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ON THE PROBLEM OF TWO-ELECTRON REDUCTION OF ARENECYCLOPENTADIENYLIRON CATIONS *

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Summary

The naphthalene-cp-iron cation (cp = cyclopentadienyl) has been studied polarographically under strictly aprotic conditions to prove the existence of the two-electron reduction product, the anion $[C_{10}H_8FeC_5H_5]^-$. The reduction of the biphenyl- and benzene-cp-iron cations with sodium amalgam in proton donor media (pentane/water) is shown to yield, together with the electroneutral arene π-complexes $AreneFeC_5H_5$, the corresponding iron cyclohexadienyl-cp derivatives, *endo*-1-$C_6H_5C_6H_6FeC_5H_5$ and $C_6H_7FeC_5H_5$. The suggestion is made that the latter are formed from the two-electron reduction products, $[AreneFeC_5H_5]^-$, under the action of protons. The $[AreneFeC_5H_5]^-$ anions cannot be detected in the reduction of $[AreneFeC_5H_5]^+$ with sodium amalgam in aprotic media as these anions react with excess $[AreneFeC_5H_5]^+$ to give two molecules of $AreneFeC_5H_5$.

For some time, we have been studying one-electron reductions of cationic arene-cp-iron derivatives (cp stands for the cyclopentadienyl ligand) and electroneutral π-complexes formed in these reactions [1—5]:

$$[AreneFeC_5H_5]BF_4 + Na/Hg \xrightarrow{-20 \text{ to } -60^\circ C} AreneFeC_5H_5$$

We invariably used sodium amalgam as the reducing agent and tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) as solvents. Under these conditions, electroneutral iron arene-cp derivatives, AreneFeCp, were isolated in 70 to 90% yields. Ferrocene and the dimers, $[AreneFeCp]_2$, were also formed as minor admixtures [2,5,6].

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* For the preliminary communication see ref. 8. The work was performed jointly with N.S. Sinitsyna.

The polarographic data [7], however, show that arene-cp-iron cations can also undergo two-electron reduction. All the compounds studied feature two one-electron waves. Under the conditions used in the work [7] (CH_3CN as solvent), the first wave was always reversible (the formation of AreneFeCp) and the second one was irreversible, that is the products of the addition of one more electron had no significant life time. The second wave was shown to be sensitive to the presence of protons.

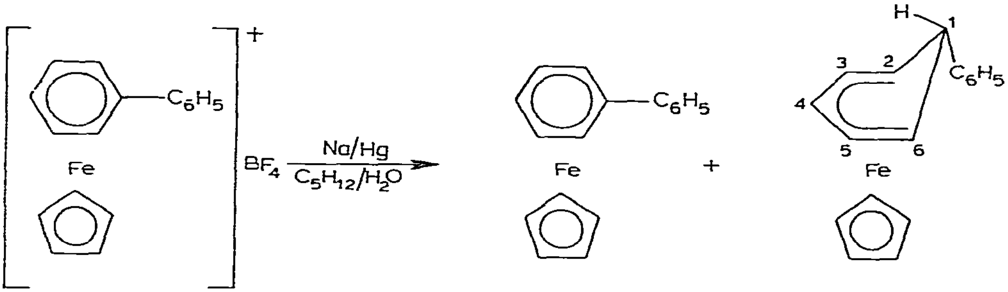
A repeated polarographic study of naphthalene-cp-iron fluoroboride under strictly aprotic conditions has shown that the second one-electron wave in the polarogram of this π-complex is also reversible.

$$[C_{10}H_8FeC_5H_5]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} C_{10}H_8FeC_5H_5 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [C_{10}H_8FeC_5H_5]^-$$

$$E^k_{1/2} = E^a_{1/2} = -1.01\text{V}\ ; \qquad E^k_{1/2} = E^a_{1/2} = -1.82\text{V}$$

The existence of the two-electron reduction product, the naphthalene-cp-iron anion, was thus proved.

Taking into consideration the data cited in ref. 7 on the low stabilities of two-electron reduction products and their sensitivity to the presence of protons, we also carried out a detailed study of the reduction of certain $[\text{Arene-FeCp}]^+$ species in proton donor media. The reaction of biphenyl-cp-iron fluoroboride with sodium amalgam in a pentane/water * two-layer system was found to yield two products.



(1)

First, one-electron reduction leading to the formation of electroneutral biphenyl-cp-iron in a 20% yield occurred. Secondly, orange crystalline *endo*-1-phenylcyclohexadienyl-cp-iron was isolated (44%, m.p. 83—85° C). In addition, 22% of initial $[C_6H_5C_6H_5FeC_5H_5]BF_4$ was recovered unreacted. The products thus account for 86% of the reagents. Decomposition products were also observed.

