Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

EFFECT OF COORDINATION WITH THE METAL ON THE REACTIVITY OF π-BONDED ORGANIC LIGANDS
III*. CHANGE OF THE ELECTRONIC EFFECT OF THE PHENYL NUCLEUS UPON COORDINATION WITH THE $Cr(CO)_3$-GROUP

S. P. GUBIN AND V. S. KHANDKAROVA
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

(Received October 10th, 1969)

SUMMARY

Ferrocenylphenylchromiumtricarbonylmethane (I) and ferrocenylphenylchromium tricarbonyl (II) were prepared. The polarographic oxidation of (I) and (II) on a platinum electrode in CH_3CN was investigated and the E_{f_0} of (I) was determined by a potentiometric titration. A set of σ-constants was calculated for the $(CO)_3Cr$-C_6H_5-group as substituent. Analysis of the results obtained led to the conclusion that a considerable change of effective positive charge on the σ-orbitals of the aromatic ring carbons took place upon coordination with the $(CO)_3Cr$-group.

Several attempts have been made to estimate the electronic effect of the phenylchromiumtricarbonyl group as substituent and to compare it with the non-coordinated phenyl effect. Nicholls and Whitting, for example, determined the dissociation constants of free benzoic acid and benzoic acid coordinated with the $(CO)_3Cr$-group[1]. Klopman and Calderazzo investigated the alkaline hydrolysis of free and coordinated methyl benzoate[2], and finally, Holmes *et al.* reported on the solvolysis of benzyl chloride coordinated with the $(CO)_3Cr$-group and made an attempt to estimate σ-constants for the "$(CO)_3Cr$-group" as a substituent[3]. However, as will be shown in our later analysis, these calculations are not quite reliable and provide no information on the nature of the metal-to-π-ligand bond. The present paper is a systematic study of the electronic effect of the phenyl nucleus as substituent, free and coordinated with the $(CO)_3Cr$-group. This was carried out by determination of the σ-constants for the $(CO)_3CrC_6H_5$-substituent and by elucidation of the separate effects defining the total polar effect of this substituent.

EXPERIMENTAL

Materials

Arenechromiumtricarbonyl complexes were obtained by the method of Nicholls and Whiting[1]. They were analytically pure specimens. IR-spectra were taken

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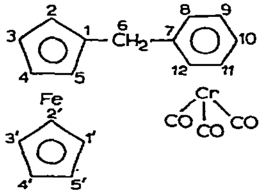
* For part II see ref. 10.

on a UR-10 model apparatus in KBr pellets. NMR-spectra were taken on a "Jeol" M-60 instrument at 60 Mcps in CCl_4 with hexamethyldisiloxane as an internal standard.

1. *Ferrocenylphenylchromiumtricarbonyl* (*I*). 5.55 g (0.02 *M*) of benzylferrocene and 1.6 g (0.0073 *M*) of chromium hexacarbonyl in 20 ml of absolute diglyme were refluxed in an argon atmosphere for 2.5 h. Sublimated hexacarbonylchromium returned mechanically into the reaction zone. After cooling to room temperature the orange-brown reaction mixture was diluted with ether (100 ml) and filtered through deactivated alumina (5 g). Solvents and unreacted hexacarbonylchromium were evaporated *in vacuo*. The residue was dissolved in pentane and carried under an argon atmosphere to an alumina column (alumina was preliminarily refluxed in pentane in an argon atmosphere). Complete light protection of the adsorbed substance was provided. Elution with pentane gave unreacted benzylferrocene (4.9 g). (I) was eluted with benzene. Double recrystallization from heptane afforded a pale yellow complex (0.160 g, 5.3% based on $Cr(CO)_6$), m.p. 145–150° (decomp.) (Found: C, 58.58; H, 3.92; Fe, 13.23. $C_{20}H_{16}FeCrO_3$ calcd.: C, 58.28; H, 3.91; Fe, 13.55%). The IR-spectrum shows the bands characteristic of π-C_5H_5 and π-C_6H_6 rings and absorption in the carbonyl region at 1967, 1943 and 1865 cm^{-1}. NMR-spectral data are listed in Table 1.

