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INTERACTION OF ELECTRONEUTRAL BENZENECYCLOPENTADIENYLIRON WITH HALOGEN DERIVATIVES

A.N. NESMEYANOV, N.A.VOL'KENAU * and V.A. PETRAKOVA

Institute of Organo-Element Compounds of the Academy of Sciences of the USSR, Moscow V-312 (USSR)

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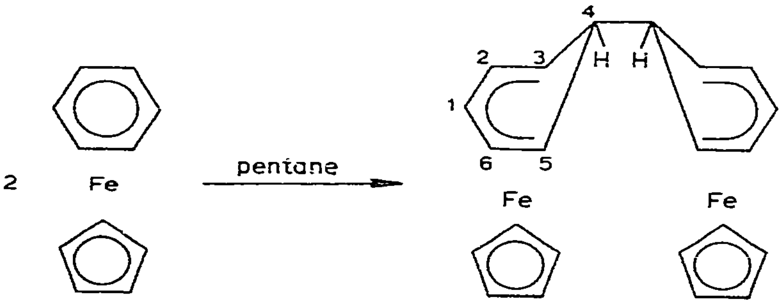
Summary

Electroneutral benzenecyclopentadienyliron, $C_6H_6FeC_5H_5$, dimerises at 20°C to give bis(cyclohexadienylcyclopentadienyliron), $C_5H_5FeC_6H_6$—$C_6H_6FeC_5H_5$, with a C—C bond between the six-membered rings of the $C_6H_6FeC_5H_5$ fragments. The title compound gives two products in its reaction with RHal, viz., the salt $[C_6H_6FeC_5H_5]$Hal and the substituted cyclohexadienylcyclopentadienyliron derivative $RC_6H_6FeC_5H_5$. The products ratio is usually close to 1 : 1. The RHal activity follows the series $CCl_4 \geqslant (C_6H_5)_3CCl > C_6H_5CH_2Cl >> C_2H_5Br > C_6H_5Br$.

Earlier [1—3] we described electroneutral benzenecyclopentadienyliron, $C_6H_6FeC_5H_5$ (referred to as benzene-cpd-iron below). In the intensely coloured, paramagnetic [2] $C_6H_6FeC_5H_5$, the central metal atom has a formally 19-electron outer shell. The "extra", unpaired electron presides over the chemical behaviour of the π-complex studied. Benzene-cpd-iron oxidises to give $[C_6H_6FeC_5H_5]^+$ extremely easily [3]. On the other hand, a π-complex possessing an unpaired electron may be expected to enter radical reactions.

We wish to report on the first reaction of the kind. Benzene-cpd-iron is transformed to its dimer I * completely, at room temperature and over 15 h.



(1)

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* A preliminary communication on reaction 1 has already been published [3].

The C—C bond between the six-membered ligands is formed by the unpaired electrons of two molecules of $C_6H_6FeC_5H_5$. The arene ligands turn into non-planar cyclohexadienyl (referred to as chd) ligands to give bis(chd-cpd-iron) (I).

Compound I is diamagnetic (^1H NMR) and its molecular weight is twice that of $C_6H_6FeC_5H_5$. The structure follows from the spectra discussed below.

A ^1H NMR spectrum of the diamagnetic $[C_6H_6FeC_5H_5]PF_6$ contains [4] two sharp singlets (δ 6.44 and 5.19 ppm) due to the arene and cpd protons respectively. The cpd signal is a singlet (4.02 ppm) in the spectrum of I as well. The strong upfield shift against $[C_6H_6FeC_5H_5]^+$ may be assigned to electroneutrality of I. The arene signal is, in contrast, absent from the spectrum of I. Instead, there is a system of multiplets characteristic of a chd ligand (see [5] and references cited therein): δ_1 3.96; $\delta_{2,6}$ 2.28; $\delta_{3,5}$ 1.33; δ_4 1.04 ppm. The spin-spin couplings are as follows: $J[(H_1 - H_2) + (H_1 - H_3)] = 4.5$, $J(H_2 - H_3) = 4.5$ Hz. All the chd signals in the I spectrum are shifted upfield compared with the chd spectra described in the literature [5]. An IR spectrum of I contains bands at 810, 1000, 1100, 1415, 3105 (a cpd ligand, see [6]), 1310, 1470, 2910, 3030, 3050 cm^{-1} (a chd ligand, see [7]). At 2750—2790 cm^{-1} there is no band and consequently [8], the H atoms at the methylene (C_4) carbons may be assumed to lie in the *endo*-position with respect to the iron. Of course, to finish the structure of I, an X-ray study is necessary. A similar dimerisation leading to a C—C bond between six-membered ligands was described [9] for bi(hexamethylbenzene)rhenium(0).

