Organometallic Chemistry

Investigation of the electrochemical behavior of some R—Fe(CO)$_2$Cp metallocomplexes containing a σ-bonded η^5-cyclopentadienylirondicarbonyl fragment attached to an sp^2-hybridized carbon atom

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Electrochemical oxidation and reduction of a large number of Cp(CO)$_2$Fe—R compounds (R = aryl, vinyl, aroyl) with a Fe—C(sp^2) σ-bond have been studied at a platinum electrode using cyclic voltammetry and rotating disk-ring electrode techniques. The mechanisms of both oxidation and reduction cannot be rationalized in terms of unified schemes and depend on the nature of the organic fragment R.

Key words: electrochemistry, organometallic complexes, iron.

Organometallic complexes containing a metal—carbon(sp^2) σ-bond are of great interest since the chemical properties that determine their practical implementation are versatile. Important practical information can be obtained when studying the electrochemical properties of metallocomplexes. These data can be used to predict the properties and reactivity of organometallic compounds not only in heterogeneous electrode reactions but also in various types of homogeneous reactions.

The little literature data on the electrochemical properties of Cp(CO)$_2$FeR complexes containing the Fe—C(sp^2) σ-bond are incomplete and, as a rule, refer to only one of the electrode processes, oxidation or reduction. Thus, for instance, reduction of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl ArFe(CO)$_2$Cp (Ar = p-CH$_3$C$_6$H$_4$, p-ClC$_6$H$_4$, C$_6$H$_5$, C$_6$F$_5$) at a dropping mercury electrode has been described previously.[1,2]

Recently, the electrochemical oxidation of mono- and di-η^5-cyclopentadienylirondicarbonyl-substituted arenes and azines ArFe(CO)$_2$Cp (Ar = C$_6$H$_{5-n}$F$_n$ (n = 0÷5), C$_5$H$_3$FN, C$_5$F$_4$N, C$_5$F$_3$ClN, C$_5$F$_2$Cl$_2$N, C$_4$Cl(SMe)$_2$N$_2$, C$_4$ClH$_2$N$_2$) and Ar'(Fe(CO)$_2$Cp)$_2$ (Ar' = C$_6$H$_4$, C$_6$F$_4$, C$_4$H(SMe)$_2$N$_2$, C$_4$Cl$_2$N$_2$) at a platinum anode has been studied.[3]

Electrochemical reduction of σ-vinyl derivatives of η^5—cyclopentadienylirondicarbonyl has not yet been studied. However, information on the oxidation of E- and Z-isomers of the PhMeC=CPhFe(CO)(P(OPh)$_3$)Cp complex at a gold anode is available.[4]

Data on the electrochemical oxidation of some acyl derivatives of η^5-cyclopentadienylirondicarbonyl RCOFe(CO)$_2$Cp and, in particular, PhCOFe(CO)$_2$Cp are known.[5,6] However, electrochemical reduction of acyl complexes containing the Fe—C(sp^2) σ-bond has not been described.

Recently, using cyclic voltammetry (CVA) and rotating disk-ring electrode (RDRE) techniques, we studied the oxidation and reduction of a number of σ-aryl

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derivatives of η^5-cyclopentadienylirondicarbonyl at a platinum electrode and proposed a mechanism for these processes.[7] In the present work we continued the systematic investigation of the electrochemical behavior of metallocomplexes containing the Fe—C(sp^2) σ-bond, increasing the number of σ-aryl complexes of η^5-cyclopentadienylirondicarbonyl, and investigating the σ-vinyl as well as σ-aroyl derivatives of η^5-cyclopentadienylirondicarbonyl.

Experimental

Measurements of electrochemical oxidation and reduction potentials were carried out using a SVA-1B-M voltammetric system at a stationary Pt-electrode and at a rotating platinum disk-ring electrode (platinum ring) with $Bu_4{}^nNBF_4$ as the supporting electrolyte in anhydrous organic solvents (DMSO, CH_3CN, CH_2Cl_2) at 20 °C. The geometric parameters of the disk—ring system were: disk radius r_1 = 2.57 mm, inner ring radius r_2 = 2.65 mm, external ring radius r_3 = 3.68 mm.

Determination of the coefficient of the efficiency of the disk—ring system was carried out according to the previously described procedure.[8] In all experiments, platinum served as the auxiliary electrode, and a saturated silver chloride electrode was used as the reference electrode. The electrochemical measurements were carried out in a cell 10 mL in volume. The concentrations of solutions of the compounds under study were $5 \cdot 10^{-4}$ mol L^{-1}.

The polarization curves were registered by CVA at a stationary Pt-electrode at potential scan rates of 50, 100, 200, and 500 mV s^{-1}, and also at a rotating Pt-electrode with a ring at 20 mV s^{-1} in the following modes: a) $i_r = f(E_d)$, E_r = const; b) $i_r = f(E_r)$, E_d = const. The rotation speed of the disk electrode was varied from 480 to 3450 rev min^{-1}.

Acetonitrile of "pure" grade was stirred for 24 h over CaH_2 and filtered, then KNO_3 (5 g) and conc. H_2SO_4 (10 mL) were added. The mixture was boiled for 3 h, distilled, boiled again for 2 h over P_2O_5, and distilled; b.p. 81—82 °C.

Dimethylsulfoxide of "pure" grade was successively stirred for 12 h over anhydrous NaOH and for 12 h over CaH_2, and then distilled under reduced pressure (2—4 Torr, b.p. 50—61 °C) under an argon flow. Distilled DMSO was kept under an argon atmosphere over molecular sieves (4 Å). Methylene chloride was distilled over lithium aluminum hydride.

Results and Discussion

σ-*Aryl derivatives of* η^5-*cyclopentadienylirondicarbonyl*

The redox properties of a large number of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl (**1**—**19**) containing various substituents in the aromatic ring have been studied. The data obtained for electrochemical reduction and oxidation of these compounds at a Pt-electrode in different solvents are presented in Table 1.

As can be seen from Table 1, reduction of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl X-$C_6H_4Fe(CO)_2Cp$ is hampered as a whole when the substituent in the aromatic ring changes from being an acceptor to being a donor. In this case 1,4-bis-(η^5-cyclopentadienylirondicarbonyl)benzene (**9**) has the most negative reduction potential.