TABLE 1

NMR SPECTRA OF THE π-COMPLEXES OF FERROCENYLPHENYLMETHANE AND PHENYLFERROCENE WITH THE $(CO)_3Cr$-GROUP (CCl_4)



Free ligand				Complex			
Compound	Type of protons	δ (ppm)	Type of signal	Compound	Type of protons	δ (ppm)	Type of signal
Ferrocenylphenylmethane	1', 2', 3', 4', 5'	4.01	singl.	I	1', 2', 3', 4', 5' 2, 3, 4, 5	4.12	mult.
	2, 3, 4, 5	3.98	mult.				
	6	3.65	singl.		6	3.49	singl.
	8, 9, 10, 11, 12	7.14	mult.		8, 9, 10, 11,12	5.15	mult.
Phenylferrocene	1', 2', 3', 4', 5'	3.94	singl.	II	1', 2', 3', 4', 5'	4.04	singl.
	2, 5	4.52	tripl.		2, 5	4.44	tripl.
	3, 4	4.18	tripl.		3, 4	4.27	tripl.
	8, 9, 10, 11, 12	7.25	mult.		8, 9, 10, 11, 12	5.33	mult.

2. *Ferrocenylphenylchromiumtricarbonyl* (*II*). 7.09 g (0.027 *M*) of phenylferrocene and 2.0 g (0.0091 *M*) of chromiumhexacarbonyl in 20 ml of absolute diglyme were refluxed in an argon atmosphere for 6 h. The reaction mixture was treated as in procedure 1. Unreacted phenylferrocene was separated by chromatography on an alumina column with hexane under an inert atmosphere. (II) was eluted with a

benzene–hexane (1/1) mixture, yield 0.480 g (13% based on starting $Cr(CO)_6$). Double recrystallization from heptane gave a crystalline orange complex, m.p. 147–150° (decomp.). (Found: C, 57.32; H, 3.77; Fe, 14.02. $C_{19}H_{14}FeCrO_3$ calcd.: C, 57.32; H, 3.54; Fe, 14.03%). The IR-spectrum contains the bands characteristic of π-C_5H_5 and π-C_6H_6 rings and intensive carbonyl absorption at 1968 and 1885 cm^{-1}. NMR-spectral data are shown in Table 1.

E_{f_0} determination

Formal redox potentials, E_{f_0}, were determined by potentiometric titration with 0.01 *N* potassium dichromate in a mixture of 98% acetic (75% v/v) and aqueous perchloric (25% v/v) acids at 25±0.1° according to a procedure already described[4].

Polarographic measurements

Polarographic measurements were conducted on a platinum electrode in absolute CH_3CN at 25±0.1° in an argon atmosphere saturated with solvent vapour. 0.1 *N* $(C_2H_5)_4NClO_4$ was used as supporting electrolyte. All potentials are referred to a saturated aqueous calomel electrode.

Calculation of σ-constants

σ-Constants were calculated from the following equation:

$$\log \frac{K_X}{K_{C_6H_5}} = \frac{\rho}{\pi'}(\sigma_X - \sigma_{C_6H_5}) \qquad (1)$$

obtained by subtracting eqn. (B) from eqn. (A).

$$\log \frac{K_X}{K_{H-Y}} = \frac{\rho}{\pi'}\sigma_X \qquad X\text{–}Y \qquad (A)$$

$$\log \frac{K_{C_6H_5}}{K_{H-Y}} = \frac{\rho}{\pi'}\sigma_{C_6H_5} \qquad C_6H_5\text{–}Y \qquad (B)$$

In all calculations π' was taken as 0.30[5]. The σ_p^0 of the $(CO)_3CrC_6H_5$-group was estimated using the data of Nicholls and Whiting[1]. The pK_a-values of $(CO)_3CrC_6H_5$-CH_2COOH (5.02), $C_6H_5CH_2COOH$ (5.64) and p-NO_2-$C_6H_4CH_2COOH$ (5.01) were measured by these authors in 50% ethanol. The value of ρ for the dissociation of substituted phenylacetic acids is known only for aqueous solutions[5–7] and thus the ρ-value for the dissociation of phenylacetic acid in 50% ethanol had to be calculated. This was carried out by two methods:

(1) It is known that ρ for the dissociation of aromatic acids in water amounts to about 80% of the value in 50% ethanol. From the Taft data, ρ for the dissociation of phenylacetic acids in water is equal to 0.489. Hence, for the dissociation of the same acids in 50% ethanol, the ρ-value is approximately 0.620.