One mole of I is oxidised to two moles of the cation complex $[C_6H_6FeC_5H_5]X$.

$$\underset{\text{I}}{C_5H_5FeC_6H_6\text{-}C_6H_6FeC_5H_5} \xrightarrow[20^\circ]{\text{oxidant}} 2[C_6H_6FeC_5H_5]X$$

Oxidant = O_2, J_2, bromosuccinimide

Pyrolysis of the dimer gives ferrocene and benzene as the main products. GLC analysis shows also a small biphenyl admixture. The results agree with the assumption that the pyrolysis starts from the C—C bond decomposition. Ferrocene, then, may be a product of the $C_6H_6FeC_5H_5$ pyrolysis.

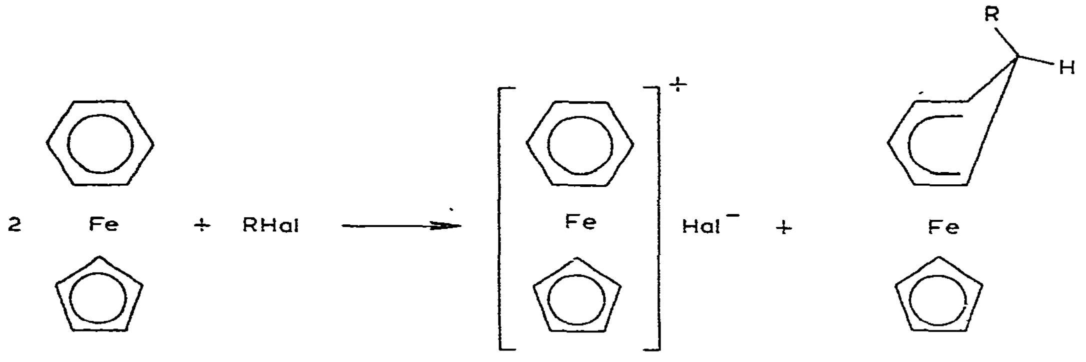
$$\underset{\text{(I)}}{C_5H_5FeC_6H_6\text{—}C_6H_6FeC_5H_5} \xrightarrow{140^\circ C} \{C_6H_6FeC_5H_5\} \rightarrow (C_5H_5)_2Fe + 2\ C_6H_6 + Fe$$

Indeed, crystals of $C_6H_6FeC_5H_5$ are in part transformed to ferrocene at as low a temperature as 20° C. However, the main process going under the mild conditions is dimerisation.

$$2\ C_6H_6FeC_5H_5 \xrightarrow{20\text{—}35^\circ C} (C_5H_5)_2Fe + 2\ C_6H_6 + Fe + C_5H_5FeC_6H_6\text{—}C_6H_6FeC_5H_5$$

The dimer is stable at 20—35° C. The fact that biphenyl is formed in trace amounts does not allow us to rule out the second route of pyrolysis involving the ring—ring bond retention. Unlike the benzene-cpd-iron monomer [1], the dimer yields no ferrocene when heated with tetrahydrofuran.

Further, we studied the interaction of benzene-cpd-iron with organic halides. The products were the benzene-cpd-iron cation halide and the chd-cpd-iron substituted at the methylene carbon atom.



II (a–e) III (a–e) (2)

RHal = (a) CCl_4 ; (b) $(C_6H_5)_3CCl$; (c) $C_6H_5CH_2Cl$; (d) C_2H_5Br ; (e) C_6H_5Br.

The various RHal differ largely in their activity in process 2; see Table 1. Chlorobenzene does not react at all. The slower reactions (Table 1) are accompanied by dimerisation.

