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ELECTRONEUTRAL HALOGEN BENZENE-CYCLOPENTADIENYL DERIVATIVES OF IRON

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Summary

The preparation and properties of electroneutral complexes, $HalC_6H_5FeC_5H_5$ (Hal = Cl, F) and their dimers, $[HalC_6H_5FeC_5H_5]_2$, are described. Mass spectra of these compounds are discussed.

The analysis of the ^1H and ^{19}F NMR spectra of $[HalC_6H_5FeC_5H_5]_2$ has shown that these compounds are mixtures of *syn*- and *anti*-isomers.

The reactivity of electroneutral $HalC_6H_5FeC_5H_5$ complexes and their dimers in nucleophilic substitution reactions has been studied and it has been shown that these compounds are inert as far as these reactions are concerned.

For some time we have been studying (see ref. 1 and ref. cited therein) the preparation, reactivity, ESR spectra [2–4] and electronic absorption spectra [5] of electroneutral arenecyclopentadienyl derivatives of iron. First, we dealt with π-complexes containing only hydrocarbon ligands. Later on we reported [6] the synthesis of the first AreneFeCp with a non-hydrocarbon substituent in the arene ligand, viz. chlorobenzenecyclopentadienyliron. Its dimer was also obtained.

This paper describes in detail the synthesis and properties of chlorobenzene- and fluorobenzene-cyclopentadienyliron as well as the preparation, properties and ^1H NMR spectra of their dimers. Both halogen-containing π-complexes were obtained by conventional procedures from the corresponding cations.

$$[HalC_6H_5FeC_5H_5]BF_4 \xrightarrow[THF]{Na/Hg} HalC_6H_5FeC_5H_5$$

(Hal = F, Cl; THF = tetrahydrofuran)

The reduction was performed both in THF and in the pentane/water system [1]. The results obtained are given in Table 1, which shows that in almost all cases the final products contain admixtures of $[HalC_6H_5FeC_5H_5]_2$ dimers. It is only at

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TABLE 1

CONDITIONS AND PRODUCTS OF REDUCTION OF CHLOROBENZENE- AND FLUOROBENZENE-CYCLOPENTADIENYLIRON CATIONS

($AreneFeC_5H_5)BF_4$	Solvent	Conditions (°C/h)	Product yields (%)	
			$HalC_6H_5FeC_5H_5$	$[HalC_6H_5FeC_5H_5]_2$
$[ClC_6H_5FeC_5H_5]BF_4$[a]	THF	−80 to −90/1	50	4
$[ClC_6H_5FeC_5H_5]BF_4$	Pentane/H_2O	−10 to −5/1	4	27
$[ClC_6H_5FeC_5H_5]BF_4$	Pentane/H_20	−10 to −5/3	-	66
$[FC_6H_5FeC_5H_5]BF_4$	THF	−70/2	64	17
$[FC_6H_5FeC_5H_5]BF_4$	Pentane/H_2O	−5/2	17	60
$[FC_6H_5FeC_5H_5]BF_4$	Pentane/H_2O	−10 to −5/15	24	54

[a] See preliminary data in ref. 6.

−90°C that the $[ClC_6H_5FeC_5H_5]_2$ dimer is formed in an insignificant amount. Mass spectrometry of the reaction mixtures also shows that deep cooling suppressed dimerization of $HalC_6H_5FeC_5H_5$. However, the π-complexes are readily dimerized in the isolation processes.

The data given in Table 1 make it possible to conclude that $[FC_6H_5FeC_5H_5]BF_4$ is reduced somewhat more readily than $[ClC_6H_5FeC_5H_5]BF_4$, while $ClC_6H_5FeC_5H_5$ is dimerized faster than $FC_6H_5FeC_5H_5$.