Using the data obtained for the redox properties of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl, one can construct dependences of the reduction potentials E^{Red} and oxidation potentials E^{Ox} on the Hammett's σ_{para} constants of substituents. As can be seen in Fig. 1, a correlation is found between those parameters (ρ = 0.13 V and ρ_2 = 0.50 V for the reduction and oxidation processes, respectively). Extrapolation of both straight lines to the values of the reduction potential E^{Red} and the oxidation potential E^{Ox} of the disubstituted complex **9** gives in both cases similar values of the Hammett's σ_{para} constant for the group —Fe(CO)$_2$Cp: $\sigma_{para} \approx -0.70$. This value is comparable to the σ_{para} constant for the —N(CH$_3$)$_2$ group (−0.66). This means that the η^5-cyclopentadienylirondicarbonyl fragment is a strong electron donor.

The ability of metal-containing groups of the ML_n type (ML_n = Cp(CO)$_2$Fe, Mn(CO)$_5$, *et al.*) to serve as both π- and σ-donors is well known.[9—12] However, the total quantitative evaluation of this effect as well as the determination of the relative contribution of the inductive (σ_I) and resonance ($\sigma^0{}_R$) factors of this effect differ significantly depending on the method used. Thus, based on the values of the inductive and resonance parameters of the metal-containing groups (which were obtained from the chemical shifts in the ^{19}F NMR spectra) in *m*- and *p*-$FC_6H_4ML_n$ type compounds (Ref. 10) the

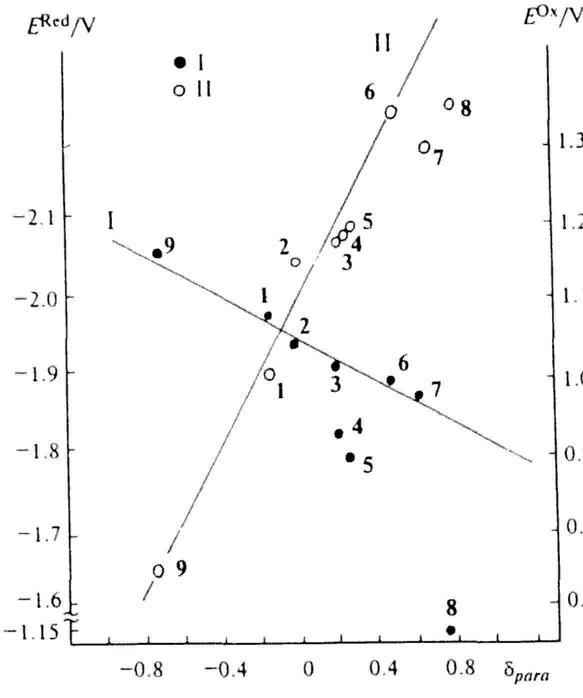


Fig. 1. Dependences of reduction potentials E^{Red} (I) and oxidation potentials E^{Ox} (II) for complexes $XC_6H_4Fe(CO)_2Cp$ on Hammett's σ_{para} constants of substituents X. The numeration of points corresponds to that of compounds in Table 1.

Table 1. Data on the electrochemical reduction and oxidation of compounds containing the η^5-cyclopentadienylirondicarbonyl fragment $-Fe(CO)_2Cp$ ($-Fp$) bonded to an sp^2-hybridized carbon atom ($c = 5 \cdot 10^{-4}$ mol L^{-1}, Pt, 0.05 M $Bu_4{}^nNBF_4$, $Ag^+/AgCl/KCl$, 20 °C)

Compound	Solvent	E^{Red}/V [a]	n [b]	N_r^- [c]	E_r^{Ox}/V	n [b]	N_r^+ [c]
$CH_3C_6H_4Fp$-*p* (**1**)	DMSO	−1.98	2.1	0.43	1.01	2.2	0.25
	CH_3CN	−2.15	1.99	0.20	1.04	0.83	0.13
					1.25	1.45	
C_6H_5Fp (**2**)	DMSO	−1.95	1.90	0.40	1.15	2.0	0.23
	CH_3CN	−2.08	1.95	0.25	1.12	0.88	
					1.37	1.5	0.15
ClC_6H_4Fp-*p* (**3**)	DMSO	−1.92	1.73	0.46	1.18	2.0	0.25
BrC_6H_4Fp-*p* (**4**)	DMSO	−1.83	1.3	0.10	1.18	2.0	0.20
	CH_3CN	−2.03	1.26	0.05	1.22	0.80	
					1.3	1.40	0.16
IC_6H_4Fp-*p* (**5**)	DMSO	−1.80	1.27	0.085	1.2	1.75	0.19
	CH_3CN	−2.0	1.25	0.02	1.2	0.86	
					1.29	1.38	0.15
$CH_3COC_6H_4Fp$-*p* (**6**)	DMSO	−1.90	1.90	0.46	1.35	1.98	0.24
NCC_6H_4Fp-*p* (**7**)	DMSO	−1.88	1.9	0.40			
	CH_3CN				1.30	1.6	0.14
$O_2NC_6H_4Fp$-*p* (**8**)	DMSO	−1.15	0.99	0.[illegible] [d]			
	CH_3CN				1.35	1.0	0.15
FpC_6H_4Fp-*p* (**9**)	DMSO	−2.05	1.70	0.40	0.5	0.81	[e]
					0.84	1.12	
	CH_3CN	2.24	1.75	0.20	0.76	1.04	[e]
					0.92	0.75	
C_6F_5Fp (**10**)	DMSO	−1.62	1.30	0.08			
	CH_3CN	−1.81	1.21	0.00	1.5	1.03	0.00
	CH_2Cl_2 [f]				1.62 [g]	1.00	0.00
NC_5F_4Fp (**11**)	DMSO	−1.68	0.90	0.00			
	CH_3CN	−1.88	1.00	0.00	1.61	0.91	0.00
	CH_2Cl_2 [f]				1.75 [g]	1.00	0.00
$Fp(C_6F_4)_2Fp$-*p* (**12**) [h]	CH_3CN	−1.80	1.4	0.00	1.62	1.5	0.00
C_6F_5COFp-*p* (**13**)	CH_3CN	−1.76	1.3	0.30	1.45	1.43	0.01
$FpCOC_6F_4Fp$-*p* (**14**)	CH_3CN	−1.85	1.00	0.25	1.3	0.9	0.03
					1.68	0.87	
E-PhCH=CHFp (**15**)	CH_3CN	−2.03	1.63	0.24	0.87	2.0	0.25
Z-PhCH=C(Ph)Fp (**16**)	CH_3CN	−2.1	1.9	0.22	1.1	1.75	0.20
Z-*tert*-C_4F_9CF=CFFp (**17**)	CH_3CN	−1.99	0.93	0.10	1.62	1.02	0.09
	CH_2Cl_2 [f]				1.69 [g]	1.04	0.01
Z-PhFC=CFFp (**18**)	CH_3CN	−2.03	0.87	0.09	1.15	0.92	0.05
E-PhFC=CFFp (**19**)	CH_3CN	−2.01	0.90	0.10	1.29	1.00	0.05

