orange solid, m.p. 40–42° (lit [36] 41·5–42°), and was identical with an authentic specimen. Ether eluted XII R = OEt: 1·2 g; 7%), which crystallized from ligroin ether as small orange needles, m.p. 123–125°. (Found: C, 61·6; H, 4·8. $C_{24}H_{22}Fe_2O_3$ requires: C, 61·3; H, 4·7%); IR (CCl_4) 5·83, 6·14 μ; PMR τ 4·9–5·7 (m; 14H; C_5H_4CO and CH_2 protons), 5·80 (s; 5H; Cp protons), 8·69 (t; 3H; Me protons). $CHCl_3$ eluted XII (R = Fc; 0·6 g; 3%), which crystallized from ligroin–$CHCl_3$ as an orange solid, m.p. 245–246° (lit.[18] 253–257°). (Found: C, 63·4; H, 4·3. $C_{32}H_{26}Fe_3O_2$ requires: C, 63·0; H, 4·3%); IR ($CHCl_3$) 6·25 μ; PMR τ 4·9–5·1, 5·35–5·55 (2m; 16H; C_5H_4CO protons), 5·80 (s; 10H; Cp protons).

(d) A soln of XII (R = OH; 0·9 g; 2 mmole) and PCl_3 (3·2 g; 23 mmole) in anhyd benzene (50 ml) was refluxed for 4 hr and then evaporated to dryness under reduced press. The residue, containing XII (R = Cl; *vide infra*), was dissolved in CH_2Cl_2 (400 ml), $AlCl_3$ (0·8 g; 6 mmole) was added, and the mixture was stirred at room temp for 24 hr and then poured into H_2O (500 ml). The CH_2Cl_2 layer was extracted with NaOHaq in order to remove unchanged XII (R = OH; 0·19 g; 21% recovery) and then evaporated. The residue was extracted with ether affording 1-chlorocarbonyl-1'-ferrocenoylferrocene (0·24 g; 26%), which crystallized from ether as red-brown needles, m.p. 141–149° (dec). (Found: C, 57·4; H, 4·3. $C_{22}H_{17}ClFe_2O_2$ requires: C, 57·4; H, 3·7%); IR (Nujol) 5·70, 6·12 μ; PMR τ 4·82 (t; 2H), 4·98 (t; 4H), 5·2–5·4 (m; 6H), 5·74 (s; 5H).

The ether-insoluble residue was chromatographed and $CHCl_3$ eluted XI (0·015 g; 3%), identical with the compound described above.

1-*Carbomethoxyferrocene-1'-carboxylic acid* (XIII; R = OH)

A soln of 1,1'-bis(carbomethoxy)ferrocene[8c] (8·23 g; 27 mmole) in MeOH (125 ml) and NaOHaq (9 ml; 10%) was refluxed for 24 hr. The mixture was then diluted with H_2O and unchanged diester (1·93 g; 23% recovery) was extracted with ether. The aqueous soln was acidified (HCl) and extracted with ether. The extract was washed (H_2O), dried (Na_2SO_4), and evaporated, giving 1-carbomethoxyferrocene-1'-carboxylic acid (5·6 g; 92%), which crystallized from ether as a yellow solid, m.p. 148–150° (lit.[19] 147–148°). (Found: C, 54·6; H, 4·6. $C_{13}H_{12}FeO_4$ requires: C, 54·2; H, 4·2%); IR (Nujol) 5·85, 6·00 μ; PMR τ 2·09 (s; 1H; OH proton), 5·04, 5·46 (2 t; 8H; Cp protons), 6·11 (s; 3H; Me protons).