(2) ρ for the dissociation of phenylacetic acids in 50% ethanol may be estimated from the following equation:

$$\log K_{NO_2} - \log K_H = \rho\sigma^0_{pNO_2} \qquad \sigma^0_{pNO_2} = +0.82$$

Hence $\rho = 0.77$.

Using the ρ-values obtained an average σ_p^0 for the $(CO)_3CrC_6H_5$-group equal to $+0.27\pm0.03$ can be calculated.

Measurements of the carbonyl vibration frequencies of metallocenyl ketones

Spectra were taken on the double beam UR-20 instrument in CCl_4 solutions, at concentrations, 0.002–0.004 *M*, and a layer thickness of 1 mm. The instrument was calibrated on water vapour absorption at 1600–1700 cm^{-1}*. All the ketones investigated were analytically pure specimens. Measurements were made of the $\nu(CO)$ frequencies for acetylferrocene and acetophenone. The values obtained are in a good agreement with published data[8], thus enabling the CO-group frequencies obtained by Traylor and Ware[8] to be used for deriving a correlational equation. Use was made only of 11 points giving a good linear dependence of $\nu(CO)$ on σ^+.

RESULTS

To elucidate the effect of coordination with the metal upon the reactivity of the π-bonded organic ligands and to understand the nature of the transition metal–π-ligand bond it should be borne in mind not only that coordination with the metal changes the reactivity of the π-bonded ligand by such or another value and to this or that side[1–3,9,10], but that the change in inductive or conjugative effects may give rise to such variation. In other words, the problem is to clarify on which orbitals of the aromatic ring occur the largest changes of charge upon coordination with the metal. In this regard our approach to a description of the arenemetalcarbonyl reactivities will be that commonly employed for reactions obeying the principle of a linear free energy change (LFE). The objects to be studied can then be represented in the following general form: X–G–Y, where substituent X is an arenemetalcarbonyl group, $(CO)_3CrC_6H_5$–, Y is the reaction center and G the conducting system or group. As in the case of other substituents, the effect of the arenemetalcarbonyl group X on the reactivity of Y will to a first approximation include the two major interactions: inductive and conjugative effects. The *p*-phenylene nucleus is most often used as a conducting system. It is more convenient, however to prepare compounds where the arenemetalcarbonyl groups and different reaction centers are directly adjacent (X–Y) without a phenylene or any other conducting group (a particular case of compounds X–G–Y without –G–). The reactivity of such compounds can usually be adequately described by the LFE principle. Furthermore, it was found[5,6] that by introducing some atomic grouping, –G–, between a substituent and the reaction center, the ρ-value varies and is quantitatively described by a multiplier π' independent of the nature of the reaction center and the character and conditions of the reaction, thus being a constant for the given conducting system. Thus, if an equation of reactivity for compounds X_i–G–Y and the value characterizing a reactivity of compounds X_i–Y (X_i—metallocenyl group) are known, the σ-values of the X_i substituent can be estimated. Equations used in the calculation of σ for the $(CO)_3Cr$-C_6H_5-group are presented in the experimental section.

For the complete characteristics of the electronic effects of the arenemetalcarbonyls as substituents, at least three types of σ should be available: the inductive

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* The error of experiment was about 0.5 cm^{-1}.

aromatic constant σ_i, the Hammett value σ_p and the electrophilic aromatic constant σ_p^+. A later analysis will successively deal with the model reaction series that provide a basis for the determination of the σ-values of $(CO)_3CrC_6H_5-$ as a substituent. In addition to our measurements we used published data that proved to be suitable for further treatment.