Note. [a] Scan rate υ = 200 mV s^{-1}. [b] n is the number of electrons. [c] N_r^- and N_r^+ are the current yields of oxidation of $[CpFe(CO)_2]^-$ and reduction of $[CpFe(CO)_2]^+$ at the ring, respectively, υ = 20 mV s^{-1}, ω = 2530 rev min^{-1}. [d] The current yield for oxidation of the radical anion $(O_2NC_6H_4Fp)^-$ at the ring. [e] Strong passivation of the disk electrode occurs in oxidation of this compound; therefore, one fails to register the products of its oxidation at the ring. [f] Potentials for 0.1 M Bu_4NBF_4 as the supporting electrolyte are given. [g] The values given correspond to $E^0 = (E^c - E^a)/2$. [h] The concentration of complex **12** was ≈ 10^{-5} mol L^{-1} due to its low solubility.

σ-bonding between the ligand and the metal is believed to be of great importance. However, data of other investigators,[9] in particular, the results of a ^{13}C NMR study on the substituent effect in $C_6H_5ML_n$ type compounds showed that the Fe(CO)$_2$Cp and Mn(CO)$_5$ groups are strong π-donors, similar to fluorine.

The electron-releasing ability of metal-containing —CH$_2$M(CO)$_n$Cp type groups (M = Fe, n = 2; M = Mo, W, n = 3) was studied in Refs. 13—15. The construction of the dependences of pK_a of the conjugated acids of the corresponding pyridine bases on Hammett's σ_{para} constants for 3- and 4-substituted pyridinium ions allowed one to determine the values of Hammett's σ_{para} constants for —CH$_2$M(CO)Cp groups (M = Fe, n = 2; M = Mo, W, n = 3).[13] Thus, for the —CH$_2$Fe(CO)$_2$Cp group, σ_{para} = −0.49 or −0.26 depending on the position of the pyridine ring (4 or 3) occupied by this substituent.[13] Hence, the value of Hammett's σ_{para} constant for the Fe(CO)$_2$Cp group (−0.70) indicates that the electron-releasing character of a metal-containing group is higher if it is not separated from the aromatic ring by a methylene unit. This is in good agreement with the data in Ref. 9.

As can be seen in Fig. 1, the reduction potentials of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl **4**, **5**, and **8** are not described by a linear $E^{\mathrm{Red}}(\sigma_{para})$ dependence. This means that reduction of these compounds and of complexes **1**—**3**, **6**, **7**, and **9** have different mechanisms. Let us consider in detail the possible mechanisms of the reduction and oxidation of the compounds under study.

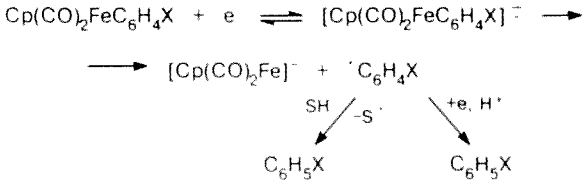
Reduction. Reduction of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl at a dropping mercury electrode proceeds irreversibly with the consumption of two electrons to yield the iron carbonylate anion [CpFe(CO)$_2$]$^-$ and a hydrocarbon ArH.[1,2] The reduction of all studied complexes CpFe(CO)$_2$C$_6$H$_4$X (X = CH$_3$, H, Cl, Br, I, COCH$_3$, CN, CpFe(CO)$_2$), CpFe(CO)$_2$C$_6$F$_5$ and CpFe(CO)$_2$C$_5$F$_4$N, at a platinum electrode (except for nitrogen derivative **8**) is chemically and electrochemically irreversible, since no peak of the reoxidation of the radical anion of the starting compound is observed on the cyclic voltammogram of the reverse scan.

As can be seen from Table 1, the experimental values of the number of electrons consumed in the reduction of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl varies from 1 to 2. The nature of the particles resulting from reduction was studied by RDRE techniques. The voltammetry curve recorded at the ring $i_r = f(E_r)$ was recorded at the potential of the disk electrode corresponding to the limiting current plateau. The particles recorded on this curve are oxidized at a potential of −0.79 V (in DMSO), which coincides with the reoxidation potential of iron carbonylate anions.[8]

Previously[8] we found that iron carbonylate anions are fairly stable in the time scale of the methods used. Hence, assuming that all radical anions formed in the reduction of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl decompose to form iron carbonylate anions, the current yield of the oxidation of the latter at the ring N_r must correspond to the calculated value of 0.42,* which is the maximum for the system under study. However, as can be seen from Table 1, the values of N_r vary between values close to the theoretical value and zero. The closer the experimental value of the number of electrons consumed in the reduction of compounds is to 1, the smaller, as a rule, the value of N_r.

Analysis of the data obtained for complexes **1**—**3**, **6**, **7**, and **9** (two-electron reduction and current yields of the oxidation of the iron carbonylate anions at the ring close to theoretical) allows one to propose the following ECE type mechanism for reduction (Scheme 1).

Scheme 1



In the case of complex **8**, which contains a NO$_2$ group in the aromatic ring, the radical anion formed is relatively stable, and its further decomposition is not observed.[7]

In the case of iodine- and bromine-containing complexes **4** and **5**, the experimental values of the number of electrons consumed during reduction are close to 1 while the current yields at the ring N_r, corresponding to oxidation of iron carbonylate anions, are much less than the theoretical values N_r (see Table 1). This means that not all radical anions formed in the reduction of the compounds under study decompose to give iron carbonylate anions. Hence, the reduction mechanism of σ-p-iodo- and σ-p-bromophenyl derivatives of η^5-cyclopentadienylirondicarbonyl must differ from the ECE type mechanism proposed above for complexes **1**—**3**, **6**, **7**, and **9**.

