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THE ELECTRONIC EFFECT OF BUTADIENYLIRON TRICARBONYL SUBSTITUENTS

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Summary

The effect of butadienyliron tricarbonyl substituents on the polarographic oxidation potentials of the ferrocenyl nucleus and the ^{19}F NMR chemical shifts in *m*- and *p*-substituted fluorobenzenes is discussed. The data obtained by different physical methods enable us to conclude that all carbon atoms in the coordinated butadiene are sp^2 hybridized.

Distribution of electronic density in dieneiron tricarbonyl π-complexes and the state of carbon atoms participating in the bonds with iron are still the subject of much discussion.

In the study of the effect of coordination upon the reactivities and physicochemical properties of the arenic [1] and cyclopentadienylic [2] ligands in metal carbonyl complexes, a transfer of positive charge from the metal to the ligand has been observed. This is also observed by measuring the dipole moments of dieneiron carbonyl complexes [3], assuming the diene is the positive pole of the dipole.

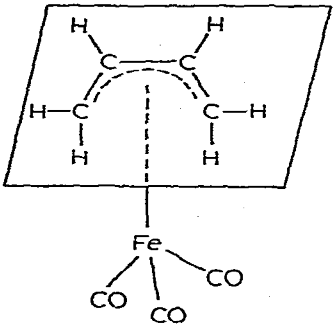
In general, the electron attractive effect of $M(CO)_3$ groups may decrease in the series Cr, Mn, Fe owing to a sequential increase in the number of *d*-electrons of the metal. This is in agreement with the effective metal charge [4] and quantum-chemical computations [5].

However, the following results of experiments provide the basis for consideration of $Fe(CO)_3$ as an electron donor with respect to the coordinated butadiene: the phenyl ring in the *para*-position of 1-phenylbutadienyliron tricarbonyl may be easily acylated [6,7], the acidity of coordinated sorbic acid has been found to decrease with respect to the free acid [6] and the data obtained by measuring the basicity of aniline compounds containing *para*-1-butadieneiron tricarbonyl substituents [8].

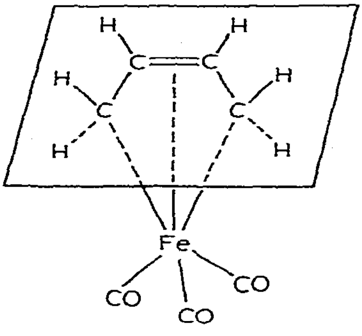
The quantum-mechanical computations of the electron density distribution in the free *s-cis*-butadiene [9] and in that coordinated with the iron tricarbonyl group [10] have demonstrated that, upon coordination, the electron density in position 2 decreases while in position 1 it increases more than two-fold, also there is a large negative charge at the iron atom.

X-Ray analysis [11] and NMR studies [12,13] lead to the conclusion that the inner carbons in the coordinated butadienic system of dieneiron tricarbonyl complexes are sp^2 hybridized (the C(1)—C(2)—C(3) angle is equal to 118° and the respective proton chemical shifts are in the "olefinic" region).

Different views are held regarding the degree of hybridization of the terminal carbon atoms [12—15], so structures A and B have been proposed for dieneiron tricarbonyl complexes.



(A)



(B)

Analysis of the metal—butadiene bond [10] and the reactivity of the coordinated butadiene show that, unlike cyclopentadienylic and arenic ligands, the electron density in the butadiene ligand is unevenly distributed. Thus, in order to estimate the change of electron density, upon coordination, of such π-ligands with unequivalent carbon atoms one should investigate the changes in reactivity and physicochemical properties for each unequivalent ligand position and then analyse the total change.

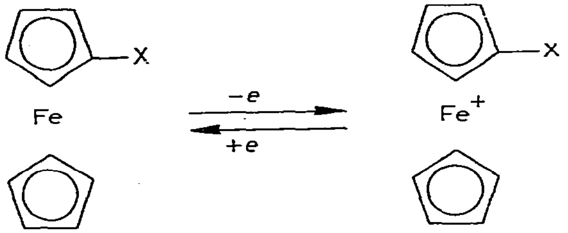
For this purpose we attempted a systematic study of the effect of coordination upon the reactivity and physicochemical characteristics of dienic ligands in iron tricarbonyl complexes for which either structure A or B is possible.