Unlike its *exo*-stereomer, *endo*-1-phenylcyclohexadienyl-cp-iron has not been described previously. The structure of this π-complex was determined as follows. Its mass spectrum contained the corresponding molecular ion, *m/e* 276, and the fragment ions characteristic of iron cyclohexadienyl-cp-derivatives [10]: 275, $C_6H_5C_6H_5FeC_5H_5^+$; 210, $C_6H_5C_6H_5Fe^+$; 186, $(C_5H_5)_2Fe^+$ **; 154,

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* It has been shown earlier [3,9] that proton donors including water oxidize electroneutral Arene-Fecp to the corresponding cations. This process is, however, hindered under reducing conditions.

** The ferrocene molecular ion is usually present in the mass-spectra of π-complexes containing the C_5H_5Fe moiety [3,4,11].

$C_6H_5C_6H_5^+$; 121, $C_5H_5Fe^+$; 56, Fe^+. The IR spectrum of the compound featured a 2765 cm^{-1} bond indicative of the presence of an *exo*-H atom at the sp^3-carbon atom [11]. The structure of the π-complex isolated was finally proved by an analysis of its ^1H NMR spectrum (for details, see below). The spectrum showed that of seven possible phenylcyclohexadienyl-cp-iron isomers, only one, the 1-*endo*-phenyl isomer, was formed in reaction 1.

Oxidation of *endo*-1-phenylcyclohexadienyl-cp-iron with bromosuccinimide in the presence of $NaBF_4$ gave biphenyl-cp-iron fluoroboride (60%), i.e. splitting off of the *exo*-H atom mainly occurred. Special experiments gave conclusive evidence that the interaction of $AreneFeC_5H_5$ (Arene = $C_6H_5C_6H_5$, C_6H_6, $CH_3C_6H_5$) with water did not yield the corresponding cyclohexadienyl-cp-iron derivatives (cf. ref. 3).

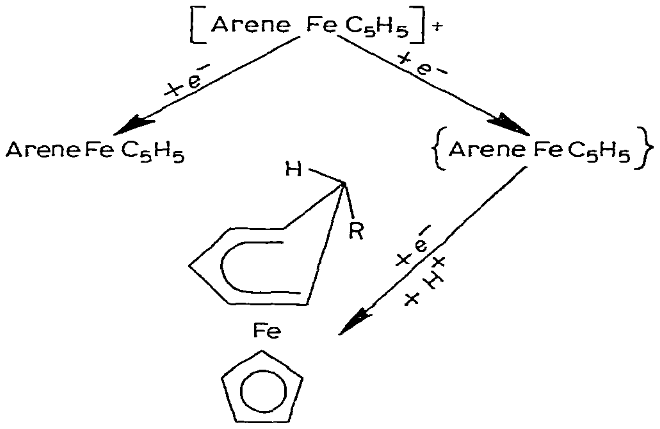
The formation of transition metal-cyclohexadienyl derivatives under the action of sodium amalgam on their arene complexes in protic media has not been described thus far. Usually, the cyclohexadienyl derivatives are made by nucleophilic addition of the hydride ion (from $LiAlH_4$, $NaBH_4$) to the arene ligand of some cationic transition metal complex (see the review, ref. 12 and references cited therein). If the arene ligand contains a substituent, the addition of H^- occurs almost exclusively at unsubstituted carbon atoms and leads to a mixture of isomers differing in the substituent position with respect to the sp^3 carbon atom [12].

We also carried out the reaction between $[C_6H_5C_6H_5FeC_5H_5]BF_4$ and $LiAlH_4$ in THF to obtain 87% of a mixture of isomeric iron phenylcyclohexadienyl-cp-derivatives. The ^1H NMR spectrum of the mixture showed that the 2-phenyl and 6-phenyl isomers predominated with all the other isomers possible being also present. Reduction of $[C_6H_5C_6H_5FeC_5H_5]BF_4$ with $NaBH_4$ in THF yielded 79% of a mixture of all phenylcyclohexadienyl-cp-iron isomers possible.

The results obtained using sodium amalgam and complex metal hydrides thus differ significantly from each other. In the first case, the reaction features high regiospecificity which is never observed in the second case. One may suppose this to be due to the specificity of reduction by dissolved metals [13]. The process occurs at the metal surface and involves consecutive addition of two electrons and (in our case) one proton. Reaction regiospecificity depends on the orientation of the molecule undergoing reduction on the surface of the metal.

Interestingly, the stereochemistry of the addition in reaction 1 is the same as in all cases of formation of metal cyclohexadienyl π-complexes: proton addition occurs exclusively at the *exo*-position.