The inductive effect of the $(CO)_3CrC_6H_5$*-group*

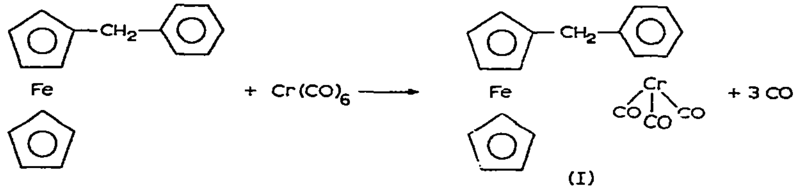
A relatively large number of model reaction series which may be used for determination of the substituent inductive constants are known. However, most of these series are unacceptable for the determination of the inductive parameters of polyatomic groups such as arenemetalcarbonyls and metallocenes. A novel approach has been worked out for estimating the substituent inductive parameters based on the reaction of the reversible oxidation of ferrocenes. Earlier we found that the E_{fo}-value of the reversible oxidation of ferrocene is exceptionally sensitive to the electronic effects of the substituent[11]. Even when a substituent is separated by a methylene moiety from the nucleus, the potential difference between the farthest removed substituents exceeds by many hundred times the maximal mean-square error of the experiment (300 and 2–3 mV, respectively). Redox potentials of the substituted ferrocenes, $C_5H_5FeC_5H_4CH_2X$, where a substituent is separated by a methylene moiety hindering the conjugation, correlate well with the inductive constants of the corresponding–X substituents both in aromatic and aliphatic scales (σ_i and σ^*). The respective equations are as follows:

$$E_{fo} = -0.34\,\sigma_i - 0.208; \quad r=0.992,\ n=8,\ S=0.023 \qquad (1)$$

$$E_{fo} = -0.055\,\sigma^* - 0.209; \quad r=0.991,\ n=7,\ S=0.111 \qquad (2)$$

In the reaction series investigated, substituents display "purely" inductive effects, since a methylene moiety is commonly accepted as hindering the transmission of the substituent conjugation effects. Moreover, as was convincingly shown by one of the present authors[12], the ferrocenyl nucleus itself transmits, of the total polar effect of the substituents, only an inductive component in the direction of the reaction center, the iron atom. The characteristics outlined above for the reaction series under analysis make the ρ-value, of high negative value*, also satisfy conditions required for the model reactions and make it suitable for the determination of the new inductive parameters.

Ferrocenylphenylchromiumtricarbonylmethane required for the determination of the $(CO)_3CrC_6H_5$-group inductive constant using this method was prepared by reaction of benzylferrocene with chromium hexacarbonyl using the conditions of Nicholls and Whiting[1]:



(I)

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* Correlation of the difference between the logarithms of equilibrium constants obtained from the corresponding potentials gives $\rho = -5.65$ [11]

The structure of (I) was confirmed on the basis of the elementary analysis and IR- and NMR-spectra. The results obtained, together with X-ray data for structurally similar compounds[13] give grounds for assuming that (I) may exist predominantly in a "*trans*" configuration with undistorted (due to the direct contacts) phenylchromiumtricarbonyl and ferrócenyl nuclei.

The reversible oxidation of the ferrocenyl nucleus in this compound was investigated by two methods: using a potentiometric procedure described earlier for the oxidation of substituted ferrocenes[4] and polarographically in acetonitrile on the platinum electrode. As can be seen from Fig. 1, under the conditions described the titration curve of (I) represents a one-electron one-stage reversible oxidation. However, the polarographic oxidation of (I) showed two well defined diffuse oxidation waves (Fig. 2). The first wave is specific to the reversible one-electron oxidation of the ferrocenyl fragment. The second wave was identified *via* the polarographic oxidation of the benzenechromiumtricarbonyl complex under analogous conditions.

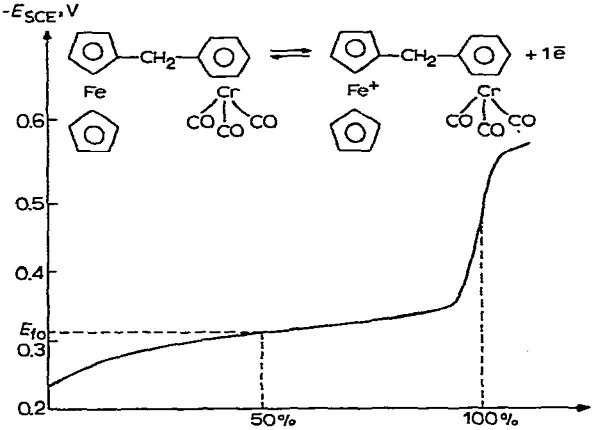


Fig. 1. Typical potentiometric oxidation curve of the ferrocenyl nucleus in ferrocenylchromiumtricarbonylmethane (total amount of iron in the sample was taken as 100%).