Electroneutral chlorobenzene- and fluorobenzene-cyclopentadienyliron as well as other AreneFeCp complexes appear to be dark-green crystals, see the mass spectrum of $ClC_6H_5FeC_5H_5$ in ref. 6. Mass spectrum of $FC_6H_5FeC_5H_5$* (*m/e*): 217 $FC_6H_5FeC_5H_5^+$, 186 $(C_5H_5)_2Fe^+$ **, 152 $FC_6H_5Fe^+$, 121 $C_5H_5Fe^+$, 96 $FC_6H_5^+$, 56 Fe^+. The ions 199 $C_6H_6FeC_5H_5^+$, 134 $C_6H_6Fe^+$ and 78 $C_6H_6^+$ are resolved in the spectrum at low intensity. The presence of these ions indicates a slight dehalogenation during reduction of $[FC_6H_5FeC_5H_5]^+$ with Na/Hg (see also ref. 6). The fragment ions with a higher mass than that of the molecular ion, $FC_6H_5FeC_5H_5^+$, resolved in the spectrum with negligible intensity, which shows that a negligible admixture of the dimer is present. The $C_6H_5C_6H_5^+$ (*m/e* 154) also resolves at low intensity in the mass spectrum of the reduction product under discussion. Since the peaks corresponding to the ions, $C_6H_5C_6H_5FeC_5H_5^+$ and $C_6H_5C_6H_5Fe^+$ are not present in the spectrum, one can suggest that, in the reduction process with Na/Hg, biphenyl is formed from C_6H_5F resulting from partial decomposition of $[FC_6H_5FeC_5H_5]^+$ or $FC_6H_5FeC_5H_5$.

In order to obtain considerably higher amounts of the dimer, $[FC_6H_5FeC_5H_5]_2$, the reduction of $[FC_6H_5FeC_5H_5]BF_4$ was performed at a higher temperature and over a longer time period (see Table 1). In this way the maximum yield (60%) of the dimer was attained.

The dimer, $[FC_6H_5FeC_5H_5]_2$, is a red crystalline substance, dec.p. 125–130°C; it dissolves readily in non-polar solvents.

The dimers of AreneFeCp investigated so far do not produce peaks of molecular ions in the mass spectra. However, their spectra always show fragments with a higher

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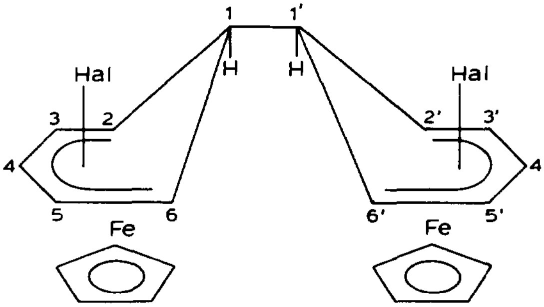
* The deeply cooled sample obtained was recorded.

** See ref. 1.

mass than that of the molecular ion of the monomer, 338 and 262, which indicate the presence of the dimer. In all other respects the mass spectra of the dimers and the corresponding monomers coincide. The masses 338 and 262 were not identified. It may be assumed that the corresponding ions are formed due to the transformation of the CpFe part of the dimeric molecule since their formation does not depend on the nature of the six-membered ligand. The ions, *m/e* 338 and 262, never resolve in the spectra of AreneFeCp (see references in ref. 1).

Taking into account the above considerations, the molecular weight of $[FC_6H_5FeC_5H_5]_2$ was determined ebullioscopically in benzene: found, 430 ± 4; calculated for $C_{22}H_{20}Fe_2F_2$, 434. The mass spectrum of $[FC_6H_5FeC_5H_5]_2$ shows the peaks (*m/e*): 338, 262, 217 $FC_6H_5FeC_5H_5{}^+$, 186 $C_5H_5FeC_5H_5{}^+$, 121 $C_5H_5Fe^+$, 96 $FC_6H_5{}^+$, 65 $C_5H_5{}^+$, 56 Fe^+. In addition, the following ions resolve with low intensities: 199 $C_6H_6FeC_5H_5{}^+$, 152 $FC_6H_5Fe^+$, 134 $C_6H_6Fe^+$, 78 $C_6H_6{}^+$.

It is well known [1,7] that the dimers of electroneutral arenecyclopentadienyliron derivatives have a bis(cyclohexadienylcyclopentadienyliron) structure with a bond between the six-membered ligands and an *endo*-position of the hydrogens at this bond. Such a structure was proved for $[ClC_6H_5FeC_5H_5]_2$ using IR and ^1H NMR spectroscopy [6].