We have also carried out the reduction of benzene- and toluene-cp-iron fluoroborides under the conditions under investigation. With $[C_6H_5C_6H_5$-$FeC_5H_5]BF_4$ the reaction was run at −6 to −8°C for 2 h, under which conditions the benzene derivative only gave the electroneutral π-complex, C_6H_6-FeC_5H_5. The reduction proceeded in an approximately 40% yield, with 5% of the electroneutral π-complex formed undergoing dimerization during the reaction. In addition, 54% of the initial $[C_6H_6FeC_5H_5]BF_4$ was recovered unreacted. No cyclohexadienyl-cp-iron was formed under these conditions. Under more forcing conditions (25°C, 2 h), the reaction gave 2% of cyclohexadienyl-cp-iron. The electroneutral π-complex, $C_6H_6FeC_5H_5$, underwent partial dimerization or decomposition. One more product was ferrocene (10%). The introduction of more sodium amalgam during the reaction and an increase of reaction duration (20° C, 25 h) did not lead to an increase of the yield of cyclohexadienyl-cp-iron. The dimer, $[C_6H_6FeC_5H_5]_2$ (23%), ferrocene (10%) and numerous decomposition products were formed. These results suggest that once AreneFecp is formed and transferred into solution, it undergoes no further reduction.



While attached to the metal surface, the AreneFecp molecule can add one more electron and proton. It may be thought that the same occurs under aprotic conditions but, in the absence of H^+, the two-electron reduction product, which is highly reactive, transfers an excess electron to the arene-cp-iron cation present in solution in excess.

$$[\text{AreneFecp}]^- + [\text{AreneFecp}]^+ \rightarrow 2\ \text{AreneFecp} \qquad (2)$$

Equation 2 explains why there is no indication of the presence of arene-cp-iron anions in aprotic media, except for the possibility of detecting them polarographically in certain cases.

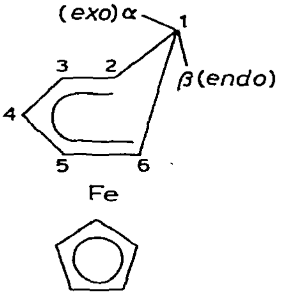
The different results obtained in the reduction of biphenyl- and benzene-cp-iron fluoroborides are easy to understand if one compares the polarographic characteristics of these compounds: [7]: $E^K_{1/2}$ of 1.30 and 2.22 in the biphenyl and 1.45 and 2.39 V in the benzene complex for the first and second waves, respectively. It is also known that free biphenyl can undergo reduction with sodium amalgam whereas monocyclic arenes containing no activating electron-withdrawing substituents can not [15]. The results obtained in the reduction of $[C_6H_6FeC_5H_5]^+$ are, however, of fundamental importance. They show that even with a monocyclic arene as ligand in $[\text{AreneFecp}]^+$, the latter may undergo two-electron reduction to a certain degree.

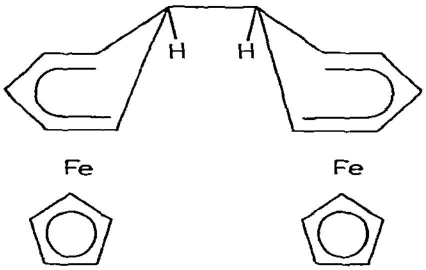
The reduction of toluene-cp-iron fluoroboride under the conditions studied only gave $CH_3C_6H_5FeC_5H_5$ in a 41% yield, of which 16% were in the dimeric

$$[CH_3C_6H_5FeC_5H_5]BF_4 \xrightarrow[C_5H_{12}/H_2O]{Na/Hg} CH_3C_6H_5FeC_5H_5 \rightarrow [CH_3C_6H_5FeC_5H_5]_2$$

form; 46% of unreacted $[CH_3C_6H_5FeC_5H_5]BF_4$ were recovered. Methylcyclohexadienyl-cp-iron was not formed under these conditions. Under more forcing conditions (ca. 25°C), deep decomposition occurred and the $[CH_3C_6H_5FeC_5H_5]_2$ was the only product. For comparison, $[CH_3C_6H_5FeC_5H_5]BF_4$ was reduced under the usual aprotic conditions (see ref. 3 for the preliminary communication) and $CH_3C_6H_5FeC_5H_5$ obtained was subjected to dimerization. Comparison of the two dimeric samples showed them to be identical to each other.

All the iron cyclohexadienyl-cp derivatives and dimers isolated in this work were studied by ^{1}H NMR spectroscopy. To interpret the results, one should first analyze the spectra of $C_5H_7FeC_5H_5$, *exo*-1-$DC_6H_6FeC_5H_5$, *endo*-$C_6H_5C_6H_6FeC_5H_5$.





In Fig. 1, the cyclohexadienyl proton signals of those compounds are only shown. One may see that the 4, 3, 5 and 2, 6 protons give triplet signals at $\delta \sim 6(1)$, $\delta \sim 4(2)$, and $\delta \sim 2(2)$ ppm (the integral intensities are given in parentheses). The α- and β-1 protons in the $C_6H_7FeC_5H_5$ spectrum (a) give rise to an AB quartet with $J(H_\alpha—H_\beta)$ of 11 Hz with the β-proton signal undergoing an additional triplet splitting caused by its interaction with the 2,6 protons. In the α-deuterated analogue (b), the β-proton signal is a triplet at δ 2.33 ppm.