Formally, the reaction 2 may be written as a two-step process. The first step is electron transfer from $C_6H_6FeC_5H_5$ to the halides RHal.

$$C_6H_6FeC_5H_5 + RHal \rightarrow \underset{(II)}{[C_6H_6FeC_5H_5]^+} + Hal^- + R^\bullet \tag{3}$$

It results in the salt II and the radical $R^\bullet$. The second step may be visualized as follows. The radical may attack the second molecule of $C_6H_6FeC_5H_5$, and the latter will react with the radical by its unpaired electron.

$$C_6H_6FeC_5H_5 + R^\bullet \rightarrow \underset{(III)}{RC_6H_6FeC_5H_5} \tag{4}$$

Similarly to the dimerisation, the arene ligand is transformed to the cyclohexadienyl ligand. An alternative assumption is that the radical $R^\bullet$ oxidises the

TABLE 1

REACTION OF $C_6H_6FeC_5H_5$ WITH ORGANIC HALIDES

RHal		Molar ratio π-complex : RHal	Reaction conditions		Yield (%)			Conversion of the starting compound (%)
			Time (h)	Temp. (°C)	II	III[a]	I	
(a)	CCl_4	1 : 1	instantly	—30	48	43		91
(b)	$(C_6H_5)_3CCl$	1 : 0.5	instantly	—30	50	50		100
(c)	$C_6H_5CH_2Cl$	1 : 3	2.5	20	25	19	11	55[b]
(d)	C_2H_5Br	1 : 11	15	20	23	8	7	38[b]
(e)	C_6H_5Br	1 : 8	16	20	35	3	27	65[b]
(f)	C_6H_5Cl	1 : 8	15	20			17[b]	

[a] The yields of chd—cpd derivatives are rough estimates, except for IIIa. [b] TLC on alumina in hexane showed ferrocene (see ref. 1).

second molecule of $C_6H_6FeC_5H_5$ to the cation $[C_6H_6FeC_5H_5]^+$ and is reduced at the same time to the carbanion.

$$C_6H_6FeC_5H_5 + R^{\cdot} \rightarrow [C_6H_6FeC_5H_5]^+ + R^- \qquad (5)$$

If so, the chd-cpd derivative III will be formed via a wellknown nucleophilic attack [8,10] of the carbanion on the π-complex cation:

$$[C_6H_6FeC_5H_5]^+ + R^- \rightarrow RC_6H_6FeC_5H_5 \qquad (6)$$

To specify the one or the other, further experiments are necessary. One more assumption is that active RHal's such as $(C_6H_5)_3CCl$, CCl_4 and, probably $C_6H_5CH_2Cl$, react via the carbanion mechanism (eqs. 3, 5, 6) whereas the less active C_2H_5Br and C_6H_5Br do so via the radical route (eqs. 3, 4).

Experimental

All operations were carried out in a dry, well purified argon atmosphere. Anhydrous, peroxide-free solvents were used throughout. All solvents were distilled in argon directly before use. The synthesis of benzene-cpd-iron has been described elsewhere [1]. An improved technique is shown below.

Benzene-cpd-iron

Suspension of $[C_6H_6FeC_5H_5]BF_4$ (1.14 g, 4 mmol) in 75 ml dimethoxyethane (DME) was stirred for 50 min at —25 to —30°C with 1% sodium amalgam prepared from 0.4 g (17 mg-at) of sodium metal. The dark green reaction mixture was diluted with 150 ml of cold (—30°C) pentane and left at —30°C until sedimentation was complete. The unreacted $[C_6H_6FeC_5H_5]BF_4$ and the $NaBF_4$ sediment were filtered off, the solvent was removed at —5 to —10°C (0.2—0.5 Torr), to give $C_6H_6FeC_5H_5$, dark green crystals of metallic lustre, 0.72 g (90%). The compound prepared in this way contains only a small admixture of ferrocene and is good for use in the experiments below.

Concentrations of $C_6H_6FeC_5H_5$ solutions may be found by titration with an ether solution of iodine [3]. The end point was indicated by disappearance of the green colour of the π-complex. The amount of $C_6H_6FeC_5H_5$ was calculated via eq. 7 *.

$$2\,C_6H_6FeC_5H_5 + J_2 \rightarrow 2[C_6H_6FeC_5H_5]J \qquad (7)$$

The accuracy was not less than 5—6%. The main source of the error is reaction 8 which, however, is as good as inexistent until $C_6H_6FeC_5H_5$ is present in the mixture.

$$[C_6H_6FeC_5H_5]J + J_2 \rightarrow [C_6H_6FeC_5H_5]J_3 \qquad (8)$$

Benzene-cpd-iron may be stored under argon at —70°C for months. At 20—35°C in an inert atmosphere, it is in part dimerised, and in part transformed to $(C_5H_5)_2Fe$, C_6H_6 (GLC data), and Fe.

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* Our earlier titration with triphenylchloromethane [1] gives incorrect results.