(A)

(Hal = F, Cl)

The absence of the band at 2800 cm^{-1} (characteristic for *exo*-CH vibration at the sp^3-carbon atom) in the IR spectrum of $[FC_6H_5FeC_5H_5]_2$ convincingly proves that the H atoms at C(1) and C(1′) are in *endo*-positions with respect to the iron atom.

Previously it was found by ^1H NMR spectroscopy [6] that the Cl atoms in the dimer, $[ClC_6H_5FeC_5H_5]_2$, are predominantly in the positions 2(6) and 2′(6′) of the cyclohexadienyl ring. The admixtures of other isomers were negligible. The ^1H NMR spectrum recorded on an instrument operating at 90 MHz suggests the analogous structure (A) for the fluorine-containing dimer, $[FC_6H_5FeC_5H_5]_2$. It should be noted that, in the spectrum of the fluorine-containing dimer, the multiplicity of signals H(1)(1′) and H(2)(2′) of the cyclohexadienyl ligands was found to be doubled. In the ^1H NMR spectra of $[HalC_6H_5FeC_5H_5]_2$ (Hal = F, Cl) obtained on a spectrometer operating at 200 MHz the multiplicity of almost all the signals was doubled. The ^{19}F NMR spectrum of the fluorine-containing dimer shows two signals at δ −81.72 and −83.62 ppm, having an integral intensity ratio of 1 and 1.2, respectively.

The doubled multiplicity in the spectra of the dimers under investigation is due to the fact that both $[ClC_6H_5FeC_5H_5]_2$ and $[FC_6H_5FeC_5H_5]_2$ appear to be mixtures

TABLE 2

PARAMETERS OF ^{1}H NMR SPECTRA OF DIMERS $[HalC_6H_5FeC_5H_5]_2$ (Hal = F, Cl)

Hal	Isomer	Content (%)	Chemical shifts of protons (ppm)						Coupling constants (Hz)
			Cp	H4, H4′	H3(5), H3′(5′)	H5(3), H5′(3′)	H6(2), H6′(2′)	H1, H1′	
F	*syn*	45	4.009 s	5.232 d of t	4.232 d of d	3.623 quadr.	2.517 d of quadr.	2.194 d of quadr.	J1-6(2) = J1′-6′(2′) ≈ 6 J5(3)-6(2) = J5′(3′)-6′(2′) ≈ 6 J3(5)-4 = J3′(5′)-4′ ≈ 6 J4-5(3) = J4′-5′(3′) ≈ 6
F	*anti*	55	4.009 s	5.209 d of t	4.232 d of d	3.623 quadr.	2.379 d of quadr.	2.102 d of quadr.	J1-F′ = J1′-F = 6 J3(5)-F = J3′(5′)-F′ = 8 J5(3)-F = J5′(3′)-F′ = 6 J4 − 6(2) = J4′-6′(2′) = 1 J6(2) − F = J6′(2′)-F′ = 6
Cl	*syn*	30	4.016 s	5.327 t	4.210 d	3.737 t	2.596 t	1.855 d	J1-6(2) = J1′-6′(2′) ≈ 6 J5(3)-6(2) = J5′(3′)-6′(2′) ≈ 6
Cl	*anti*	70	4.016 s	5.313 t	4.381 d	3.737 t	2.282 t	1.948 d	J3(5)-4 = J3′(5′)-4′ ≈ 6 J4-5(3) = J4′-5′(3′) ≈ 6.

of stereoisomers. This isomerism is due to the *syn*- and *anti*-positions of the two halogen atoms of the dimer with respect to the plane passing through the C(1)–C(1′) bond and both iron atoms. Table 2 cites the parameters for the ^{1}H NMR spectra of the dimers, $[HalC_6H_5FeC_5H_5]_2$ (Hal = F, Cl). In the spectra of the dimers, the signals measured at higher fields are assigned to *anti*-isomers. Such an assignment results from the assumption that the transoid effect of the two halide atoms on the proton shielding (mainly in positions 1 and 2) prevails over the cisoid effect. The ratio of isomers in the mixture was calculated according to their spectra (see Table 2). In the case of $[FC_6H_5FeC_5H_5]_2$, the isomers occur in almost equal amounts in the mixture. In the case of $[ClC_6H_5FeC_5H_5]_2$ the *anti*-isomer is markedly predominant (70%).