The spectrum of β-1-phenylcyclohexadienyl-cp-iron (c), obtained in this work by reduction with sodium amalgam, contains the α-proton signal as a

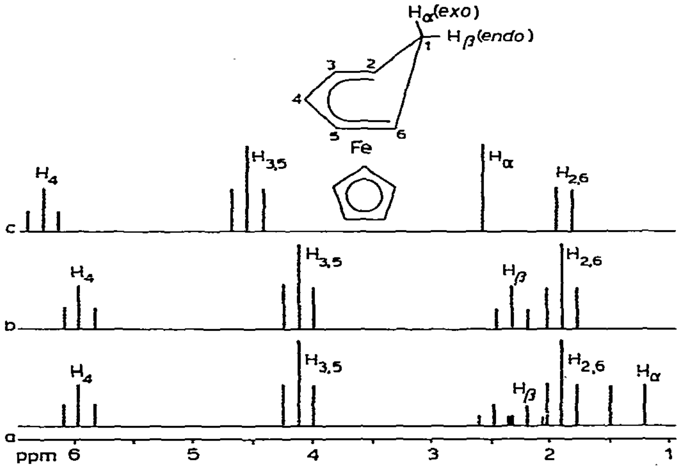


Fig. 1. Proton NMR patterns of cyclohexadienyl ligands in the compounds: a, $C_6H_7FeC_5H_5$; b, α-1-$DC_6H_6FeC_5H_5$; c, β-1-$C_6H_5C_6H_6FeC_5H_5$.

singlet and the 2,6 proton signals as a doublet at δ 2.59 and 1.93 ppm, respectively. The spin-spin coupling constants for the position 4 and 3(5); 3(5) and 2(6); 2(6) and β-1 are practically the same, of ca. ~5 Hz, accordingly the spectral pattern is rather simple.

The α-proton signal in β-1-phenylcyclohexadienyl-cp-iron (c) is strongly shifted to the lower field from its unsubstituted counterpart because of the anisotropy of the phenyl ring. The complete ^{1}H NMR spectrum of β-1-$C_6H_5C_6H_6FeC_5H_5$ is shown in Fig. 2b. The phenyl ring protons give rise to a poorly resolved multiplet at 7.26 to 8.10 ppm. The cp fragment protons give a sharp singlet at δ 4.28 ppm with a peak area corresponding to five protons.

The substituted cyclohexadienyl ligand in (b) gives a triplet at δ 6.18 ppm having an integral intensity corresponding to one proton, a triplet at δ 4.38 ppm (two protons), a singlet at δ 2.59 ppm (one proton), and a doublet at δ 1.93 ppm (two protons). These cyclohexadienyl ligand signals arise from the protons in the positions 4, 3(5), *exo*-1, and 2(6), respectively. The absence of spin-spin coupling between the 1 proton and 2 and 6 protons clearly indicates that the phenyl group is in the *endo*-position.

The spectrum of phenylcyclohexadienyl-cp-iron obtained from $[C_6H_5C_6H_5FeC_5H_5]BF_4$ and $LiAlH_4$ is shown in Fig. 2a. The analysis of the spectrum suggests that the major components are the 2- and 6-phenylcyclohexadienyl-cp-iron isomers. In fact, in addition to the complex phenyl ring proton multiplet at 7.64 to 8.5 ppm, the spectrum contains signals at δ 6.89 ppm (H_4, triplet, $J_{3,4} = J_{4,5} = 7$ Hz); δ 5.38 ppm (H(5) or H(3), doublet, $J_{4,5 \text{ or } 3} = 7$ Hz); δ 5.14 ppm (H(3) or H(5), triplet, $J_{3,4 \text{ or } 4,5} = J_{2,3 \text{ or } 5,6} = 7$ Hz); δ 3.71 ppm (β-1-H, doublet of doublets, $J_{\beta,\alpha} = 11$ Hz, $J_{\beta,2 \text{ or } 6} = 7$ Hz); δ 3.20 (H(2) or H(6), triplet, $J_{\beta,2 \text{ or } 6} = J_{2,3 \text{ or } 5,6} = 7$ Hz); δ 2.56 ppm (α-1-H, doublet, $J_{\beta,\alpha} = 1$ Hz). Apart from the signals of the 2- and 6-isomers, the spectrum contains the signals corresponding to other phenyl group positions. The spectrum of phenylcyclohexadienyl-cp-iron obtained from $[C_6H_5C_6H_5FeC_5H_5]BF_4$ and $NaBH_4$ closely resembles that shown in Fig. 2a and is also indicative of the presence of a number of isomers.