Dimerisation of benzene-cpd-iron (synthesis of I)

A pentane solution (50 ml) of $C_6H_6FeC_5H_5$ (0.7 g, 3.5 mmol) was maintained at 20°C for 15 h. It turned orange, and red crystals of I were precipitated. The crystals were filtered, washed with small portions of pentane and ether, and dissolved in benzene. The filtered solution was evaporated to dryness to give I, 0.55 g (75%), m.p. 142—143°C (dec.) after recrystallisation from benzene. Analysis: Found: C, 66.60; H, 5.54; Fe, 27.38. $C_{22}H_{22}Fe_2$ calcd.: C, 66.30; H, 5.57; Fe, 28.05%. Mol weight: Found: 399 (cryoscopy in C_6H_6); calcd.: 398.1. The solid I is moderately stable to the action of O_2 and irradiation, soluble in benzene and THF, less soluble in ether, and almost insoluble in pentane or alcohol. It decomposes in $CHCl_3$, CCl_4 or nitrobenzene.

Oxidation of bis(chd-cpd-iron) (I)

Oxidation with oxygen from air. Air was bubbled through a mixture of I (0.2 g, 0.5 mmol), benzene (50 ml), $NaBF_4$ (2.2 g, 20 mmol), and water (50 ml), for two days at 20°C. The red organic layer gradually turned colourless, and the aqueous layer became yellow. The layers were separated, the aqueous layer was treated with $Na[BPh_4]$ to give a precipitate of $[C_6H_6FeC_5H_5][BPh_4]$, 0.43 g (83%), m.p. 248—249°C (dec.).

Oxidation with iodine. A solution of iodine (0.128 g, 0.5 mmol) in 36 ml ether was added to a solution of I (0.2 g, 0.5 mmol) in 50 ml benzene under stirring. The mixture became colourless, and a precipitate of $[C_6H_6FeC_5H_5]J$ was formed, 0.32 g (98%), decomposing at 229—230°C after recrystallisation from acetone (lit. [11] dec. 230—230.5°C). Analysis: Found: C, 40.63; H, 3.37; J, 38.44; Fe, 17.03. $C_{11}H_{11}FeJ$ calcd.: C, 40.55; H, 3.39; J, 38.96; Fe, 17.13%.

Oxidation with bromosuccinimide. Bromosuccinimide (0.178 g, 1.0 mmol) was added to compound I (0.2 g, 0.5 mmol) in 50 ml C_6H_6. A yellow precipitate of $[C_6H_6FeC_5H_5]Br$ formed almost immediately. It was extracted by water and treated with $Na[BPh_4]$ to give $[C_6H_6FeC_5H_5][BPh_4]$, 0.45 g (87%), m.p. 249—250°C after dissolving the compound in CH_3NO_2, filtering the solution, and removing the solvent.

Pyrolysis of bis(cpd-chd-iron) (I)

Crystalline I (0.15 g, 0.38 mmol) was heated at 140°C (0.5 Torr) for 1 h. The compound darkened, and orange crystals sublimated on the walls. The product was treated with heptane, the dark precipitate (exclusively inorganic iron) was filtered off, and the heptane solution was chromatographed on alumina to give ferrocene, 0.061 g (85%), m.p. 170—171°C (lit. [12] m.p. 173—174°C). In a similar experiment the reaction mixture was subjected to GLC analysis that also showed benzene as a main product. Trace amounts of biphenyl were also found.

A THF solution of I (0.3 g, 0.75 mmol) was stirred at 50°C for 1.5 h and at 65°C for 4 h. A dark precipitate indicative of partial decomposition was observed. The precipitate was filtered off, and the solvent was removed from the filtrate, to give I, 0.2 g (66%), m.p. 142—143°C (dec.). The compound I was the only organo-iron product isolated.

Interaction of benzene-cpd-iron with organic halides

The conditions and the results are summarised in Table 1. A typical isolation and identification technique is given below, for II and III.