Further, we investigated the reactivity of electroneutral $HalC_6H_5FeC_5H_5$ and their dimers, $[HalC_6H_5FeC_5H_5]_2$. It is known [8] that the halides in both ligands of the $[AreneFeCp]^+$ cations are highly mobile. They are not comparable with inert halides of non-coordinated C_6H_5Hal. The source of such activity is certainly due to delocalization positive charge of the π-complex on the ligands. It is less clear whether it is affected by arene coordination on the transition metal resulting from the transition of π-electrons of the ligand on the d-orbitals of the metal (donor–acceptor component of the ligand–metal bond). Electroneutral AreneFeCp complexes have no charge, which makes it possible to investigate the pure effect of coordination upon the behaviour of halides in the arene ligand as such.

In the present work we studied the interaction of $ClC_6H_5FeC_5H_5$ and $FC_6H_5FeC_5H_5$ with CH_3ONa, C_2H_5ONa and piperidine. It was necessary that the reactions were performed at low temperatures (from −50 to −10°C) because electroneutral π-complexes tend to transform into dimers or ferrocene (depending on the solvent) at higher temperatures [1].

The reaction mixtures obtained were thoroughly investigated and no products of fluorine or chlorine substitution (for nucleophilic groups *) were found. The initial

$HalC_6H_5FeC_5H_5$ remained partly unreacted (they were oxidized and then isolated in the form of salts of the corresponding cations), partly dimerized or changed into ferrocene. Thus, under the conditions used in our experiments, chlorine and fluorine in the arene ligands of electroneutral $HalC_6H_5FeC_5H_5$ were found to be inert to nucleophilic substitution. Hence, we can assume that in $[HalC_6H_5FeC_5H_5]^+$, the halide is activated by the positive charge of the π-complex, delocalized on the ligands.

The effect of coordination on the metal either does not become manifest or is suppressed by the influence of the dative component of the metal–arene bond which increases the electron density on the arene ligand (see ref. 9 for details).

We also investigated the behaviour of the halides in the dimers, $[HalC_6H_5FeC_5H_5]_2$. This was the first attempt to carry out substitution in the cyclohexadienyl ligand. This ligand is considered to resemble the cyclopentadienyl ligand [10] (see, however, ref. 11). The halide atoms in haloferrocenes are not active under conditions of simple nucleophilic substitution, but can be replaced by other groups in the presence of copper salts [12]. We studied the behaviour of halides in $[HalC_6H_5FeC_5H_5]_2$ (Hal = Cl, F) under conditions typical for the substitution of halides in haloferrocenes as well as under simple nucleophilic substitution conditions.

$$[HalC_6H_5FeC_5H_5]_2 \not\xrightarrow{\text{AlkONa}} [AlkOC_6H_5FeC_5H_5]_2 + NaHal$$

$$(Hal = F, Cl;\ Alk = CH_3, C_2H_5)$$

$$[HalC_6H_5FeC_5H_5]_2 \not\xrightarrow{Cu(OCOCH_3)_2} [CH_3COOC_6H_5FeC_5H_5]_2$$

$$(Hal = F, Cl)$$

None of the reactions described resulted in substitution of the halide in the cyclohexadienyl ligand of the complexes investigated.

Experimental

All the experiments described below were carried out under dry, well-purified argon. The spectra described were recorded on the following instruments: ^1H NMR spectra were measured on a "Bruker SXP 4-100 (90-MHz) and a "Bruker WP-200SY" (200, 13 MHz); ^{19}F NMR on a "Bruker SXP 4-100" (84.67 MHz); IR spectra on an UR-20; mass spectra were obtained on a Finnigan 4021. The conditions were: inlet temperature 30°C, temperature of ionization chamber 150°C, ionizing voltage 70 V. Molecular weights were determined on a Hitachi–Perkin–Elmer 115 instrument. GLC analyses were performed on an instrument with steel columns 1.5 × 4 mm (packing: 3% SE-30 on a Varopot, 100–200 mesh).