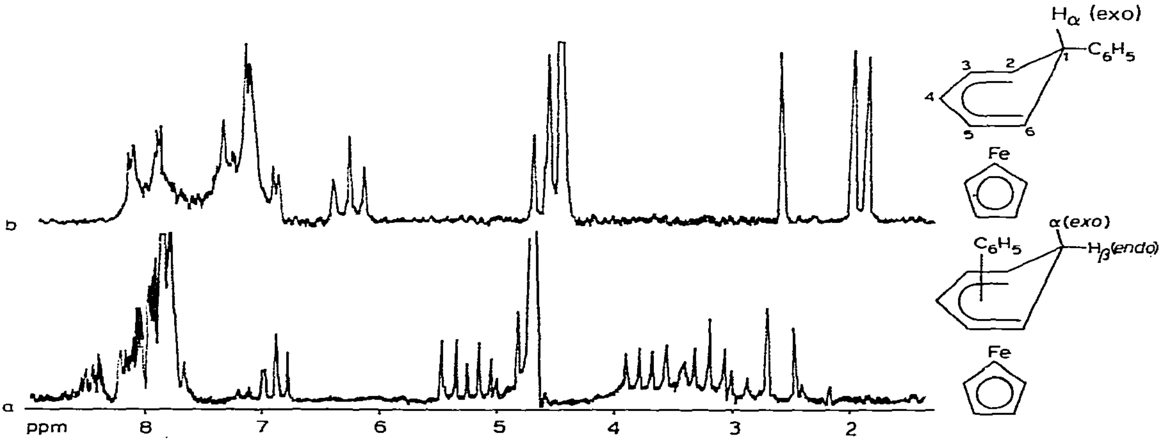


Fig. 2. Proton NMR spectra: a, $(C_6H_5)C_6H_6FeC_5H_5$, a mixture of isomers; b, β-1-$C_6H_5C_6H_6FeC_5H_5$.

The ^{1}H NMR spectra of the dimer, $[CH_3C_6H_5FeC_5H_5]_2$, samples obtained by reacting $[CH_3C_6H_5FeC_5H_5]BF_4$ with sodium amalgam in THF and in a pentane/water system are identical to each other. The spectral pattern is highly complicated because of a large number of positions that may be occupied by the methyl groups in both cyclohexadienyl rings of the dimer.

The cyclohexadienyl ring protons give rise to poorly resolved multiplets because of overlapping of the signals from various possible isomers differing in the methyl group position (δ_4 5.69, $\delta_{3,5}$ 4.14 and 3.79, δ_{endo} 2.11; $\delta_{2,6}$ 1.83; $\delta(CH_3)$ 1.48, 1.46 and 1.40 ppm). The results point to equal probabilities of finding the methyl group at any cyclohexadienyl ring position, i.e. to a statistical distribution.

Experimental

The polarographic study of naphthalene-cp-iron borofluoride was carried out in dimethoxyethane solution in the presence of $[Bu_4N]BF_4$ of a Radelkis OH-102 polarograph with a dropping mercury electrode as cathode. A saturated calomel electrode was used as reference. Reversibility of the waves was proved by measurements with a Kalousek commutator. Naphthalene-cp-iron for the polarographic study was prepared by the literature procedure [16], and purified by repeated crystallizations from ethanol (m.p. 132—133°C, decomp.). Its ^{1}H NMR spectrum showed it to be free of admixtures. The mass spectra of the compounds studied were obtained on an AEI MS-30 instrument equipped with a DS-50 data processing system. The conditions were: inlet temperature 30°C, temperature of ionisation chamber 150°C, ionizing voltage 70 V.

The ^{1}H NMR spectra were measured in CS_2 at —50°C on Hitachi-Perkin-Elmer R-20 (60 MHz) and R-32 (90 MHz) instruments and also on a RYa-2309 (90 MHz) instrument. The IR spectra (KBr pellets) were recorded on an UR-20 spectrometer.

All the reactions described below were run in inert atmosphere.

Electroneutral biphenyl-cp-iron *

A suspension of $[C_6H_5C_6H_5FeC_5H_5]BF_4$ (1 g, 2.7 mmol) in 100 ml DME was stirred with 4% Na/Hg (2 g, 87 mg-at Na; 4 ml Hg) at —20°C for 5 min and at —50 to —60°C for 2 h. Cooled pentane (100 ml) was then added and the dark-green solution was filtered; unreacted $[C_6H_5C_6H_5FeC_5H_5]BF_4$ (0.06 g, 6%) was recovered. The percentage of $C_6H_5C_6H_5FeC_5H_5$ was 81% as determined by titration with iodine in DME ($T = 0.00375$ [2]). A portion of the solution was oxidized by atmospheric oxygen in the presence of aqueous $NaBF_4$ to determine that the yield of $C_6H_5C_6H_5FeC_5H_5$ was 80%. The oxidation gave $[C_6H_5C_6H_5FeC_5H_5]BF_4$, m.p. 132—134°C, decomp. (lit.: m.p. 134—135°C, decomp. [6]). In addition, 0.1 g of a mixture of ferrocene and the dimer $[C_6H_5C_6H_5FeC_5H_5]_2$ was isolated (TLC on Al_2O_3 in pentane).