It is likely that in the case of CpFe(CO)$_2$C$_6$H$_4$Hal compounds (Hal = Br, I) two processes proceed in parallel (Scheme 2).

Judging by the amount of the iron carbonylate anions formed, the contribution of process *b* is insignificant. However, if only process *a* occurs, abstraction of the halogen must proceed close to the surface of the electrode (since iodine- and bromine-containing radical anions have, as a rule, a very short lifetime). Therefore, further reduction of the η^5-cyclopentadienyliron-dicarbonyl radical at the electrode should dominate over

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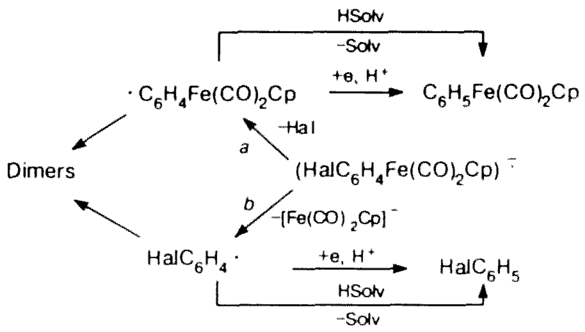
* It should be noted that the stability of [CpFe(CO)$_2$]$^-$ and [CpFe(CO)$_2$]$^+$ in MeCN is lower than that in DMSO, and the experimental values of the current yield of oxidation of [CpFe(CO)$_2$]$^-$ and reduction of [CpFe(CO)$_2$]$^+$ in MeCN (N_r), generated from dimer [CpFe(CO)$_2$]$_2$, are 0.3 and 0.25 V, respectively.

Scheme 2



Solv — solvent

other pathways of its stabilization. The total number of electrons consumed in the reduction of complexes **4** and **5** in this case should be close to 2; however, it was found to be somewhat smaller (see Table 1). Stabilization of the *p*-iodo- and *p*-bromophenyl-η^5-cyclopentadienyliron-dicarbonyl radical anions can follow a third parallel pathway. This assumption is supported by the formation of a new reversible redox couple in the less cathodic region of potentials observed in the reduction of complexes **4** and **5**. The potentials $E^0{}_\mathrm{I}$ of the given couple for the compounds investigated are presented in Table 2.

The same situation was also observed for σ-perfluoroaryl derivatives of η^5-cyclopentadienylirondicarbonyl. The number of electrons consumed in the reduction of these compounds is close to 1, while the current yield of the oxidation of iron carbonylate anions at the ring is virtually equal to zero, *i.e.*, $[\mathrm{CpFe(CO)_2}]^-$ is not formed. In this case, as in the reduction of complexes **4** and **5**, the formation of a new reversible couple was observed (see Fig. 2, *a* and Table 2), which was even more pronounced than in the preceding case.

Reduction of η^5-cyclopentadienylirondicarbonyl-pentafluorobenzene at the dropping mercury electrode also involves one electron and is irreversible.[1] The authors of Ref. 1 assume that the carbonylate anion $[\mathrm{CpFe(CO)_2}]^-$ (is contradictory to the above mentioned RDRE data) and C_6F_5 (whose further transformations were not considered in Ref. 1) can be the reaction products.

Since the formation of radical anions in the reduction of complexes **4**, **5**, **10**, and **11** is irreversible, and, at the same time, no iron carbonylate anions were found among their decomposition products, it is natural to assume a chemical transformation of these radical anions, for instance, dimerization.

Dimerization reactions are characteristic of radical anions containing at least one electron-withdrawing group, CN, CHO, CO_2CH_3, NO_2, as well as for radical anions of heteroaromatic compounds (see Ref. 16 and references cited therein).

Thus, to explain the presence of the reversible couple $E^0{}_\mathrm{I}$ in the case of σ-perfluoroaryl complexes $C_6F_5Fe(CO)_2Cp$ and $NCC_6F_4Fe(CO)_2Cp$, one can assume "tail-to-tail" type dimerization with the formation of dianion **A**, which is capable of reversible transformation into biradical **B** (Scheme 3).

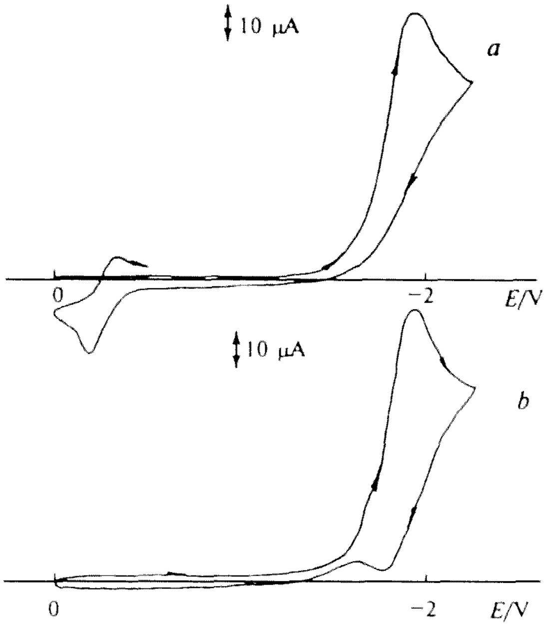


Fig. 2. Cyclic voltammograms of a solution of $\mathrm{Cp(CO)_2FeC_5F_4N}$ ($9.8 \cdot 10^{-4}$ mol L^{-1}): *a*, in the absence of CO; *b*, in a solution saturated with CO (Pt, CH_3CN, 0.05 *M* $\mathrm{Bu_4{}^nNBF_4}$, 200 mV s^{-1}, Ag/AgCl/KCl, 20 °C).