Electroneutral fluorobenzenecyclopentadienyliron

(a) Synthesis in THF. A mixture of $[FC_6H_5FeC_5H_5]BF_4$ (0.5 g, 1.65 mmol), THF (100 ml) and 0.5% Na/Hg (0.5 g, 20 mg-at. Na and 8 ml of Hg) was stirred for

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[***] Only in one case, using the ^1H NMR method, was $[CH_3OC_6H_5FeC_5H_5]BF_4$ found in the oxidation products of the reaction mass. However, it is impossible to assess with any certainty that fluorine substitution was not preceded by oxidation of $FC_6H_5FeC_5H_5$ to $[FC_6H_5FeC_5H_5]^+$.

2 h at −70°C, the mixture became dark-green. Then pentane (100 ml) was added to the mixture, the green reaction solution was decanted from Na/Hg, filtered, and a small quantity was taken for mass-spectral determination. 0.1 g (20%) of unreacted $[FC_6H_5FeC_5H_5]BF_4$ was extracted from the reaction flask and identified by means of TLC (Al_2O_3; dichloroethane/ethanol, 25/4). The green THF/pentane filtrate was oxidized with atmospheric oxygen in the presence of a saturated aqueous solution of $NaBF_4$ (50 ml) and benzene.

0.32 g (64%) of $[FC_6H_5FeC_5H_5]BF_4$ with a slight admixture of $[C_6H_6FeC_5H_5]BF_4$ was isolated from the yellow aqueous layer. The admixture was identified by GLC analysis of the thermolysis products (150°C) of the fluoroborates obtained. 0.04 g (18%) of $[FC_6H_5FeC_5H_5]_2$ was isolated from the organic layer (for identification, see below).

The experiment was repeated under the same conditions. The solvents were removed from the filtered THF/pentane solution in vacuo at −10°C. Pentane (10 ml) was added to the red-brown residue and the mixture was left for 1 h at 0°C. Then, in the presence of atmospheric O_2, a saturated aqueous solution of $NaBF_4$ and benzene was added and the layers were intermixed. 0.22 g (63%) of the dimer, $[FC_6H_5FeC_5H_5]_2$, was isolated from the benzene layer and 0.05 g of $[FC_6H_5FeC_5H_5]BF_4$ with an admixture of $[C_6H_6FeC_5H_5]BF_4$ was isolated from the aqueous layer as shown by GLC of the thermolysis products.

(b) Synthesis in pentane/water. A mixture of $[FC_6H_5FeC_5H_5]BF_4$ (0.5 g, 1.65 mmol), pentane (100 ml), water (20 ml) and 0.8% Na/Hg (from 34 mg-at Na and 8 ml Hg) was stirred at −10 to −5°C for 15 min. Then the temperature was decreased to −40°C and the green pentane solution was decanted from Na/Hg, filtered, and a small quantity was selected for mass-spectral determination. 0.08 g (16%) of unreacted $[FC_6H_5FeC_5H_5]BF_4$ was removed from the reaction flask. The green pentane solution was oxidized by atmospheric oxygen in the presence of an aqueous solution of $NaBF_4$ and benzene in the same way as in the previous experiment. 0.12 g (24%) of $[FC_6H_5FeC_5H_5]BF_4$ was isolated from the aqueous layer (GLC analysis of the thermolysis products showed a negligible admixture of $[C_6H_6FeC_5H_5]BF_4$). 0.19 g (54%) of the dimer, $[FC_6H_5FeC_5H_5]_2$, was isolated from the benzene solution and from the reaction flask.