Reaction with CCl_4. The experiment was carried out with $C_6H_6FeC_5H_5$ (0.7 g) in 70 ml DME plus 150 ml pentane. The green solution turned orange directly after the CCl_4 had been added, and a yellow precipitate of $[C_6H_6FeC_5H_5]Cl$ was formed. It was filtered and dried in argon. It was identical with the chloride resulting from the reaction with $C_6H_5CH_2Cl$ (see below), as shown by TLC on alumina in a dichloroethane ethanol mixture. The filtrate was evaporated under reduced pressure, to give ruby-red crystals of IIIa, m.p. 90.5—92°C (from pentane). Analysis: Found: C, 45.85; H, 3.55; Cl, 33.20; Fe, 17.47. $C_{12}H_{11}Cl_3Fe$ calcd.: C, 45.41; H, 3.39; Cl, 33.51; Fe, 17.59%. Compound IIIa is easily soluble in ether or benzene. The mass spectrum revealed an ion at *m/e* 316 assignable as $[Cl_3CC_6H_6FeC_5H_5]^+$. The IR spectrum (KBr) contained no band at 2790 cm^{-1}, so the Cl_3C group is in the *exo*-position to the iron [8]. The CCl_4 excess in the experiments with this halide should not be too high since CCl_4 may react with IIIa.

Reaction with $(C_6H_5)_3CCl$. The experiment was carried out with $C_6H_6FeC_5H_5$ (0.56 g) in 70 ml DME plus 150 ml pentane. A solution of $(C_6H_5)_3CCl$ in ether was gradually added to the green solution of the iron compound. The $[C_6H_6FeC_5H_5]Cl$ precipitated was filtered, dissolved in water, and treated with $Na[BPh_4]$ to give $[C_6H_6FeC_5H_5][BPh_4]$, 0.7 g, (48% in terms of the chloride), m.p. 249—250°C (dec.). A solution of iodine in ether was added dropwise to the filtrate containing IIIb until precipitation was complete. The precipitate was $[C_6H_6FeC_5H_5]J$, and the solution contained the second oxidation product, triphenylmethyl iodide. The precipitate was dissolved in an acetone/water 1 : 1 mixture and converted into $[C_6H_6FeC_5H_5][BPh_4]$, 0.070 g. The filtrate gave $(C_6H_5)_3CJ$, m.p. 131°C (dec.) [lit. [13] m.p. 132—133°C (dec.)] after recrystallisation from ethyl acetate. The $(C_6H_5)_3CC_6H_6FeC_5H_5$ (IIIb) could not be isolated per se, owing to its low stability. The $C_6H_6FeC_5H_5$: RHal ratio should be 1 : 0.5 in the experiments with $(C_6H_5)_3CCl$, otherwise only $[C_6H_6FeC_5H_5]Cl$ is formed because $(C_6H_5)_3CCl$ oxidises IIIb.

Reaction with $C_6H_5CH_2Cl$. The reaction was carried out with $C_6H_6FeC_5H_5$ (0.72 g) in 100 ml ether. After the green colour had disappeared the $[C_6H_6FeC_5H_5]Cl$ precipitated was filtered and converted into $[C_6H_6FeC_5H_5]$-$[BPh_4]$, 0.47 g, m.p. 249—250°C (dec.). The filtrate was evaporated at 30°C, and the excess $C_6H_5CH_2Cl$ was distilled off at 60°C (0.2 Torr). The residue was a mixture of the chd-cpd derivative IIIc, the dimer I, and an insignificant amount of ferrocene. The mixture was treated with some pentane, filtered, and it was shown that the precipitate was I, 0.08 g, m.p. 142—143°C (dec.). The pentane filtrate gave 0.52 g of an orange mixture of ferrocene and IIIc. The mixture was treated with 0.40 g bromosuccinimide in 20 ml pentane plus 5 ml methanol for 5 min. The compound IIIc was oxidised to $[C_6H_6FeC_5H_5]Br$ [14], and the ferrocene to $[(C_5H_5)_2Fe]^+$. Benzene-cpd-iron bromide was extracted by water and converted into $[C_6H_6FeC_5H_5][BPh_4]$ which was recrystallised from CH_3NO_2 to purify it from the $[(C_5H_5)Fe]^+$ decomposition products. The yield of $[C_6H_6FeC_5H_5][BPh_4]$ was 0.35 g, m.p. 250—251°C (dec.). This corresponds to a 19% yield of IIIc in the principal reaction. The real yield may be even higher since the IIIc oxidation with bromosuccinimide is not quantitative (80—85%, cf. [14]). However, the yield of 19% allows one to roughly estimate the II : III ratio as being close to 1 : 1.

