

EFFECT OF COORDINATION WITH THE METAL ON THE REACTIVITY OF π -BONDED ORGANIC LIGANDS
IV*. DETERMINATION OF THE INDUCTIVE CONSTANT FOR THE $(\text{CO})_3\text{CrC}_6\text{H}_5$ -SUBSTITUENT BY ^{19}F NMR METHOD

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SUMMARY

The σ_i and σ_R^0 components of the total polar effect of $(\text{CO})_3\text{CrC}_6\text{H}_5$ -group as a substituent have been determined by ^{19}F NMR study of some fluorine-containing arenachromium tricarbonyl complexes. The data obtained led to the conclusion that effective positive charge on the carbon σ -orbitals of aromatic ring increases due to its coordination with $(\text{CO})_3\text{Cr}$ -group.

INTRODUCTION

In the foregoing communication¹ a new method has been proposed for determination of an inductive constant of $(\text{CO})_3\text{CrC}_6\text{H}_5$ group as substituent where a reversible oxidation of some substituted ferrocenes ($\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{X}$) was selected as a model reaction series.

From the correlational equations combining the redox potentials of substituted ferrocenes ($\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{X}$) and the inductive constants of the respective X-substituents, the σ_i constant was determined for $(\text{CO})_3\text{CrC}_6\text{H}_5$ -group as a substituent. This was found to be +0.31, thus comparable with the values of σ_i for such strong electron-withdrawing substituents as CH_3CO -, CH_3COO - and CHO -groups.

On the other hand, σ_R , σ_R^0 and σ_R^+ constants estimated from the corresponding reaction series were found to be close both for the free C_6H_5 -group as well as that coordinated with $\text{Cr}(\text{CO})_3$ -fragment.

The results obtained led us to the conclusion that a significant portion of the known electron deficiency of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ is defined by a high positive inductive aromatic constant, i.e. by an increasing effective positive charge on the σ -carbon orbitals of aromatic ring as a result of interaction with $(\text{CO})_3\text{Cr}$ -group. In the latter the chromium atom is known to possess^{2,3} considerable effective positive charge due to the strong electron-withdrawing effect of three carbonyl groups.

In the present study the electronic properties of $(\text{CO})_3\text{CrC}_6\text{H}_5$ -group as a

* For Part III see ref. 1.

substituent in some fluorine substituted arenechromium tricarbonyl complexes have been determined with the use of ^{19}F NMR technique.

Earlier, Taft *et al.*^{4,5} have established for a number of compounds that ^{19}F chemical shifts are highly sensitive to the electronic changes occurring at the substitution in arene ring. They also found a possibility to separate the effects (inductive and conjugation). Although a theoretical background of Taft's equations was recently criticized⁶⁻⁸, his approach for the determination of σ 's often led to the results which are in close agreement with the data on reactivities of the corresponding compounds.

EXPERIMENTAL

Arenechromium tricarbonyl complexes were prepared by Nicholls and Whiting's method⁹ and were analytically pure.

(3'-Fluorobiphenyl)chromium tricarbonyl (I)

3.2 g (0.0186 M) of 3-fluorobiphenyl and 8.2 g (0.0372 M) of chromium hexacarbonyl were refluxed in 20 ml of absolute diglyme for 10 h in an atmosphere of argon. The work up of the reaction mixture was conducted as in ref. 9. The unreacted 3-fluorobiphenyl was separated by chromatography on alumina column under inert atmosphere using heptane. Adsorbent with the substance was thoroughly light-protected. Compound (I) was eluted with benzene/heptane (1/4). Double recrystallization from heptane gave 0.240 g (4.2% from the initial 3-fluorobiphenyl) of the yellow crystalline complex, m.p. 102–103.5°. (Found: C, 58.44; H, 3.24; F, 6.34. $\text{C}_{15}\text{H}_9\text{CrFO}_3$ calcd.: C, 58.45; H, 2.94; F, 6.16%.) IR-spectrum showed the bands characteristic of $\pi\text{-C}_6\text{H}_6$ -ring and intense band at 1981 and 1919 cm^{-1} corresponding to the carbonyl vibrations.

(4'-Fluorobiphenyl)chromium tricarbonyl, (II)

This compound was obtained analogously to (I) M.p. 115–117°, $\nu(\text{CO})$ 1980 and 1916 cm^{-1} [cf. ref. 10 m.p. 118–120°, $\nu(\text{CO})$ 1982 and 1918 cm^{-1}].

(Fluorobenzene)chromium tricarbonyl

This compound was prepared and purified by the procedure described earlier⁹. M.p. 116.5–117.5°, $\nu(\text{CO})$ 1991 and 1925 cm^{-1} (cf. ref. 9 122.5–124.9° and ref. 10 $\nu(\text{CO})$ 1996 and 1930 cm^{-1}].