Dimer of fluorobenzenecyclopentadienyliron

Fluorobenzenecyclopentadienyliron fluoroborate (0.5 g, 1.65 mmol) was reduced in pentane/water as in the previous experiment. The reaction proceeded at −5°C for 2 h. The green coloration of the pentane solution gradually changed to red-brown; a red precipitate was formed. The content of the reaction flask was decanted from Na/Hg and poured into a separatory funnel. The red precipitate was carefully extracted from the flask using benzene. The benzene solution was also poured into the funnel. An aqueous solution of $NaBF_4$ was added and after shaking, the layers were separated. 0.08 g (17%) of $[FC_6H_5FeC_5H_5]BF_4$ was obtained from the aqueous layer, identified by TLC on Al_2O_3 and by GLC analysis of the pyrolysis products. 0.21 g (60%) of a red crystalline dimer, $[FC_6H_5FeC_5H_5]_2$, with traces of ferrocene (shown by TLC on Silufol in hexane, with reference to standards) was obtained from the benzene/pentane layer after removal of the solvents under low pressure. After triple recrystallization from benzene/pentane, the dimer decomposes at 125–130°C; Found: C, 60, 69; H, 4.83; F, 8.21; Fe, 25.52. $C_{22}H_{20}Fe_2F_2$ calcd.: C, 60.88; H, 4.65, F, 8.75; Fe, 25.74%.

Electroneutral chlorobenzenecyclopentadienyliron

A mixture of [$ClC_6H_5FeC_5H_5$]BF_4 (0.5 g, 1.50 mmol), THF (100 ml), 0.5% Na/Hg (0.5 g, 20 mg-at Na and 8 ml Hg) was stirred at −70 to −80°C for 2 h. Pentane (100 ml) was added to the reaction mixture, the green solution was decanted from Na/Hg, filtered off and oxidized with atmospheric oxygen in the presence of saturated aqueous $NaBF_4$ (50 ml) and benzene. 0.29 g (58%) of [$ClC_6H_5FeC_5H_5$]BF_4 with a negligible admixture of [$C_6H_6FeC_5H_5$]BF_4 was isolated from the yellow aqueous layer. The admixture was traced by TLG and GLC of the thermolysis products of the fluoroborates obtained.

0.15 g (30%) of unreacted [$ClC_6H_5FeC_5H_5$]BF_4 was removed from the reaction flask, and 0.03 g (8%) of [$ClC_6H_5FeC_5H_5$]$_2$ was obtained from the organic layer.

Attempts at substitution of chlorine in $ClC_6H_5FeC_5H_5$

(a) Interaction of $ClC_6H_5FeC_5H_5$ with C_2H_5ONa. Chlorobenzenecyclopentadienyliron was obtained in THF by reduction of [$ClC_6H_5FeC_5H_5$]BF_4 (0.5 g, 1.5 mmol) on sodium amalgam. After reduction pentane was added to the reaction mixture, its temperature was decreased to −70°C. Then the green solution obtained was filtered off into a C_2H_5ONa solution (0.1 g, 4.34 mg-at Na) in ethanol (5 ml). The mixture was kept at −30 to −20°C for 1 h and at −5 to 0°C for an additional hour. The green coloration of the solution gradually changed to red-brown and a dark precipitate was formed. The reaction mixture was then oxidized by atmospheric O_2 in the presence of an aqueous solution of $NaBF_4$ (50 ml) and benzene. 0.17 g (49%) of [$ClC_6H_5FeC_5H_5$]$_2$ with traces of ferrocene was isolated from the benzene layer. These products were proved by TLC on Silufol in hexane, with reference to standards.

0.11 g (22%) of [$ClC_6H_5FeC_5H_5$]BF_4 with an admixture of [$C_6H_6FeC_5H_5$]BF_4 (TLC on Al_2O_3 in dichloroethane with i-C_3H_7OH, 4/1, with reference to standards; GLC of the pyrolysis products) was isolated from the aqueous layer. Only ClC_6H_5 and C_6H_6 were traced in the pyrolysis products; phenetole was absent. Thus, in this experiment, $ClC_6H_5FeC_5H_5$ was mainly dimerized and remained partly intact upon prolonged contact with C_2H_5ONa. It did not react with C_2H_5ONa; the experiment was repeated many times. The reaction temperatures varied from −60 to 0°C, the time from 2 to 6 h. The synthesis of $ClC_6H_5FeC_5H_5$ was performed both in THF and in pentane/water. However, in neither case was the substitution of the Cl atom for a C_2H_5O group observed.