A similar experiment was carried out with 0.4 g of $C_6H_6FeC_5H_5$. The $[C_6H_6FeC_5H_5]Cl$ precipitated was filtered, dried on the filter in argon, and reprecipitated with ether from CH_3NO_2. It is a yellow extremely hygroscopic crystalline compound, without distinct melting point. Analysis: Found: Fe, 24.06; Cl, 15.24. $C_{11}H_{11}Cl$ calcd.: Fe, 23.83; Cl, 15.13%. The filtrate was treated as in the preceding experiment and the resulting mixture of IIIc and ferrocene was fractionated at 2×10^{-2} Torr. The fraction collected at 140—150°C was (TLC on alumina in heptane) IIIc containing a small ferrocene admixture *. Five successive recrystallisations from pentane gave IIIc, m.p. 64—65°C, the IR spectrum being identical with that of the compound obtained from $[C_6H_6FeC_5H_5]BF_4$ and C_6H_5MgCl [10]. The spectrum contained no band at about 2790 cm^{-1}, so the $C_6H_5CH_2$ group lies in the *exo*-position to the iron. Analysis: Found: C, 75.0; H, 6.66. $C_{18}H_{18}Fe$ calcd.: C, 74.50; H, 6.25%.

Reaction with C_2H_5Br. The experiment was carried out with $C_6H_6FeC_5H_5$ (0.7 g) in 70 ml DME plus 150 ml ether. The yellow, hygroscopic precipitate of $[C_6H_6FeC_5H_5]Br$ was isolated by filtration. It decomposes at 202—204°C after reprecipitation with ether from nitromethane. Analysis: Found: C, 47.47; H, 3.92; Fe, 20.94. $C_{11}H_{11}BrFe$ calcd.: C, 47.34; H, 3.99; Fe, 20.01%. The bromide was converted into the tetraphenylborate, m.p. 248—250°C (dec.), 0.42 g (23% in terms of the bromide). The organic filtrate was evaporated under reduced pressure, the residue was washed with 10 ml pentane, to give red bis(chd-cpd-iron) (I) crystals, 0.05 g, m.p. 141—142°C (dec.). A quantity of the pentane solution was evaporated and the residue was studied with mass spectroscopy techniques. The parent ions of the chd-cpd derivative IIId, *m/e* 228, and ferrocene, *m/e* 186, were found. The main body of the pentane solution was treated with bromosuccinimide (0.2 g, 1.5 mmol) in 5 ml methanol plus 20 ml light petroleum. The mixture was worked up as in [14]. The resulting $[C_6H_6FeC_5H_5]^+$ was precipitated in the form of tetraphenylborate, 0.15 g, m.p. 248—250°C (dec.). No $[C_2H_5C_6H_5FeC_5H_5]^+$ was found, because the IIId oxidation proceeds with the C_2H_5 group being abstracted entirely [14]. Based on the oxidation product yield, the IIId yield was of about 8%. It was shown that C_2H_5Br did not react with IIId.

Reaction with bromobenzene. The reaction was carried out with $C_6H_6FeC_5H_5$ (0.68 g) in 70 ml DME. Ether (120 ml) was added to the mixture, the $[C_6H_6FeC_5H_5]Br$ precipitate was filtered and dried in argon, to give 0.33 g of the compound decomposing at 202—204°C after two reprecipitations with ether from CH_3NO_2. Analysis: Found: C, 47.43; H, 4.37; Br, 28.47; Fe, 19.87. $C_{11}H_{11}BrFe$ calcd.: C, 47.34; H, 3.99; Br, 28.65; Fe, 20.01%. The organic layer was worked up as in the preceding experiment, to give dimer I, 0.19 g, m.p. 141—142°C. The pentane solution contained IIIe (mass spectrum, *m/e* 276). The IIIe yield was very low, and the compound could not be purified from ferrocene. The pentane fractions obtained from several runs were combined, and oxidised with bromosuccinimide [14]. Chromatography on alumina in dichloroethane/ethanol (25 : 4) showed the presence of $[C_6H_6FeC_5H_5]^+$ and $[C_6H_5C_6H_5FeC_5H_5]^+$ salts. The salts were pyrolysed, and C_6H_6 and $C_6H_5C_6H_5$

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* Ferrocene is not only a side product of any reaction involving $C_6H_6FeC_5H_5$ in THF or DME [1] but also formed through pyrolysis of IIIc during the distillation [10,14].

were found in the products (GLC). Consequently, in contrast with the data [8], both the *endo*-hydrogen and the *exo*-phenyl are split during the oxidation of IIIe. A special experiment showed that C_6H_5Br did not react with IIIe, so the RHal excess could not interfere. Chlorobenzene did not react with $C_6H_6FeC_5H_5$ under the conditions shown above (Table 1).

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