The ^{19}F NMR spectra were recorded on Hitachi-Perkin-Elmer Model R-20 spectrometer at 56.4 MHz and 34°. All the measurements were conducted in the diluted solutions (at concentrations below 0.2 M). Chemical shifts were measured by a substitution method with respect to an external reference, fluorobenzene in the same solvent taken in a concentration almost equivalent to that of the substance under study.

Chemical shifts corresponded to a separation of centers of the ^{19}F NMR signals and were estimated with an accuracy of ± 0.05 ppm. IR-spectra were taken in cyclohexane on UR-20 spectrometer.

RESULTS AND DISCUSSION

I. Effect of coordination with $\text{Cr}(\text{CO})_3$ -group on the fluorine chemical shift of fluorobenzene

Numerous PMR studies of arenechromium tricarbonyl complexes showed a 1.5–2 ppm upfield shift of the aromatic proton on the coordination with $\text{Cr}(\text{CO})_3$ -group^{10–15}. Interpretation of this result in terms of a certain negative charge appearing at the ring carbon atoms as a result of their coordination obscures the known electron-withdrawing effect of the $(\text{CO})_3\text{Cr}$ -group.

Such effect has yet received no exhaustive explanation and the two basic reasons were advanced by the most investigators: decreasing π -ring current in the arene cycle as a result of its coordination with $(\text{CO})_3\text{Cr}$ -group, and the magnetic anisotropy of the chromium–arene bond. It can be noted that the protons separated by at least one atom from the aromatic ring are far less sensitive to the effect of $\text{Cr}(\text{CO})_3$ -group at the formation of π -complexes. The proton shifts of substituents are smaller than those of ring protons, and are often nonspecific, *i.e.* there are either upfield or downfield chemical shifts.

In this work we used the known advantages of the ^{19}F NMR method and studied the ^{19}F NMR spectra of fluorobenzene coordinated with $(\text{CO})_3\text{Cr}$ -group. The NMR spectra of ^1H and ^{19}F of fluorobenzenechromium tricarbonyl were measured in benzene and DMSO. A ^{19}F resonance signal of the complex was found to shift over 21.9 (C_6H_6) and 19.2 ppm (DMSO) upfield with respect to fluorobenzene, while after coordination the ring proton chemical shifts changed only over 1.35 (DMSO) and 2.86 (benzene) ppm upfield with respect to a noncoordinated arene*.

Apparently the ^{19}F resonance upfield shift over 20 ppm can be explained neither by a magnetic anisotropy of the metal–ring bond which should equivalently contribute to the chemical shifts of both ^{19}F and ^1H [$\sigma_A(\text{H})/\sigma_A(\text{F}) \approx 1.06$]**, nor by a reduced π -ring current after coordination, since simple model of the ring current¹⁶ also gives close shielding values for ^{19}F and ^1H nucleus. It was confirmed by the ^{19}F spectral study of fluorosubstituted naphthalenes¹⁷. Probably, one should not consider an even explanation involving enhancing shielding of ^{19}F due to the total increase in benzene ring electron density at the coordination with $(\text{CO})_3\text{Cr}$ -group, because this is inconsistent with the numerous studies of reactivity^{1,9,18–21}, IR spectra^{10,15,22}, and with the results of quantum chemical calculations of the arenechromium tricarbonyl complexes^{2,3}. Furthermore, the ^{19}F chemical shifts of fluorosubstituted biphenyls both free and coordinated with $\text{Cr}(\text{CO})_3$ -group presented in the II-nd section of this paper are a convincing proof of an effective positive charge appearing at the arene ring carbon atoms at their coordination.

Thus, an upfield shift of the ^{19}F resonance signal should probably result from some specific sensitivity of the fluorine chemical shifts to the changes in its electronic environment. It is known that in the Ramsey equation for the nuclear shielding constant

* Attention can be drawn to the fact that unlike biphenyl complexes a considerable solvent effect on the ^1H and ^{19}F chemical shifts is observed (*cf.* Table 1). Probably this phenomenon can be a subject of special investigation.

** Moreover, approximate calculations show that for an explanation of the observed proton chemical shifts (to say nothing of fluorine) the magnetic anisotropy of the chromium–aromatic ring bond should be assumed unreasonably high $\sim 10^{-4}$.

based on the second approximation of the perturbation theory, a paramagnetic term of the second order has a major contribution in the shielding of ^{19}F nucleus. This is explained by the presence of valence p -electrons in the fluorine atom which may essentially distort spherical symmetry at the formation of interatomic bonds. It can be assumed that the observed increase in electronegativity of the aromatic ring carbon atoms at their coordination with $(\text{CO})_3\text{Cr}$ -group¹ means their partial $sp^2 - sp$ rehybridization which may result in the stronger shielding of ^{19}F nucleus.