Interaction of $[C_6H_5C_6H_5FeC_5H_5]BF_4$ with sodium amalgam in pentane/water

Water (20 ml) free of O_2 was added to a mixture of 1% Na/Hg (0.4 g, 17

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* We here give an improved technique for $C_6H_5C_6H_5FeC_5H_5$ (cf. ref. 5).

mg-at Na) and [$C_6H_5C_6H_5FeC_5H_5$]BF_4 (0.6 g, 1.6 mmol) in 100 ml pentane. The mixture was stirred at —6 to —8°C for 2 h. The pentane layer turned gradually dark-green. The mixture was cooled to —60°C, the pentane solution was filtered in air into 100 ml of saturated aqueous $NaBF_4$, and the layers were intermixed. The water layer became yellow and the pentane layer turned orange. The water layer gave [$C_6H_5C_6H_5FeC_5H_5$]BF_4 (0.12 g which corresponds to a 20% yield of $C_6H_5C_6H_5FeC_5H_5$). Biphenyl-cp-iron fluoroboride isolated had m.p. of 133—135°C (decomp.) after recrystallization from ethanol. Found: C, 56.47; H, 4.18; F, 21.32; Fe, 14.97. $C_{17}H_{15}FeBF_4$ calculated: C, 56.41; H, 4.18; F, 21.00; Fe, 15.43%.

The pentane layer gave *endo*-1-phenylcyclohexadienyl-cp-iron (0.20 g, 44%), m.p. 83—85°C after triple crystallization from pentane. Found: C, 73.99; H, 6.06; Fe, 19.57%. $C_{17}H_{16}Fe$ calculated: C, 73.94; H, 5.84; Fe, 20.23%. Molecular weight (ebullioscopy in C_6H_6): found, 279 ± 3; calculated for $C_{17}H_{16}Fe$, 276. The IR spectrum (KBr pellets) contained a 2770 cm^{-1} band.

Oxidation of endo-1-phenylcyclohexadienyl-cp-iron with bromosuccinimide

A mixture of $C_6H_5C_6H_6FeC_5H_5$ (0.35 g, 1.2 mmol) in petroleum ether (20 ml), bromosuccinimide (0.22 g, 1.2 mmol) and $NaBF_4$ (0.3 g) in methanol (20 ml) was stirred for 0.5 h. The mixture was then diluted with 30 ml H_2O and extracted with ether. The aqueous layer gave [$C_6H_5C_6H_5FeC_5H_5$]BF_4 (0.28 g, 60%), m.p. 132—134°C, decomp.. Found: C, 56.16; H, 4.16; Fe, 15.06. $C_{17}H_{15}FeBF_4$ calculated: C, 56.41; H, 4.18; Fe, 15.43%.

Interaction of $C_6H_5C_6H_5FeC_5H_5$ BF_4 with lithium aluminium hydride (or sodium borohydride)

$LiAlH_4$ (0.25 g, 6.5 mmol) or $NaBH_4$ (0.31 g, 6.5 mmol) was added to [$C_6H_5C_6H_5FeC_5H_5$]BF_4 (1.2 g, 3.3 mmol) in 100 ml THF. The mixture was stirred at —5°C for 1 h and at 20°C for 1 h. Aqueous ether and then water were added, the mixture was filtered and extracted with pentane. The pentane layer gave deep-red crystalline $C_6H_5C_6H_6FeC_5H_5$ (0.8 g, 87%). The product was recrystallized from pentane 3 times, m.p. 68—70°C. Found: C, 73.93; H, 5.94; Fe, 20.12%. $C_{17}H_{16}Fe$ calculated: C, 73.94; H, 5.84; Fe, 20.23%. The IR spectrum of the product contained the band at 2780 cm^{-1}. The mass spectrum contained the molecular ion, *m/e* 276, $C_6H_5C_6H_6FeC_5H_5^+$, and lighter fragments, *m/e* 275, $C_6H_5C_6H_5FeC_5H_5^+$, 210, $C_6H_5C_6H_5Fe^+$, 154, $C_6H_5C_6H_5^+$, 121, $C_5H_5Fe^+$, 56, Fe^+.