To estimate correctly the electronic changes in the ligand after coordination, the reactivity and physicochemical characteristics of the non-coordinated ligand and its π-complexes should be studied under the same conditions. Only by analysing the differences observed, can one draw any conclusions about the electronic changes in the ligands after coordination. One of the necessary conditions is maximum possible retention of ligand geometry upon coordination. Until now, no such condition has been fulfilled in the study of butadienyliron tricarbonyl. The butadienyl ligand belongs to the class of "hard" ligands and its ready polymerization quite often hinders a quantitative estimation of butadiene reactivity in many reactions. Moreover, under normal conditions, 1,3-dienes exist in the form of an isomeric mixture, with the *s-trans*-isomer dominant (for butadiene it is > 95%), while coordinated dienes possess a *s-cis*-configuration. Data are rather scarce on the difference in properties between the two configurations. In the rare cases, however, when such measurements have been available their values could not be ignored [16].

Two methods were used in estimating the effect of the butadienyl substituent. Firstly, the electronic effect of substituents was estimated from changes in redox potentials of the respective substituted ferrocenes and secondly, using the Taft method, by correlation of the ^{19}F NMR chemical shifts in fluorobenzene derivatives with the substituent reactivity parameters in the benzene ring.

Oxidation potentials of the ferrocenyl nucleus in 1- and 2-ferrocenylbutadiene-iron tricarbonyls * *[17]*

The polarographic method was employed for measuring the reversible oxidation potentials of the ferrocenyl nucleus in these compounds. The change of the half-wave oxidation potential of ferrocene under the effect of substituents has been used repeatedly for estimating the electronic effects of various substituents, including π-complexes [18]. This reaction involves a transfer of an electron from the ferrocenyl nucleus to the electrode.



Numerous experiments have demonstrated that the substituents display a predominantly inductive effect on the value of E_0 or equilibrium constant of the reaction.

The polarographic method employed possesses lower sensitivity toward substituent effects than potentiometric techniques. It does enable one, however, to use inert solvents and thus study the electronic effect of the non-coordinated butadiene, although only in *s-trans*-form. The results are shown in Table 1.

It was shown that introduction of a substituent into the ferrocene cyclopentadienyl ring does not change the wave characteristics only the $E_{1/2}$ value; the wave corresponds to a reversible one-electron transfer. It is seen from the data of Table 1 that the presence of butadienyl or vinyl groups in the ferrocene cyclopentadienyl ring shifts the value of $E_{1/2}$ for ferrocene oxidation over 0.01 V towards the positive potential, which is greater than that comparable with experimental accuracy. A comparison of the electronic effect of the vinylic and 1-butadienyl substituents show that the measured half-wave potential is insensitive to a replacement of one β-hydrogen atom of the vinylic group with a $CH{=}CH_2$ grou It is clear that the *s-trans*—*s-cis* transition does not affect the value of $E_{1/2}$, within experimental accuracy. The $E_{1/2}$ value also changes negligibly upon coordination of the butadienyl substituent with the $Fe(CO)_3$ group when the ferrocenyl group resides at position 1 of butadiene; $E_{1/2}$ shifts over 0.02 V towards the negative value. This means that when butadiene coordinates with the $Fe(CO)_3$ group

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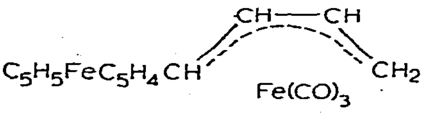
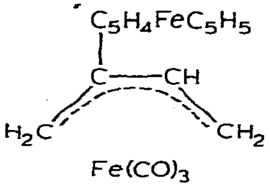
* The polarographic measurements were performed by Drs. L.I. Denisovich and I.A. Suskina.

TABLE 1

THE $E_{1/2}$ VALUES OF THE REVERSIBLE OXIDATION OF FERROCENE AND ITS DERIVATIVES (CH_3CN, 0.1 N $(C_2H_5)_4NClO_4$, $c = 1.10^{-3}$ M, 25°C, WITH RESPECT TO S.C.E. ±0.01 V)

Compound	$E_{1/2}$ (V)
$C_5H_5FeC_5H_5$	0.41
$C_5H_5FeC_5H_4CH{=}CHCH{=}CH_2$	0.42
$C_5H_5FeC_5H_4CH{=}CH_2$	0.42
	0.40
	0.49

the electron density of position 1 of the dienic ligand increases somewhat with respect to the non-coordinated diene. However, when ferrocene is located at position 2 of the butadiene ligand the $E_{1/2}$ value for ferrocenyl oxidation changes considerably ($E = 0.07$ V). In this case the $E_{1/2}$ shift to the positive potential with respect to unsubstituted ferrocene may serve as evidence of rather strong electron-accepting properties of the butadienyliron tricarbonyl group, e.g. comparable to the electron attractive effect of the CH_2OR group in ferrocenyl [19]. This suggests that the electron density at position 2 in butadienyl decreases considerably upon coordination with the $Fe(CO)_3$ group compared to the slight increase in electron density observed at the terminal carbons. In general, the ferrocenyl oxidation potential changes by 0.09 V upon its transfer from position 1 to 2 of the butadienyl system, thus there is an essential charge separation in the dienic system.