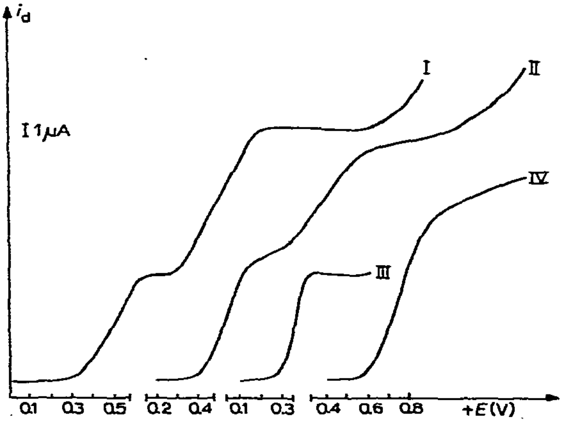


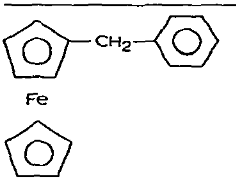
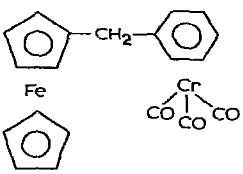
Fig. 2. Polarographic oxidation waves on the Pt electrode (C, $1 \cdot 10^{-3}$ mol·l^{-1}; CH_3CN; 0.1 N $(C_2H_5)_4NClO_4$). (I) ferrocenylphenylchromiumtricarbonylmethane; (II) ferrocenylphenylchromium tricarbonyl; (III) ferrocene; (IV) benzenechromium tricarbonyl.

One diffuse oxidation wave was found on the polarogram. Thus, the second wave on polarograms of (I), having $E_{\frac{1}{2}}$ shifted by about 0.5 V to more positive potentials (because of the electron-withdrawing effect of the $C_5H_5Fe^+C_5H_4$-group) corresponds to the oxidation of the phenylchromiumtricarbonyl fragment. The values of E_{f_0} and $E_{\frac{1}{2}}$ obtained are listed in Tables 2 and 3.

TABLE 2

THE FORMAL REDOX POTENTIALS OF BENZYLFERROCENE, FREE AND COORDINATED WITH THE CHROMIUMTRICARBONYL GROUP

(75% CH_3COOH, 0.066 *N* $HClO_4$, 25±0.1°)

Compound	E_{f_0} (V *vs.* SCE)
	−0.227±0.003
	−0.304±0.007

Thus, the potentiometric oxidation of (I) shows only the first oxidation stage —the oxidation of the ferrocenyl nucleus*.

It can be seen from these results that coordination of the phenyl nucleus in a benzylferrocene molecule with the $(CO)_3Cr$-group results in a substantial hindering of ferrocenyl oxidation in this compound. The absolute magnitude of the formal redox potential increases by approximately 90–100 mV, whereas, as we have found in a recent study, introduction of any substituents into the phenyl ring of a benzylferrocene molecule increases this value by no more than 40 mV[14].

Thus, the strong electron-withdrawing effect of the $(CO)_3Cr$-group appears even when a conjugation chain between substituent and a reaction center is broken. This confirms the inductive nature of this effect. The inductive constants of the $(CO)_3CrC_6H_5$-group were calculated from the oxidation potential obtained (Table 4). It is known that the carbon electronegativity of the phenyl ring as substituent exceeds that of hydrogen (also as a substituent) taken as zero value in the scale of aromatic inductive constants; in this regard the inductive aromatic constant of phenyl is, although small, of positive magnitude.