Interaction of $C_6H_5C_6H_5FeC_5H_5$ with water

Oxygen-free (25 ml) H_2O was added to a solution of $C_6H_5C_6H_5FeC_5H_5$ (0.6 g, 2.16 mmol) in THF (100 ml). The mixture was stirred at —5 to —8°C. Hydrogen (9 cm^3) was evolved and identified by GLC. Pentane and saturated aqueous $NaBF_4$ were then added, the layers were intermixed and separated. The aqueous layer gave [$C_6H_5C_6H_5FeC_5H_5$]BF_4, m.p. 131—134°C, decomp. (0.35 g, 45%). The organic layer gave a mixture (0.3 g) containing ferrocene, diphenyl, and the dimer [$C_6H_5C_6H_5FeC_5H_5$]$_2$ (TLC on Al_2O_3 in hexane). The absence of the IR band at ca. 2800 cm^{-1} in the spectrum of the mixture showed it to be free of even traces of *endo*-phenylcyclohexadienyl-cp-iron.

Ferrocene and diphenyl were separated by vacuum sublimation and the sublimate was resolved by converting ferrocene to $(C_5H_5)_2Fe^+$ under the action of $FeCl_3$ and subsequent reduction of the cation with ascorbic acid. The yields of ferrocene and diphenyl were 0.03 g (15%) and 0.08 g (25%), respectively. The residue after the sublimation contained 0.12 g (22%) of $[C_6H_5C_6H_5FeC_5H_5]_2$ m.p. 123—125° C, decomp. (from pentane); lit.: decomposes at 123—125° C [5]. $C_6H_6FeC_5H_5$ and $CH_3C_6H_5FeC_5H_5$ were subjected to similar treatment. Cyclohexadienyl-cp-iron derivatives were not detected in these experiments.

Interaction of $[C_6H_6FeC_5H_5]BF_4$ with sodium amalgam in pentane/water

a) At —2° C. Oxygen-free water (6 ml) was added to a mixture of 1% Na/Hg (0.5 g, 21.5 mg-at of Na) and $[C_6H_6FeC_5H_5]BF_4$ (1.44 g, 5 mmol) in 200 ml pentane. The mixture was stirred at —2° C for 2 h upon which it turned dark green. The mixture was then cooled to —60° C, filtered in the air into saturated aqueous $NaBF_4$, and the layers were intermixed. The yellow aqueous layer was separated, neutralized with 5% HCl and subjected to treatment with $[Ph_4B]Na$ to give 0.89 g of $[C_6H_6FeC_5H_5]BPh_4$ precipitate, which corresponds to a 34% yield of $C_6H_6FeC_5H_5$. The pentane layer gave a mixture of the dimer, $[C_6H_6FeC_5H_5]_2$, and traces of ferrocene (TLC on Al_2O_3 in heptane). The mixture contained no cyclohexadienyl-cp-iron, judging from the absence of the 2790 cm^{-1} IR band. The mixture was dissolved in benzene and oxidized with atmospheric oxygen in the presence of aqueous $NaBF_4$. The aqueous layer gave 0.13 g of $[C_6H_6FeC_5H_5]BF_4$ which corresponds to a 5% yield of $[C_6H_6FeC_5H_5]_2$. The benzene layer contained ferrocene (TLC, Al_2O_3 in heptane).

The starting $[C_6H_6FeC_5H_5]^+$ (54%) was recovered unreacted as the tetraphenylborate (1.4 g).

b) At 25° C. A mixture of $[C_6H_6FeC_5H_5]BF_4$ (1.3 g, 4.5 mmol), 1% Na/Hg (21.5 mg-at Na) and 12 ml H_2O in 200 ml pentane was stirred at 25° C in a flask equipped with a cock at the bottom for 2 h. The aqueous layer and sodium amalgam were then separated. The green pentane solution was twice washed with water in the air and the washings were added to the aqueous layer. The quantity of monomeric $C_6H_6FeC_5H_5$ thus was not controlled in this experiment: it was oxidized, combined with unreacted $[C_6H_6FeC_5H_5]^+$, and isolated as tetraphenylborate (0.27 g, 11%, decomposes at 250—251° C). The pentane layer gave a red-coloured mixture whose IR spectrum contained a band at 2790 cm^{-1}. The mixture was subjected to sublimation (35—40° C/1 mmHg) to give 0.07 g of sublimate containing cyclohexadienyl-cp-iron and ferrocene (TLC on Al_2O_3, in heptane). The IR spectrum of the sublimate showed the band at 2790 cm^{-1}. The sublimate was oxidized with atmospheric oxygen as described in (a) to give 0.045 g of $[C_6H_6FeC_5H_5]BPh_4$ which corresponds to a 2% yield of $C_6H_7FeC_5H_5$. In addition, 0.04 g (10%) of ferrocene was isolated. The nonvolatile residue was purified by recrystallization from benzene to give 0.23 g (21%) of $[C_6H_6FeC_5H_5]_2$, m.p. 141—143° C, decomp..