Table 2. Potentials of reversible redox couples observed in the cyclic voltammograms of certain σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl (Pt, CH_3CN, $\mathrm{Bu_4{}^nNBF_4}$, Ag^+/AgCl/KCl, 20 °C)

Compound	$E_1{}^0$/V	$E_2{}^0$/V
$\mathrm{Cp(CO)_2FeC_6H_4Br}$	−0.275	–
$\mathrm{Cp(CO)_2FeC_6H_4I}$	−0.275	–
$\mathrm{Cp(CO)_2FeC_6F_5}$	−0.320	+0.735
$\mathrm{Cp(CO)_2FeC_5F_4N}$	−0.230	+0.820

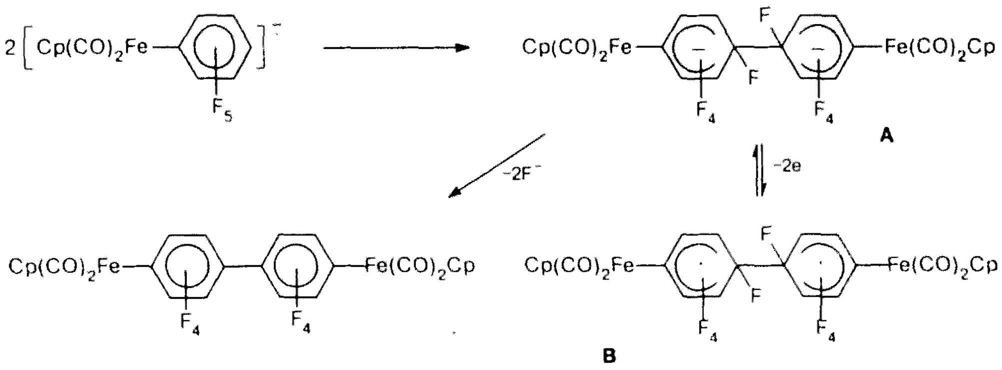
However, analogous "tail-to-tail" type dimerization for compounds $\mathrm{CpFe(CO)_2C_6H_4X}$ (X = Br, I) to yield a dianionic complex similar to **A** without "instantaneous" abstraction of iodine or bromine atoms appears to be highly improbable.

Another pathway of dimerization of the radical anions formed in reduction is dimerization of the "head-to-tail" type. One can propose the following scheme for the reaction:

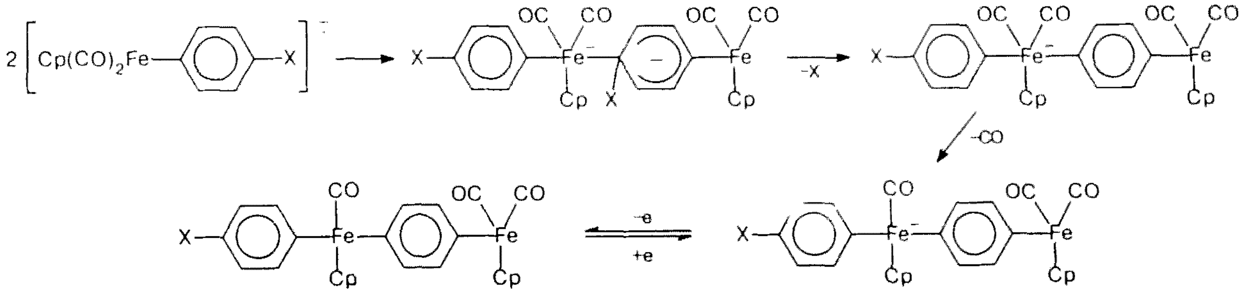
It is likely that this pathway could occur only for those σ-aryl derivatives of η^5-cyclopentadienyliron-dicarbonyl that contain a good leaving group in the aromatic ring, *i.e.*, X = Br, I.

One more possible way the radical anions could dimerize is "head-to-head" type dimerization, *i.e.*, over the metal-containing centers (Scheme 5).

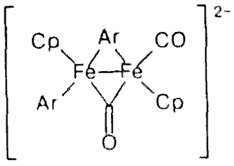
Scheme 3



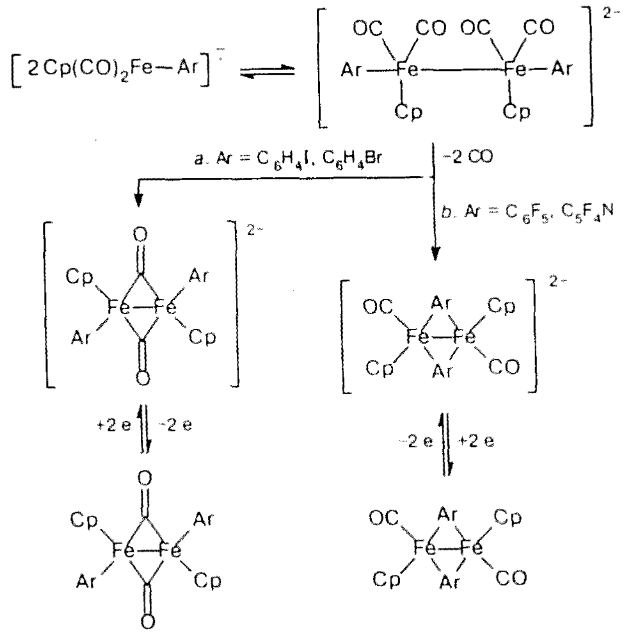
Scheme 4



In the case of σ-perfluorophenyl (**10**) and σ-perfluoro-4-pyridyl (**11**) complexes, formation of an asymmetric dianion with a three-center bond between one of the aryl (hetaryl) ligands and two iron atoms is also possible.



Scheme 5



Each of the two dimerizing radical anions loses one of its CO-ligands to yield a bridging dianion capable of transformation into a neutral complex, which explains the presence of the reversible redox couple $E^0{}_1$. Platinum complexes with this structure containing perfluoroaryl ligands are known to exist.[17,18] One can assume the formation of complexes of this type for substrates containing strong electron-withdrawing substituents in the aromatic ring, which favors delocalization of the negative charges at Fe atoms. If the aromatic ring contains no acceptor substituents, the formation of a dimeric structure containing carbonyl bridges appears to be more probable (Scheme 5, route *a*). In order to prove the possibility of such dimerization, we reduced complexes **4**, **5**, **10**, and **11** in a CO atmosphere. It was found (Fig. 2, *b*) that saturation of the solution with gaseous CO leads to reversibility of the reduction wave for the compounds under study and to disappearance of the peaks of the reversible redox couple $E^0{}_1$.