The change of the inductive aromatic constant of the phenyl ring as substituent ($\Delta\sigma_i = 0.22$) testifies to an appreciable increase in the ring carbon electronegativities

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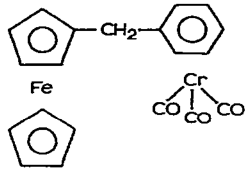
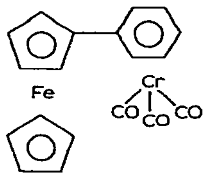
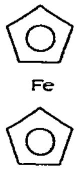
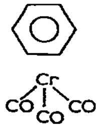
* We have shown earlier that no oxidation can be observed under these conditions for ferrocenes having strong electron-withdrawing substituents which are by 0.35 V more difficult to oxidize with respect to unsubstituted ferrocene[4].

TABLE 3

POLAROGRAPHIC CHARACTERISTICS OF THE OXIDATION WAVES OF THE COMPLEXES (CH_3CN, 0.01 N $(C_2H_5)_4NClO_4$, $C=1\cdot10^{-3}$ M)

No.	Compound	$+E_{\frac{1}{2}}^{I}$ (V vs. SCE)	i_d (μA)	$+E_{\frac{1}{2}}^{II}$ (V vs. SCE)	i_d (μA)
(I)		0.49 ±0.02	9.3	0.96 ±0.03	13.2
(II)		0.55 ±0.01	9.9	0.96 ±0.02	9.6
(III)		0.39 ±0.01	9.1	—	—
(IV)		—	—	0.74 ±0.01	15.4

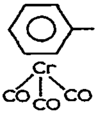
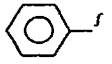
in the Pauling electronegativity scale, upon its coordination (by 0.4 unit, see Table 4). The following example may be considered for comparison: the introduction of chlorine instead of hydrogen into the CH_3-group alters the electronegativity of carbon by 0.5 unit. The inductive aromatic constant of the $(CO)_3CrC_6H_5$-group in the σ_i scale[5-7] is close to that of strong electron-withdrawing substituents such as $-COCH_3$ ($\sigma_i=0.28$), and $-CHO$ ($\sigma_i=0.31$). This comparison shows that a considerable part of the known electron deficiency of $C_6H_6Cr(CO)_3$ is determined by the highly positive inductive aromatic constant, in other words, by an essential enhancement of effective positive charge on the aromatic ring carbon σ-orbitals. This charge appears upon interaction with the $(CO)_3Cr$-group, which is known to have a significant effective positive charge at chromium[16], as a result of the strong electron-withdrawing effect of the three CO-groups.

Determination of σ_p^0 for the $(CO)_3CrC_6H_5$-group

σ_p^0 constants are known to characterize the inductive effect of the *para*-sub-

TABLE 4

σ-CONSTANTS OF THE $(CO)_3CrC_6H_5$-GROUP AS SUBSTITUENT

Substituent	σ_i	σ^*	σ_p^0	σ_p	σ_p^+	σ_c	σ_c^+	$\Delta\sigma_c^+$	Group electronegativity[g]
	+0.31	+1.96	+0.26[a] 0.27[b]	+0.18[c] +0.23[d]	−0.15	−0.13[e]	−0.46	−0.33	2.79 ±0.01
	+0.09	+0.60	0.00	−0.01	−0.179	−0.10	−0.27	−0.17	2.37

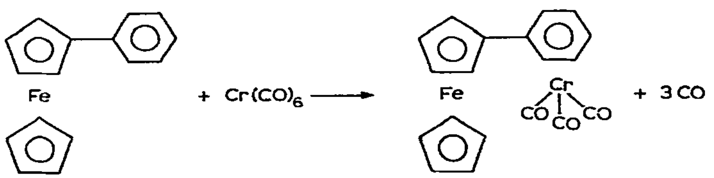
[a] From oxidation reaction of $C_5H_5FeC_5H_4C_6H_5Cr(CO)_3$. [b] From dissociation constant of $(CO)_3CrC_6H_5CH_2COOH$. [c] From dissociation constant of $(CO)_3CrC_6H_5COOH$. [d] From the alkaline hydrolysis rate constant of $(CO)_3CrC_6H_5COOCH_3$. [e] σ_p was taken as +0.18. [f] Values taken from refs. 5–7. [g] Calculated from equations: $\chi_1=0.37\sigma^*+2.06$; $\chi_2=0.26\sigma^*+2.30$; values of $\chi=\frac{1}{2}(\chi_1+\chi_2)$ are presented in ref. 15.