Moreover, Caldow²⁴ has found that a significant contribution into the ^{19}F shielding may be imported by the second order term of the field effect, responsible for the so-called Van der Waals shift²⁵. The latter term as well as paramagnetic term were found to determine changes in the ^{19}F chemical shifts which are observed when passing from *para*- to *ortho*-substituted di- and polyfluorobenzenes²⁴. In this view it should be pointed out that there exists a formal analogy between the introduction of a substituent in the *ortho*-position of fluorobenzene and coordination of the latter molecule with $(\text{CO})_3\text{Cr}$ -group. In both cases separations of ^{19}F nucleus from the "substituents" are approximately the same (~ 2.8 and 3.2 \AA respectively). Probably the ^{19}F NMR chemical shift observed at the coordination may be also determined by a contribution of the second order term of the field effect into the shielding constant. If these assumptions were correct, an introduction of any conducting group between the reaction center (fluorine atom) and aromatic ring coordinated with $(\text{CO})_3\text{Cr}$ -group should substantially decrease the Van der Waals shift since the latter is known to decrease rapidly with distance²⁵. Moreover, in this case a possible specific effect of $(\text{CO})_3\text{Cr}$ -fragment should not distort symmetry of the electronic environment of fluorine. In general, the observed chemical shifts in such case will be determined by a transmission of charge from a "substituent" to the reaction center in accordance with the properties of conducting system. Thus we investigated the arenechromium tricarbonyl complexes in which fluorine is separated by *para*- or *meta*-phenylene nucleus from the coordinated arene.

II. The effect of coordination with $\text{Cr}(\text{CO})_3$ -group on the chemical shifts of fluorine in fluorobiphenyls

Earlier the PMR-spectra of the chromium tricarbonyl biphenyl complexes have been studied by Brown and Raju¹⁰. Similar to benzene complexes, proton shift of the ring combined with $\text{Cr}(\text{CO})_3$ -group in (4'-fluorobiphenyl)chromium tricarbonyl is 1.85 ppm upfield while that of the free ring is only 0.06 ppm upfield (CDCl_3) with respect to the corresponding values of the noncoordinated arene.

It is evident that if the ^{19}F NMR signal upfield shift in (fluorobenzene)chromium tricarbonyl were determined by an increasing total electron density in the arene ring, one might expect this effect in the 4'-fluorobiphenyl complex in the same direction. A magnitude of the effect should be determined by a transmission factor π' for the *para*-phenylene system ($\pi' \approx 0.3$ ref. 26), *i.e.* one should expect a three fold weaker ^{19}F upfield shift for the complex. The ^{19}F chemical shifts were determined in several solvents for 4- and 3-fluorobiphenyls both free and coordinated with the chromium tricarbonyl group (Table 1).

It can be seen from Table 1 that introduction of phenyl substituent to the *para*-position of fluorobenzene molecule causes 2.97 ppm* upfield shift of the ^{19}F resonance

* The data discussed were obtained in benzene.

TABLE I

FLUORINE CHEMICAL SHIFTS^a IN THE ARENECHROMIUM TRICARBONYL COMPLEXES WITH RESPECT TO FLUOROBENZENE

Compound No.	Structure	Solvent			
		Benzene	Acetone	Dimethyl sulphoxide	Benzene/ HClO ₄ (0.3 N)/ CH ₃ COOH (98%) (1/1/4)
(I)		-0.66	-0.72	-0.50	-0.64
(II)		-0.55		-0.44	-0.55
(III)		+0.05		-0.25	
(IV)		+2.97		+2.50	

^a ppm.

signal (the weak + *R* effect), whereas the latter was almost the same in case of *meta*-substitution (0.05 ppm upfield shift in benzene, and 0.25 ppm downfield shift in DMSO).

On the other hand, coordination of the unsubstituted phenyl ring of *para*- and *meta*-fluorobiphenyls with (CO)₃Cr-group causes respectively 0.55* and 0.66* ppm downfield shifts of ¹⁹F which is in accordance with an assumed electron-withdrawing effect of (CO)₃Cr-group. Thus, it confirms our suggestion that the 20 ppm upfield shift of ¹⁹F in fluorobenzene at its coordination with (CO)₃Cr-group is not associated with increasing negative charge at the aromatic ring carbon atoms. It should be noted that the ¹⁹F chemical shifts of the complexes are almost independent of the nature of the solvent.