c) At 25° with addition of Na/Hg. Experiment (b) was repeated with the same reagent quantities except that additional Na/Hg (21.5 mmol) and water (12 ml) were introduced during the reduction. The mixture was stirred at 25° C for 20 h.; it had dark-green colouration in the beginning of the reaction but then turned orange. A red-brownish residue was formed. Pentane and water were decanted, the residue was dissolved in benzene, and the benzene solution was combined with the pentane layer. The aqueous layer contained nothing but decomposition products. The combined organic layer gave a mixture of $[C_6H_6FeC_5H_5]_2$, ferrocene and cyclohexadienyl-cp-iron which was then treated as in (b) to obtain 0.28 g (23%) of $[C_6H_6FeC_5H_5]_2$, m.p. 141—143°C, decomp. (lit.: m.p. 142—143°C [6]), 0.056 g of ferrocene (10%), m.p. 173—174°C and 2.5% of cyclohexadienyl-cp-iron. The latter product was identified mass-spectrometrically: the molecular ion, *m/e* 200, $C_6H_7FeC_5H_5^+$, 199, $C_6H_6FeC_5H_5^+$, 121, $C_5H_5Fe^+$, 78, $C_6H_6^+$, 56, Fe^+. The IR spectrum of the product contained the band at 2790 cm^{-1}. Its yield was determined by oxidation to $[C_6H_6FeC_5H_5]^+$ (see experiment (b)).

Electroneutral toluene-cp-iron *

A suspension of $[CH_3C_6H_5FeC_5H_5]BF_4$ (1 g, 3.3 mmol) in DME (100 ml) was stirred with 4% Na/Hg (2 g, 87 mg-at Na, 4 ml Hg) at —20°C for 5 min and at —50 to —60°C for 2 h. Cooled pentane (100 ml) was then added and the dark-green solution was filtered. The residue filtered off was unreacted $[CH_3C_6H_5FeC_5H_5]BF_4$ (0.2 g, 20%). The yield of $CH_3C_6H_5FeC_5H_5$ was determined by titration with iodine solution in DME (70.5%) and by oxidation with atmospheric oxygen in the presence of aqueous $NaBF_4$ (68%) (for details, see the synthesis of $C_6H_5C_6H_5FeC_5H_5$).

Dimeric toluene-cp-iron

A solution of $CH_3C_6H_5FeC_5H_5$ (0.28 g, 1.32 mmol) in 10 ml pentane was kept at —10°C for 1 h. The solution colouration turned from green to deep-red. After the removal of pentane, a red crystalline dimer, $[CH_3C_6H_5FeC_5H_5]_2$ (0.2 g, 71%) containing traces of ferrocene (TLC on Al_2O_3 in pentane) was isolated. After recrystallization from pentane, the product contained no ferrocene and had m.p. 87—88°C.

Its IR spectrum contained no band in the 2800 cm^{-1} region. Found: C, 67.40; H, 6.24; Fe, 26.06. $C_{24}H_{26}Fe_2$ calculated: C, 67.64; H, 6.15; Fe, 26.21%. Molecular weight (ebullioscopy in C_6H_6): found 430 ± 4, calculated for $C_{24}H_{26}Fe_2$, 426.

Interaction of [$CH_3C_6H_5FeC_5H_5$]BF_4 with sodium amalgam in pentane/water

Oxygen-free water (20 ml) was added to a mixture of 2.5% Na/Hg (2 g, 87 mg-at Na, 6 ml Hg) and $[CH_3C_6H_5FeC_5H_5]BF_4$ (1 g, 3.3 mmol) in 100 ml pentane. While the mixture was stirred at —2 to —5°C for 2 h its colouration turned to dark green. A portion of the pentane solution was removed to obtain a green product whose mass spectrum contained the molecular ion of toluene-cp-iron, *m/e* 213, and the ions *m/e* 148, $CH_3C_6H_5Fe^+$, 121, $C_5H_5Fe^+$, 56, Fe^+. The reaction mixture was cooled to —70°C, the pentane solution was filtered in the air into 100 ml saturated aqueous $NaBF_4$, the layers were intermixed and then separated. The water layer gave 0.25 g of $[CH_3C_6H_5FeC_5H_5]BF_4$ m.p. 157—159°C, decomp. (lit.: m.p. 159—160°C, decomp. [16]), which corresponds to a 25% yield of $CH_3C_6H_5FeC_5H_5$. The pentane layer gave 0.16 g (62%)

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* For a short communication on the synthesis of $CH_3C_6H_5FeC_5H_5$ see ref. 3.

of deep-red crystalline dimer, $[CH_3C_6H_5FeC_5H_5]_2$. After triple recrystallisation from pentane, the product had m.p. of 86—88°C and did not show depression of m.p. compared with the product from the preceeding experiment. The IR spectrum of the dimer contained no band at about 2800 cm^{-1}. The pentane layer did not contain any other products. In this run 0.46 g (46%) of $[CH_3C_6H_5FeC_5H_5]BF_4$ was recovered unreacted.

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