stituted phenyl ring. It is customary to determine these constants from the dissociation constants of *para*-substituted phenylacetic acids. We used the p*K*-values of $C_6H_5CH_2COOH$ and $(CO)_3CrC_6H_5CH_2COOH$ reported by Nicholls and Whiting[1] for calculation of the σ_p^0 of the $(CO)_3CrC_6H_5$-group. The value obtained is shown in Table 4. This value was also estimated by another method. In our previous paper[4] the substituent effects in the five-membered aromatic ring of ferrocene on E_{f_0} were found to be satisfactorily described by the σ_p^0 constants of the corresponding substituents. The reaction center—metal atom—is highly sensitive to changes of the electronic effects of the substituents thus affording exceptionally high ρ. The corresponding equation has the form:

$$E_{f_0} = -0.272+0.5\,\sigma_p^{0\star};\quad r=0.992,\ n=17,\ S=0.019$$

and completely satisfies all the requirements for the reaction series employed for determination of new σ-values.

Ferrocenylphenylchromiumtricarbonyl (II) required for the determination of the σ_p^0 constant for the $(CO)_3CrC_6H_5$-group was prepared by reaction of phenylferrocene with chromiumhexacarbonyl[1]. The structure of (II) was confirmed by elementary analysis and IR- and NMR-spectra.



(II)

The reversible oxidation of ferrocenyl nucleus in (II) was investigated using a potentiometric titration, and polarography in acetonitrile on the platinum electrode.

★ Correlation of the differences between the logarithms of the equilibrium constants obtained from the respective potentials gives ρ equal to −8.81 [11].

It was found that (II) is unstable in acidic media and during the potentiometric titration gives only the titration curve of a decay product—the initial phenylferrocene. The polarographic oxidation of (II) exhibits two well defined diffuse oxidation waves in CH_3CN. The first corresponds to a reversible one-electron oxidation of the ferrocenyl fragment, the second to the oxidation of the phenylchromiumtricarbonyl moiety (Fig. 2). The half-wave potentials obtained are shown in Table 3.

These results show that coordination of the phenyl nucleus of phenylferrocene with the $(CO)_3Cr$-group significantly hinders the oxidation of ferrocenyl in this compound. The oxidation potential increases by 160 mV, while on introduction of any substituent into the phenyl ring of the phenylferrocene molecule this increase is as high as 130 mV[17]. The difference between the oxidation potentials of ferrocene and (II) ($\Delta E_{\frac{1}{2}} = 0.16$ V) was used to calculate the σ_p^0 of the $(CO)_3CrC_6H_5$-group employing eqn. (3) (Table 4). This value differs very slightly from that estimated from the dissociation constants of phenylacetic acids.

Hammett σ constants of the $(CO)_3CrC_6H_5$-group

Hammett σ_p constants were estimated for the $(CO)_3CrC_6H_5$-group from the standard reaction series—dissociation of benzoic acids in 50% aqueous ethanol and a hydrolysis of the methyl esters of benzoic acids in 56% aqueous acetone. Quantitative data on the reactivities of the corresponding phenylchromiumtricarbonyl derivatives are taken from the papers by Nicholls and Whiting[1] and Klopman and Calderazzo[2]. The σ-constants calculated are listed in Table 4. These data show that there is a considerable agreement between values obtained from two different reaction series.

Electrophilic aromatic constant of the $(CO)_3CrC_6H_5$-group

Solvolysis of the substituted tert-cumyl chlorides serves as a standard reaction series for the determination of electrophilic aromatic constants. There are no data for these compounds coordinated with the $(CO)_3Cr$-group*. The linear dependence between the CO stretching frequencies in $X{-}C_6H_4{-}COCH_3$ and the σ^+ constants of the X-substituents was employed for the determination of the electrophilic aromatic σ^+ constant. Earlier, the CO stretching vibrations were found to depend substantially upon the carbon positive charges and to be mechanically independent of other bond vibrations in the molecule, *i.e.*, were highly characteristic. Stretching CO vibrations *versus* σ constants have been studied in some papers for aromatic ketones[18]. Since the conjugation (+C)-effect of the substituents has been found to be rather high for the given reaction series, it could thus be satisfactorily described only by the σ_p^+ constants. Also, it has been found that the CO stretching frequencies in $X{-}C_6H_4$-COR correlate linearly with the S_N1 solvolysis rates of chlorides or acetates of the corresponding carbinols. Thus a given "reaction series" can be used for the determination of new electrophilic aromatic constants. An equation calculated by the