The results obtained lead us to conclude that butadienyl ligand coordination with the $Fe(CO)_3$ group causes charge transfer from the ligand to the metal similar to that found in other metal carbonyl π-complexes.

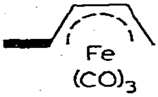
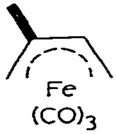
The ^{19}F NMR data interpretation using Tafts's approach

The Taft approach may be helpful in separating the total substituent electronic effect into its inductive and resonance components. In order to determine the characteristics of the electronic effects of the π-$C_4H_5Fe(CO)_3$ substituents from fluorine chemical shifts in 1- and 2-(m-, p-fluorophenyl)butadieneiron tricarbonyls [17], using the Taft equations, $\delta(m\text{-F}) = -7.10\sigma_I + 0.60$ [20] and $\delta(p\text{-F}) = -29.5\sigma_R^0 + \delta(m\text{-F})$ [21], we computed the inductive (σ_I) and resonance (σ_R^0) substituent constants shown in Table 2.

As can be seen from the data of Table 2 the total polar effect (the sum of in-

TABLE 2

THE ^{19}F NMR CHEMICAL SHIFTS (δ, PPM) AND THE VALUES σ_I AND σ_R^0 OF m- AND p-RC_6H_4F (CCl_4, C_6H_5F AS AN OUTER STANDARD ±0.05 PPM)

R	$\delta(m\text{-F})$	$\delta(p\text{-F})$	σ_I	σ_R^0
	−0.14	+1.98	+0.10	−0.07
	−0.19	−0.11	+0.11	0.00

ductive and resonance effects) of the 1-π-$C_4H_5Fe(CO)_3$ substituent (a rather weak acceptor) differs negligibly from that of the hydrogen atom and the 2-π-$C_4H_5Fe(CO)_3$ group possesses a considerable attractive ability. The electron attractive effect of the substituents investigated, is explained by negative inductive components comparable to those of such groups as $N(CH_3)_2$ or CH_2Cl. The 1-π-$C_4H_5Fe(CO)_3$ group is a rather weak electron acceptor via an inductive mechanism and a weak conjugative donor *, while the 2-π-$C_4H_5(CO)_3$ group is an electron-attractive substituent of the same strength via an inductive mechanism but displays no resonance effect on the neighbouring ferrocenyl. Since inductive effects are always associated with bonds, the equivalent and positive values of σ_I confirm a regular distribution of the effective positive charge over the σ-bonds of all butadiene carbons.

The absence of resonance interaction between the 2-π-$C_4H_5Fe(CO)_3$ substituent and the phenyl ring may be explained by geometric and electronic factors. A non-coplanarity of the phenyl ring with the π-dienic ligand plane and free rotation of the phenyl group about the C(phenyl)—C(diene) bond may hinder a transfer of conjugation. X-ray analysis of 1,4-diphenylbutadieneiron tricarbonyl [22,23] confirms conjugation between the phenyl rings and the coordinated butadiene fragment. The phenyl substituent should have the same geometry at both positions 1 and 2 of butadiene, so steric factors probably do not hinder conjugation, if it ever takes place. Since π-electrons participate in conjugation the absence of any resonance effect with the 2-π-$C_4H_5Fe(CO)_3$ group on the phenyl ring indicates low π-electron density at position 2 of the coordinated butadiene.

Combined analysis of the potentials and σ constants, obtained for π-$C_4H_5Fe(CO)_3$ substituents bonded to ferrocenyl or phenyl nuclei via positions 1 and 2 of the butadiene ligand revealed that; coordination of the butadiene ligand with iron tricarbonyl may result in negative charge transfer from the ligand to the $Fe(CO)_3$ group; upon coordination the electron density at position 1 of butadiene increases slightly but it is essentially lower at position 2; there is considerable electron density partitioning between the terminal and central butadiene

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* Comparable to ferrocenyl ($\sigma_R^0 = -0.11$).

carbons; the σ-core of the coordinated diene bears an effective positive charge distributed evenly over the carbon atoms; and the different effects are due to the higher π-electron density at the terminal carbons of the butadiene ligand.