Neither of the effects observed contradict in anyway the suggested scheme of reductive dimerization: the presence of dissolved CO suppresses the loss of the CO ligand by the radical anion, which leads to its stability and, hence, to the reversibility of its reduction. No formation of a dimeric complex responsible for the reversible redox couple $E^0{}_1$ occurs. It should be noted that the picture of reduction observed returned to the original picture immediately after removal of the dissolved CO from the solution by a flow of argon.

The results of experiments on the effect of CO on the voltammetry curve observed in reduction allow one to reject the dimerization according to Scheme 3. The choice between Schemes 4 and 5 is less obvious, however, the close values of the $E^0{}_1$ potentials for compounds with such different kinds of aromatic ligands could be evidence that for compounds **4**, **5**, **10**, and **11** dimerization proceeds with the formation of an Fe—Fe bond, and in the case of compounds **4** and **5** the iron atoms are bonded through carbonyl bridges (Scheme 5, route *a*) while in the case of compounds **10** and **11** perfluoroaryl bridges are also possible (Scheme 5, route *b*). Similar dimeric bridge complexes of iron with aryl ligands have not been reported in the literature as yet. However, based on the experimental data and a detailed theoretical consideration of the feasible transformations of the radical anions, the formation of such complexes in the time scale of the methods used seems to be plausible.

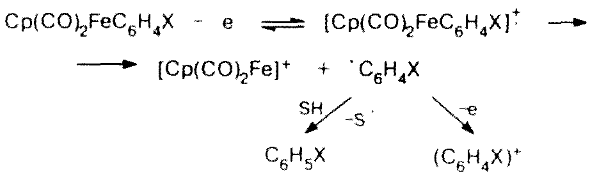
Oxidation. As can be seen from the data of Table 1, oxidation of all σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl studied is irreversible, and the number of electrons consumed in oxidation is between 1 and 2 depending on the substituent in the aromatic ring. Two closely spaced irreversible waves with total height corresponding to the transfer of two electrons are present on the cyclic voltammograms of complexes **1**—**7** and **9** in acetonitrile. One irreversible two-electron wave is observed in DMSO.

The products of the oxidation of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl were identified by the RDRE technique, as in their reduction. The curve of the dependence of the ring current on the ring potential, $i_r = f(E_r)$, was recorded at a constant potential of the disk electrode corresponding to the limiting current of the second oxidation wave of the complexes under study in CH_3CN. The particles located on this curve are reduced at the potential corresponding to the reduction potential of the $[CpFe(CO)_2]^+$ cation. The current yield at the ring N_r is less than its calculated (theoretical) value (see Table 1). However, according to our study,[8] the current yield of the reduction of $[CpFe(CO)_2]^+$ at the ring in the oxidation of the dimeric complex $[CpFe(CO)_2]_2$ is also less than the theoretical value, which indicates that $[CpFe(CO)_2]^+$ cations are less stable than $[CpFe(CO)_2]^-$ anions.

Thus, both oxidation and reduction of the most investigated σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl follow the ECE mechanism (Scheme 6).

If the aromatic ring contains a nitro group, oxidation involves one electron, however, no reversed peak of reoxidation of a radical cation is observed on the cyclic voltammogram. At the same time, RDRE data indicate that the radical cation formed undergoes decomposition into $[CpFe(CO)_2]^+$ and $C_6H_4NO_2{}^{\cdot}$; the latter of which abstracts hydrogen from the solvent to give nitrobenzene.

Scheme 6



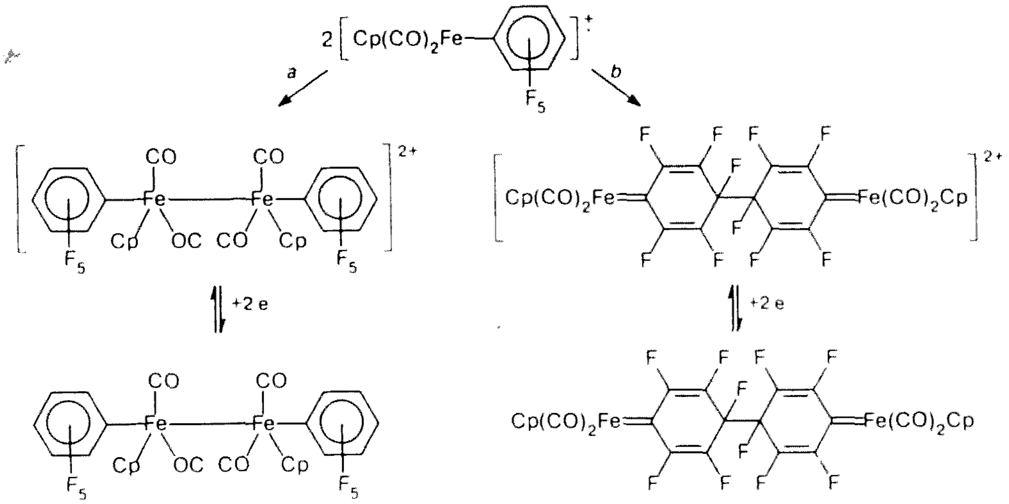
The proposed scheme of the oxidation of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl is in agreement with the data of Ref. 3. The observation of the one-electron irreversible oxidation wave for complexes $CpFe(CO)_2C_6H_5$ and $CpFe(CO)_2C_6H_4Fe(CO)_2Cp$ at a platinum anode in methylene chloride allowed the authors of Ref. 3 to draw the conclusion that the initially formed radical cations $[CpFe(CO)_2C_6H_5]^{+\cdot}$ and $[CpFe(CO)_2C_6H_4Fe(CO)_2Cp]^{+\cdot}$ are unstable. Further transformations of these radical cations were not considered. It was only noticed that other peaks are also present on the cyclic voltammograms, but they were not analyzed.[3]

As follows from a consideration of our data (see Table 1), the proposed scheme of the oxidation of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl gives no explanation for the behavior of the perfluoroaryl complexes $CpFe(CO)_2C_6F_5$ and $CpFe(CO)_2C_6F_4N$. Oxidation of these compounds involves one electron and is irreversible, however, no decomposition of a radical cation similar to that of $[CpFe(CO)_2C_6H_4NO_2]^+$ is observed, since the reduction current yield at the ring for $[CpFe(CO)_2]^+$ cations is equal to zero. At the same time, in the oxidation of σ-perfluoroaryl complexes **10** and **11** we observed the formation of a new reversible redox couple (see Fig. 3, *a*), whose potential $E^0{}_2$ (see Table 2) is more negative than the oxidation potentials of compounds **10** and **11**. Notice that the oxidation of compounds **10** and **11** in CH_2Cl_2 involves one electron and is reversible.[3] No mention was made in this case about the formation of new reversible redox couples, just as in reduction in CH_3CN. The results of electrochemical oxidation of complexes **10** and **11** in CH_2Cl_2 we conducted are in agreement with the data in Ref. 3 (see Table 1).