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* Data available on solvolysis of benzyl and benzhydryl chlorides[3] free, and coordinated with the $(CO)_3Cr$-group, were not obtained under standard conditions and thus cannot be used for a correct determination of σ-constants. Furthermore, this experimental work is described so briefly and controversially that the reliability of the results obtained cannot be estimated. In particular, there is no evidence as to where the authors obtained $K = 1 \cdot 10^{-9}$ sec^{-1} for the solvolysis of non-coordinated benzyl chloride in 80% acetone, since the reference given by the authors contains no data corresponding to 80% and 50% acetone.

present authors from the frequencies of ref. 8 and those obtained in this work is as follows:

$$\nu = 11.30\,\sigma^+ + 1690.9; \quad r=0.997,\ n=11,\ S=0.494$$

The CO stretching frequency measured in acetophenonechromiumtricarbonyl (1692 cm^{-1}) differs only slightly from that of free acetophenone (1691 cm^{-1}). The electrophilic aromatic σ_p^+ constants of these substituents are also similar (Table 4). The electrophilic aromatic σ_p^+ constant estimated is in a good accord with the known data[20] indicating that the reactivity of the coordinated arene is somewhat below that of the non-coordinated compound under conditions of electrophilic aromatic substitution.

DISCUSSION OF RESULTS

The main result of the present study is the fact that coordination of the phenyl ring with the $(CO)_3Cr$-group considerably influences the effective positive charge on the aromatic ring carbon σ-orbitals, thus increasing their electronegativity. At first glance this may be surprising. It is usually assumed that the π-electrons of an aromatic system participate in coordination with the metal atom, whereas the contribution of a σ-framework into the total bonding with the metal is rather slight and is usually ignored. At the present time such an approach should be regarded as unsatisfactory. In this we are supported not only by experimental results but also by the self-consistent Mulliken–Wolfsberg–Helmholtz calculations of ferrocene carried out by McGlynn taking into account the ring σ-framework. The contribution of σ-electrons into the total bonding has been shown to be not lower than the π-contribution*. Attention can also be drawn to the fact that according to the data of Table 4, there is no decrease in the π-electron density in the benzene molecule upon its coordination; moreover the π-electron cloud polarizability even increases somewhat. In the light of the general theory of the bond in the transition metal π-complexes developed by Chatt and Duncanson[22], in principle there can be no significant from-metal-to-ligand (or reverse) charge transfer upon coordination with the metal. Since there are certain connections and mutual compensations between two interaction mechanisms—direct donor–acceptor interaction from the ligand to metal and a back-donation from the metal to ligand—it was quite natural to suggest that in the π-ligand bonded with various metals and other ligands, a total π-electron density on the bonding and antibonding orbitals should be approximately invariant and be equal to the π-electron density in a non-coordinated ligand. Thus with regard only to the π-electron density in the ligand, there should be no significant change in its reactivity upon its coordination with the metal and after replacement of one ligand at the metal atom with another one. Actually, there are substantial changes in the ligand reactivities after coordination. In the present work they were shown to be governed by a varying ring σ-framework effective charge upon coordination. Prob-

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* An analogous calculation of the benzenechromiumtricarbonyl molecule has been provided in the recent work by Carrol and McGlynn[16]. An effective positive charge (+0.261) was found at the aromatic ring. Unfortunately, there are no data showing the distribution of the positive charge obtained on the π- and σ-ring orbitals, thus giving no possibility of comparison of such interesting data with our experimental results.

ably it should be accepted that coordination with the metal concerns σ- rather than π-orbitals of the ligand.

ACKNOWLEDGEMENTS

The authors thank Mrs. I. F. Leshcheva for the measurements and discussion of the NMR spectra and Dr. L. A. Leites for measurement of the IR-spectra.

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