The ¹⁹F chemical shifts found in benzene were further employed for estimating the σ_i inductive and σ_R^0 resonance constants, characterizing the total polar effect of (CO)₃CrC₆H₅-group. Treatment of the data of Taft *et al.*^{4,5} for a set of substituents in benzene (solvent) using the common methods of the statistical analysis afforded the following equations:

$$\int_H^{m-x} = -6.87 \sigma_i + 0.708 \quad n=17 \quad r=0.969$$

$$\int_H^{p-x} - \int_H^{m-x} = -34.7 \sigma_R^0 - 1.26 \quad n=9 \quad r=0.961$$

* The data obtained in benzene are discussed.

from which σ_i and σ_R^0 constants of $C_6H_5Cr(CO)_3$ -group were estimated employing the data obtained in benzene (Table 1). These were found to be +0.21 and -0.04 respectively. Notice should be made that use of equations of Taft *et al.*^{4,5} based on the experimental data averaged for all the solvents does not alter the character of σ constants ($\sigma_i = +0.17$, $\sigma_R^0 = -0.00$). Calculation of the inductive and resonance constants of phenyl substituent from the data of Table 1 for fluorobiphenyls led to the values ($\sigma_i = +0.10$, $\sigma_R^0 = -0.09$) which do not differ from those obtained from the analysis of reactivity ($\sigma_i = +0.09$, $\sigma_R^0 = -0.10$, ref. 26). Analysis of the changes of σ_i and σ_R^0 for phenyl coordinated with $(CO)_3Cr$ -group leads to the conclusion that there is a significant increase of the phenyl electron-withdrawing ability of the inductive type, whereas its tendency to conjugation is almost the same. It can be noted that the differences of σ_i 's obtained from analysis of reactivity²⁶ and with the ^{19}F NMR method are determined by the peculiarities of both techniques. Considering the σ 's obtained by different methods one may arrive at the following conclusion: different reactivities of arene ligands observed at coordination with $(CO)_3Cr$ -group are explained mainly by change of an inductive constant of $(CO)_3CrC_6H_5$ -substituent. In other words, coordination of benzene with $(CO)_3Cr$ -group essentially changes effective positive charge on the σ -carbon orbitals of aromatic ring while the total π -electron density changes negligibly. This major conclusion is in agreement with the data of McFarlane and Grim¹¹, who found significant change of additive contribution of the *meta*-methoxy group into the ring proton chemical shift of methoxybenzenes at their coordination with $(CO)_3Cr$ -group. Basing on the Taft concept that the effect of *meta*-substituent on the aromatic ring is determined mainly by an inductive effect, the authors¹¹ came to an idea that an ability of the aromatic ring to transmit the conjugative effect varies negligibly at coordination with $(CO)_3Cr$ -group whereas its ability to deliver the inductive effect changes considerably. Moreover, Fritz and Kreiter¹² studied change of spin-spin coupling constants of *ortho*-protons of the aromatic ring in some substituted toluenechromium tricarbonyl complexes and assumed that the aromatic ring σ -core may change on the coordination with $(CO)_3Cr$ -group. Further, in close agreement with the conclusions of the present study are both the results and their interpretation as given by Emanuel and Randall²⁷. The authors consider the increase (approx. by 3 Hz) of $J(^{13}C-H)$ for carbon atoms in methyl groups of *p*-xylene and mesitylene at coordination with $(CO)_3Cr$ -group as due to the increase of effective electronegativity in the aromatic ring connected with them. In the same publication a value of $J(^{13}C-H) = 173 \pm 1$ Hz is given for ring carbon atoms in melted benzenechromium tricarbonyl. In the present study a value of $J(^{13}C-H) = 175 \pm 1.5$ Hz* has been obtained for this compound in CS_2 solution, which is in good agreement with the results given above.

It seems rather strange that Emanuel and Randall do not use the same reasoning for the explanation of a still greater increase of $J(^{13}C-H)$ for carbon atoms as they employed for explaining the change of $J[^{13}C-H(\text{methyl})]$ ** while it is precisely this increased effective electronegativity of ring carbon atoms at coordination with $Cr(CO)_3$ -group that allows to understand the differences observed.

Calculations of McGlynn *et al.*² also confirm conclusion of an important

* The value obtained for saturated solution of $C_6H_6Cr(CO)_3$ in CS_2 on Hitachi-Perkin-Elmer Model R-20 Spectrometer with Spectrum accumulator.

** Similar effects can be observed in bis(benzene)chromium²⁸ and ferrocene²⁹, so it seems not quite logical to employ magnetic anisotropy of $Cr(CO)_3$ -fragment for their explanation.

σ -electron contribution of aromatic ring into the total bonding with the metal in a π -complex. Probably, at present along with two effects advanced by Chatt and Duncanson³⁰ and confirmed by a number of experiments (donor-acceptor, and back-donation), in describing the metal- π -ligand bond one should also take account of the essential change of charge on the σ -orbitals of the ligand.

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