The state of carbon atoms in the coordinated butadiene

In the PMR spectra of various dieneiron tricarbonyl complexes the proton resonance line of the terminal carbons of butadiene is shifted to the higher field "aliphatic" region. This shift has been explained [14] by a transfer of electron density from the metal atom to the ligand. On the other hand [12], the terminal protons of the conjugated dienic fragment become aliphatic owing to σ-bond formation between the metal atom and terminal carbons. The analysis of ^{13}C NMR spectra of butadieneiron tricarbonyl [13] shows that a delocalized π-system of the dienic ligand participates in the metal bond formation and there is no σ-metal—carbon bond in the molecule. By assuming that the values $J(^{13}C—H)$ are proportional to the carbon hybridization, sp^2 hybridization of all butadiene carbon atoms has been suggested for h^4-$C_4H_6Fe(CO)_3$ [24].

In Crews' opinion [25], structure A is favoured by the values of long-range coupling constants in the PMR spectra of dieneiron tricarbonyl complexes manifesting the coplanarity of protons at C(1) and C(2).

According to the data determined previously [6,22,23]; when the terminal atom of the diene has a substituent, a comparison of bond length between this atom and the substituent carbon (1.44—1.49 Å) with the distance computed for the sp^2- and sp^3-hybridized terminal carbon (1.48 or 1.52—1.54 Å) indicates its hybridization state. On the other hand, the substituents at the terminal carbon atoms are actually bent from the diene plane toward the metal. These results confirm the sp^3 character of the metal—terminal atom bond *.

The polarographic investigation of ferrocenyl substituted butadieneiron tricarbonyls and the treatment of fluorine chemical shifts in 1- and 2-(*m*-, *p*-fluorophenyl)butadieneiron tricarbonyls using Taft's approach, suggest a high electron attractive ability of the central carbon atoms. This could be due to higher electronegativity of these atoms (tne electronegativity of sp^2-hybridized carbon is greater than that of sp^3-hybridized carbon atoms). However, using Taft's method we found that the conjugative ability toward the phenyl ring is higher in the terminal carbons. Since conjugation is transmitted via carbon at position 1, it should not be saturated (i.e. sp^3-hybridized), since π-electrons take part in transmittance of conjugation.

It is evident from this analysis that there could be different interpretations of the experimental data which would only indirectly confirm the hybridization of the carbon bonded to the metal. Only a combined analysis of the data with those obtained by different physicochemical methods, first of all X-ray data, will provide a solution of the structure of a molecule of a complex compound.

X-ray investigation of the complexes with open-chain ligands [22,23] clearly confirms the sp^3-hybridization of dienic carbons participating in the metal bond formation. Thus in 1,4-diphenylbutadieneiron tricarbonyl the dihedral angles between the butadiene plane and rings are equal to 26 and 17°. These different angles may be explained by packing effects, while phenyl rotation itself is a result

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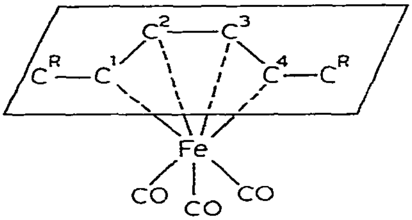
* Such deviations have been revealed by X-ray analysis of the complexes with cyclic ligands (e.g. [15]).

of spatial strain of the biphenyl type in the ligand. This fact is evident from the shorter intramolecular nonbonding distances C···C and C···H between the atoms of phenyl and butadienyl with respect to the sum of the respective Van der Waals radii (3.60 and 3.00 Å). In spite of rotation of phenyl groups about the butadiene plane this contraction is still high: C···C 2.83—2.89 and C···H 2.55—2.65 Å. Such strain in the ligand manifests itself in a tendency to coplanarity and thus conjugation may be retained in spite of the above-mentioned rotations. Moreover the carbon of a substituent combined with butadiene located in the same plane as the coordinated part has C(R)—C(1)—C(2) angles close to the ideal value, 120° for sp^2 carbons, while Fe—C(1)—C(2) and Fe—C(2)—C(1) angles for h^4-$C_4H_6Fe(CO)_3$ are 69 and 71° [22] or 67 and 73° respectively [11].



The interatomic distances and bond angles of the coordinated unsaturated molecules are usually close to the respective parameters in their lower excited state [26,27]. A geometric model of coordinated butadiene corresponds roughly to a mixture of ground and excited states of free butadiene [26].

Thus from analysing the results of experiments on the electronic structures and geometry of ligands in dieneiron tricarbonyl π-complexes it is evident that the carbons of coordinated butadiene retain their sp^2-hybridization but the molecule transfers into its excited state when the negative charge from ligands is transmitted to the metal and electron-density redistribution occurs. It is quite obvious that the apparent inconsistency of the results obtained by different physicochemical methods reflect objectively the structure of the complex.

All the available data do not support structure B although it is hard to postulate that structure A can account for all the properties of dienic complexes.

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