The formation of the new reversible redox couple in the oxidation of complexes **10** and **11**, analogously to their reduction, may be due to different processes of the dimerization of the radical cations formed (Scheme 7).

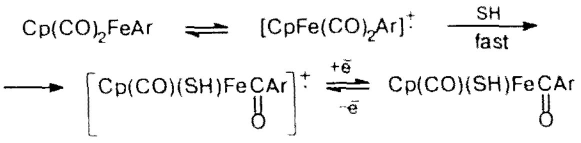
However, the formation of dimeric complexes following both routes *a* and *b* does not explain the observed effect of the solvent on the oxidation of complexes **10** and **11**. The absence of reversibility of their oxidation in

Scheme 7



CH$_3$CN and the appearance of a new reversible redox couple may be related to changes in the ligand environment of Fe atoms. For example, the migration of the CO group initiated in the course of the oxidation of these compounds and its further inclusion in an aryl—metal bond leaves a site free that can be occupied by any other ligand (for instance, by a solvent molecule). As a result, a new aroyl radical cation capable of reversible reduction to a neutral aroyl complex can be formed (Scheme 8).

Scheme 8



The higher the coordinating ability of the solvent (SH) used, the more plausible such a process.

A similar electrochemically initiated carbonylation of σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl is unknown, while an analogous reaction of σ-alkyl derivatives of η^5-cyclopentadienylirondicarbonyl has been studied in much detail.[19–26] Based on the approaches used in those works, we attempted to confirm the assumption that carbonyl rearrangement proceeds in the course of the electrochemical oxidation of the σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl **10** and **11**. It is known[19–23] that new reversible redox couples are formed in the electrochemical oxidation of σ-methyl-η^5-cyclopentadienyldicarbonyl complex of iron(II) CpFe(CO)$_2$CH$_3$ in various solvents at a reduced temperature (below –78 °C). These couples correspond to mutual transitions of the acyl radical cation [CH$_3$COFe(CO)(L)Cp]$^{+\cdot}$ into a neutral acyl complex CH$_3$COFe(CO)(L)Cp (L is the solvent molecule). In addition to CH$_3$CN, even s poorly coordinating solvents as acetone[19] and methanol[21] can be used as ligands. The introduction of strong ligands (for example, pyridine or triphenylphosphine) into the reaction leads to the appearance of additional redox couples corresponding to electrochemical transformations of acyl complexes containing pyridine or triphenylphosphine as one of the ligands.[23,24] However, no changes in the electrochemical behavior were observed in the oxidation of complexes **10** and **11** in CH$_3$CN in the presence of triphenylphosphine. On the other hand, the addition of

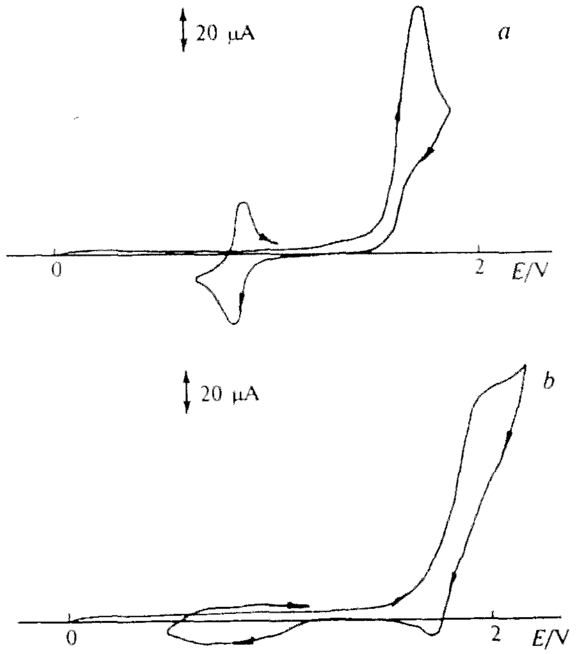


Fig. 3. Cyclic voltammograms of a solution of Cp(CO)$_2$FeC$_5$F$_4$N ($1.0 \cdot 10^{-3}$ mol L^{-1}): *a*, in CH$_3$CN with 0.05 *M* Bu$_4$^{n}NF$_4$ as the supporting electrolyte; *b*, in CH$_2$Cl$_2$ with 0.1 *M* Bu$_4$^{n}NF$_4$ as the supporting electrolyte (Pt, 200 mV s^{-1}, Ag/AgCl/KCl, 20 °C).

pyridine in the oxidation of η^5-cyclopentadienylirondicarbonylperfluoropyridine **11** resulted in the formation of one additional reversible redox couple (E^0 = 0.71 V), but had no effect on the general view of the cyclic voltammogram of σ-perfluorophenyl complex **10**.

Electrochemical oxidation of the σ-methyl derivative of η^5-cyclopentadienylirondicarbonyl in CH_2Cl_2 under a CO atmosphere results in the formation of the σ-acyl complex $CH_3COFe(CO)_2Cp$.[27–29] We studied the electrochemical oxidation of complexes **10** and **11** in various solvents under a CO atmosphere. To identify the probable product of carbonyl rearrangement of σ-perfluorophenyl complex **10** in the presence of CO, the σ-aroyl complex $C_6F_5COFe(CO)_2Cp$ (**13**) was synthesized[30] and its spectral and redox properties were studied in detail.[30]

It was found that aroyl complex **13** is oxidized more readily than σ-perfluorophenyl complex **10**. However, the aroyl radical cation formed is unstable as demonstrated by the absence of the anodic peak of its reduction. Neither the appearance of additional redox couples in the region of potentials corresponding to oxidation of $C_6F_5COFe(CO)_2Cp$, nor the disappearance of the initially formed redox couple was observed in the electrochemical oxidation of complexes **10** and **11** in acetonitrile in the presence of CO and with a simultaneous decrease in the temperature to −30 °C.