(b) Interaction of $ClC_6H_5FeC_5H_5$ and $FC_6H_5FeC_5H_5$ with CH_3ONa. The experiment was repeated several times. The reduction of [$ClC_6H_5FeC_5H_5$]BF_4 (0.5 g, 1.5 mmol) to $ClC_6H_5FeC_5H_5$ was carried out on Na/Hg in THF or in pentane/water. The $ClC_6H_5FeC_5H_5$ solution was added to dry CH_3ONa. In various experiments, the reaction temperature varied from −10 to −60°C, and the duration from 2 to 5 h. The reaction mixtures were treated as in experiment (a). In all cases, the dimer [$ClC_6H_5FeC_5H_5$]$_2$ was obtained from the benzene layer; [$ClC_6H_5FeC_5H_5$]BF_4 with an admixture of [$C_6H_6FeC_5H_5$]BF_4 was obtained from the aqueous layer. The products were identified in the same way as in experiment (a). Their ratio varied depending on the temperature and duration of the reaction. In neither case were CH_3O for Cl substitution products observed.

The interaction of $FC_6H_5FeC_5H_5$ with CH_3ONa under the conditions described above did not result in the substitution of fluorine by the CH_3O group.

(c) Interaction of $ClC_6H_5FeC_5H_5$ with piperidine. A mixture of $ClC_6H_5FeC_5H_5$ (from 0.5 g, 1.5 mmol of $[ClC_6H_5FeC_5H_5]BF_4$) and piperidine (1 ml, 1 mmol) in THF or pentane was kept at −50°C for 3 h (in another experiment the temperature was −40 to −30°C). Then the mixture was oxidized by atmospheric O_2 in the presence of 20 ml of a saturated aqueous solution, of $NaBF_4$ and extracted many times with benzene and ether. 0.22 g of $[ClC_6H_5FeC_5H_5]BF_4$ was isolated from the aqueous solution, identified by TLC on Al_2O_3 (dichloroethane with isopropyl alcohol, 4/1, as eluent) and compared with an authentic sample as reference. Attempts at chlorine substitution for NC_6H_5, $[C_5H_{10}NC_6H_5FeC_5H_5]$ were unsuccessful. The experiment was repeatedly carried out under different conditions.

Attempts at substituting the halide in the dimers $[HalC_6H_5FeC_5H_5]_2$ (Hal = Cl or F)

(a) Interaction of $[HalC_6H_5FeC_5H_5]_2$ with sodium methylate. A solution of 0.4 mmol of $[HalC_6H_5FeC_5H_5]_2$ in 50 ml of benzene was poured under argon into CH_3ONa in methyl alcohol (4 mg-at Na, 5–10 ml of CH_3OH) and the mixture was stirred at 50°C for 4 h. The reaction products were isolated by chromatography on Al_2O_3 (benzene as eluent). The ^1H NMR spectra of the compounds obtained corresponded to halide-substituted dimers.

Prolonged stirring (10–12 h) of $[HalC_6H_5FeC_5H_5]_2$ with dry CH_3ONa at room temperature did not result in substitution products either.

(b) Interaction of $[HalC_6H_5FeC_5H_5]_2$ with copper acetate. A suspension of 1 mmol of anhydrous $Cu(OCOCH_3)_2$ in benzene of $[HalC_6H_5FeC_5H_5]_2$ (0.4 mmol) was stirred under argon at room temperature for 10–20 h. The benzene solution was filtered off and removed under reduced pressure. The reaction products were oxidized by $[C_6H_5]_3CBF_4$ to the corresponding cations. TLC on Al_2O_3 with standard reference samples showed the reaction products to be $[ClC_6H_5FeC_5H_5]BF_4$ or $[FC_6H_5FeC_5H_5]BF_4$.

In the IR spectra of the products obtained, the absorption characteristic of the CO group (1750 cm^{-1}) was absent.

Similar experiments with an alcohol solution of $Cu(OCOCH_3)_2$ (5–10 ml of absolute C_2H_5OH) did not lead to substitution of the halogen atom for the CH_3COO group either.

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