1-*Carbomethoxy-1'-ferrocenoylferrocene* (XII; R = OMe)

A soln of XIII (R = OH; 3·69 g; 0·012 mole) and PCl_3 (6·4 g; 0·046 mole) in anhyd benzene (150 ml) was refluxed for 4 hr and then evaporated to dryness under reduced press. The residue, containing the crude XIII (R = Cl), was dissolved in CH_2Cl_2 (150 ml), ferrocene (6·0 g; 0·032 mole) and $AlCl_3$ (3·3 g; 0·024 mole) were added, and the mixture was stirred for 24 hr and then poured into H_2O (400 ml). Unchanged XIII (R = OH; 0·32 g; 9% recovery) was removed by extraction of the CH_2Cl_2 layer with NaOHaq. The acid-free CH_2Cl_2 soln was washed (H_2O), dried (Na_2SO_4), and evaporated, and the residue was chromatographed. Ligroin eluted ferrocene (3·89 g; 65% recovery). Ether–CH_2Cl_2 (3:1) eluted XII (R = OMe; 3·1 g; 58%), which crystallized from ligroin–ether as red-orange needles, m.p. 180–182°. (Found: C, 60·5; H, 4·5. $C_{23}H_{20}Fe_2O_3$ requires: C, 60·5; H, 4·4%); IR (Nujol) 5·90, 6·33 μ; PMR τ 4·92 (q; 4H; Cp protons), 5·11 (t; 2H; Cp protons), 5·41 (q; 4H; Cp protons), 5·55 (t; 2H; Cp protons), 5·77 (s; 5H; Cp protons), 6·21 (s; 3H; Me protons).

1-*Ferrocenoylferrocene-1'-carboxylic acid* (XII; R = OH)

The keto-ester XII (R = OMe; 2·28 g; 5 mmole) was dissolved in MeOH (75 ml), NaOHaq (10 ml; 10%) was added, and the mixture was refluxed for 24 hr and then diluted with H_2O. CH_2Cl_2 extracted unchanged keto-ester (0·35 g; 15%). The aqueous soln was acidified (HCl) and XII (R = OH; 0·5 g; 26%) was precipitated as a dark brown solid, m.p. >300°. (Found: C, 58·8; H, 4·7. $C_{22}H_{18}Fe_2O_3$ requires: C, 59·7; H, 4·1%); IR (Nujol) 6·00, 6·21 μ. Because of the limited amount of product available, further purification was not attempted. The poor solubility of the product precluded determination of its PMR spectrum.

The same acid could be similarly obtained by alkaline hydrolysis of XII (R = OEt) isolated from a previous experiment.

1,1'-*Bis(ferrocenylmethyl)ferrocene*

The diketone XII (R = Fc; 0·5 g; 0·8 mmole) was added to a stirred suspension of LAH (0·38 g; 10 mmole) and $AlCl_3$ (1·35 g; 10 mmole) in ether (100 ml). The mixture was stirred for 2 hr and then poured carefully into crushed ice (200 ml). The organic layer was separated and combined with 2 ether extracts of the aqueous layer The total extract was washed (H_2O), dried (Na_2SO_4), and evaporated giving 1,1'-bis(ferrocenylmethyl)ferrocene (0·44 g; 92%), which crustallized from benzene as a yellow solid, m.p. 165–167° (lit. 166–168°[17a]; 164–166°[17b]) and was identical with an authentic sample.[17b]

[1.1]*Ferrocenophane* (II; R = R' = H)

(a) The diketone XI (2·4 g; 5·7 mmole) was reduced with LAH (3·8 g; 0·1 mole) and $AlCl_3$ (13·4 g; 0·1 mole) in ether (200 ml) as described in the preceding experiment. The product (II; R = R' = H; 1·9 g; 87%) crystallized from ligroin–ether as a yellow solid, m.p. 254–256° (lit.[21] 245–248°). (Found: C, 66·6;

H, 5·1%; *M*, 396. $C_{22}H_{20}Fe_2$ requires: C, 66·7; H, 5·1%; *M*, 396); PMR see Table 1; λ_{max} 320 (shoulder) (ε = 245), 438 nm (ε = 180).

(b) BuLi (0·063 mole) in hexane (20 ml) was added to a soln of freshly distilled bis(cyclopentadienyl) methane[20] (2·5 ml; ca. 0·017 mole) in THF (200 ml). The soln was stirred for 2 hr, $FeCl_2$ (2·2 g; 0·018 mole) was then added, and the mixture was stirred for a further 48 hr. The mixture was diluted with H_2O (200 ml), and filtered, and the filtrate was extracted with ether. The extract was dried (Na_2SO_4) and evaporated. The mass spectrum of the residual material contained groups of molecular ions corresponding (mass measurement) to $C_{22}H_{20}Fe_2$, $C_{33}H_{30}Fe_3$, and $C_{44}H_{40}Fe_4$ of relative abundance 2:5:4 respectively (Ref. 21). [1.1]Ferrocenophane (II; R = R′ = H) could be separated from this mixture by repeated chromatography in ligroin. This compound is more conveniently extracted by oxidation of the mixture of oligomers in benzene soln with MnO_2 (*vide supra*). The corresponding XI can then be obtained by chromatography of the product as described below.