It is known[22] that the stability and reduction potentials of acyl radical cations $[CH_3COFe(CO)(L)Cp]^{+\cdot}$ are strongly dependent on the nature of the ligand L. Thus, the half-periods of the lifetimes $\tau_{1/2}$ and reduction potentials E^{Red} of radical cations $[CH_3COFe(CO)_2Cp]^{+\cdot}$ and $[CH_3COFe(CO)(CH_3CN)Cp]^{+\cdot}$ at 20 °C in CH_3CN are equal to 0.44 and 22 s, and 0.94 and 0.18 V, respectively.[22] It is likely that the aroyl radical cation $[C_6F_5COFe(CO)(CH_3CN)Cp]^{+\cdot}$, which contains an acetonitrile ligand, is also more stable than $[C_6F_5COFe(CO)_2)Cp]^{+\cdot}$. In this case, the reversible couple observed would correspond to mutual transitions of this radical cation into the neutral complex $C_6F_5COFe(CO)(CH_3CN)Cp$.

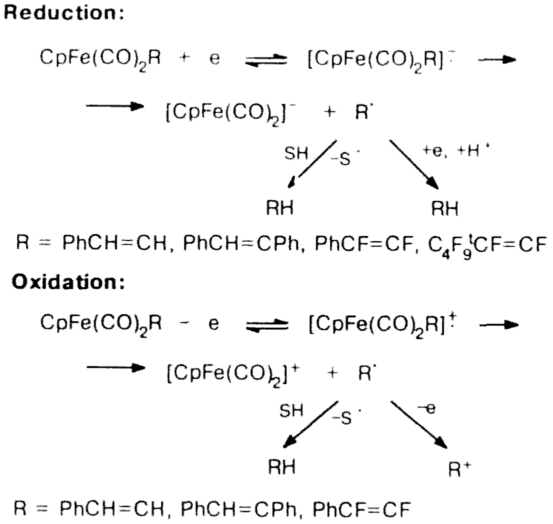
σ-Vinyl derivatives of η^5-cyclopentadienylirondicarbonyl

As can be seen from the data in Table 1, both reduction and oxidation of σ-vinyl derivatives of η^5-cyclopentadienylirondicarbonyl **15** and **16** are two-electron and irreversible. The value of N_r at the ring electrode in the oxidation of $[CpFe(CO)_2]^-$ and in the reduction of $[CpFe(CO)_2]^+$ are close to the corresponding theoretical values.

A one-electron reduction peak is present on the cyclic voltammograms of fluorine-containing σ-vinyl complexes **17**—**19**. An inflection, which likely corresponds to oxidation of the radical anions of complexes **17**—**19** that form, appears on the voltammetry curve during the reverse potential scan. The poorly pronounced peak of the oxidation of the radical anions of these compounds indicates that, despite the fact that they are more stable than the radical anions of complexes **15** and **16**, some of them disintegrate, yielding a vinyl radical and $[CpFe(CO)_2]^-$. This is confirmed by the values of the current yield of oxidation of $[CpFe(CO)_2]^-$ at the ring, which, however, in this case are appreciably smaller than the theoretical values.

The same picture is observed in oxidation of fluorine-containing σ-vinyl derivatives of η^5-cyclopentadienylirondicarbonyl except the complex **17**. Thus, the mechanism of ECE type (analogous to discussed above for σ-aryl derivatives of η^5-cyclopentadienylirondicarbonyl) can be proposed for both reduction and oxidation of almost all studied σ-vinyl derivatives of η^5-cyclopentadienylirondicarbonyl (Scheme 9).

Scheme 9



The results obtained are in agreement with the data of Ref. 4 in which the oxidation of *E*- and *Z*-isomers of the alkenyl complex $CpFe(CO)(P(OPh)_3C(Ph)=C(Ph)Me$ in methylene chloride at a gold electrode was studied.

The oxidation of σ-perfluorovinyl complex **17** is one-electron and irreversible; at the same time, the appearance of a new reversible redox couple (E^0 = 0.825 V) is observed, as in the oxidation of perfluoroaryl complexes **10** and **11**. The oxidation of complex **17** becomes reversible with methylene chloride in place of MeCN as the solvent, and no new reversible redox couples are observed in this case. It is obvious that the nature of the processes occurring in the oxidation of alkenyl complex **17** is analogous to that considered previously for aryl complexes **10** and **11**.

σ-Aroyl derivatives of η^5-cyclopentadienylirondicarbonyl

Reduction of aroyl complexes **13** and **14** is irreversible, and the number of electrons is close to 1. The current yield of the oxidation of $[CpFe(CO)_2]^-$ anions at the ring electrode is close to the theoretical value (see Table 1). It is likely that the aroyl radical anions formed undergo decomposition involving the release of CO and the formation of $[CpFe(CO)_2]^-$ and the corresponding radicals (Scheme 10).

Scheme 10

$$C_6F_5COFe(CO)_2Cp + e \rightleftharpoons [C_6F_5COFe(CO)_2Cp]^{\bar{\cdot}} \longrightarrow$$

$$\longrightarrow C_6F_5^{\cdot} + CO + [Fe(CO)_2Cp]^-$$

The number of electrons observed in the oxidation of complex **13**, is equal to 1.45. These data are in agreement with Refs. 5,6, where oxidation of the acyl complex $PhCOFe(CO)_2Cp$ was shown to be one-electron, yielding $[COFe(CO)_2Cp]^+$ and a phenyl radical. No formation of $[CpFe(CO)_2]^+$ was observed in the case of $C_6F_5COFe(CO)_2Cp$ (see Table 1), which allows one to propose the following scheme of oxidation.

Scheme 11

$$C_6F_5COFe(CO)_2Cp - e \rightleftharpoons [C_6F_5COFe(CO)_2Cp]^{+\cdot} \longrightarrow$$

$$\longrightarrow C_6F_5^{\cdot} + [COFe(CO)_2Cp]^+$$

However, the cyclic voltammograms have a number of peaks of low intensity, which is evidence for some additional processes resulting in larger experimental values of the number of electrons.

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