The estimated yield of [1.1]ferrocenophane from this reaction was very low (3–5%).

Oxidation of [1.1]*ferrocenophane*

(a) Active MnO_2 (ca. 10 g) was added to a soln of [1.1]ferrocenophane (0·18 g; 0·46 mmole) in $CHCl_3$ (25 ml). The mixture was shaken for 8 hr, then filtered, and the filtrate was concentrated and chromatographed. Ligroin–$CHCl_3$ (1:2) eluted XVI (0·16 g; 86%), which crystallized from the same solvent as red needles, m.p. 284–286°. (Found: C, 64·8; H, 4·5; *M*, 410. $C_{22}H_{18}Fe_2O$ requires: C, 64·6; H, 4·4%; *M*, 410). PMR see Table 1; IR 6·15 μ.

(b) Active MnO_2 (ca. 10 g) was added to a soln of [1.1]ferrocenophane (0·26 g; 0·66 mmole) in benzene (50 ml) and the mixture was heated under reflux with stirring for 6 hr. The mixture was filtered and the residue was washed with $CHCl_3$. The total filtrate was evaporated giving XI (0·25 g; 89%), identical with the compound described in a previous experiment.

1,12-*Dimethyl*[1.1]*ferrocenophane*-1,12-*diol* (II; R = Me, R′ = OH)

The diketone XI (0·32 g; 0·75 mmole) was added to a soln of MeMgI [from Mg (0·24 g; 10 mg at) and MeI (1·50 g; 10 mmole)] in ether–THF (1:7) (240 ml) and the mixture was stirred and heated under reflux for 24 hr. The soln was then diluted with H_2O (500 ml) and the organic layer was separated and combined with three ether extracts of the aqueous layer. The total extract was washed (H_2O), dried (Na_2SO_4), and evaporated, and the residue was dissolved in benzene and chromatographed Benzene–ether mixtures eluted traces of coloured products which were not examined. Ether–MeOH (99:1) eluted II (R = Me, R′ = OH; 0·17 g; 50%), which decomposed sharply at its m.p. 189–191°. (Found: C, 63·2; H, 5·4; *M*, 456. $C_{24}H_{24}Fe_2O_2$ requires: C, 63 2; H, 5·3%; *M*, 456); PMR see Table 1, IR 2·9 μ. The compound was unstable in soln.

Mixed hydride reduction (LAH/$AlCl_3$) of this diol gave 1,12-dimethyl[1.1]ferrocenophane (90%), identical with the product previously obtained from I (R = Me)

2,2-*Diferrocenylpropane*

A soln of 6-ferrocenyl-6-methylfulvene[14] (5·52 g; 0·02 mole) in THF (50 ml) was added to a soln of MeLi (0·02 mole) in ether (50 ml) and the mixture was stirred until formation of the yellow cyclopentadienide salt was complete. A soln of sodium cyclopentadienide (ca. 0·02 mole) in THF (100 ml) followed by $FeCl_2$ (ca. 2 g) was then added and the mixture was stirred overnight. The product was isolated as in previous experiments and chromatographed. Ligroin eluted ferrocene (2·3 g) followed by an unstable unsaturated product [probably (α-cyclopentadienyl-α-methyl)ethylferrocene], which was not characterized. Ligroin eluted 2,2-diferrocenylpropane (0·88 g; 11%), which crystallized from ligroin as an orange-yellow solid, m.p. 127·5–128·5°. (Found: C, 66·7; H, 5·9. $C_{23}H_{24}Fe_2$ requires: C, 67·0; H, 5·9%); PMR see Table 1; λ_{max} 325 (shoulder) (ε = 230), 445 nm (ε = 240).

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