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THE EFFECT OF COORDINATION WITH THE METAL ON THE REACTIVITY OF π-BONDED ORGANIC LIGANDS

VI. SOLVOLYSIS OF CUMYL CHLORIDES COORDINATED WITH THE $Cr(CO)_3$-GROUP. DETERMINATION OF σ_p AND σ_p CONSTANTS OF $(CO)_3CrC_6H_5$-SUBSTITUENT

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Summary

The kinetics of S_N1 solvolysis of π-(tricarbonylchromium)cumyl chloride and *p*-[π-(tricarbonylchromium)phenyl]cumyl chloride was investigated at different temperatures in 90% aqueous acetone and the thermodynamic activation parameters were estimated. It was shown that the rates of solvolysis of cumyl chloride and *p*-phenylcumyl chloride coordinated with $Cr(CO)_3$ group are respectively 28 and 2.4 times greater than that of non-coordinated cumyl chloride. The apparent dissociation constant of *p*-[π-(tricarbonylchromium)phenyl]benzoic acid and ν(CO) mode of ketonic group in *p*-[π-(tricarbonylchromium)phenyl] acetophenone were determined. The experimental data obtained were used in computation of the σ_{p^+} and σ_p constants for the $(CO)_3CrC_6H_5$-substituent.

Introduction

After the synthesis of the first representatives of arene metal carbonyls [1] a large number of papers dealing with the effect of coordination with the metal on the electronic properties of arenic ligand were published [2 - 10]. In the series of studies carried out at our laboratory [11 - 13] it has been shown that no essential change of the π-electronic charge of the arene takes place upon its coordination with $Cr(CO)_3$ group and the total electron attractive effect of the $(CO)_3CrC_6H_5$ substituent is determined by its positive inductive aromatic constant σ_i.

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. The established change of the electronic properties of phenyl substituent provides a satisfactory interpretation to all experimental data obtained on the change of reactivity and some physico-chemical properties of the arenes during coordination with the $Cr(CO)_3$ group [14,15]. Only the data of Pettit [16] and Trahanovsky et al. [17] on the stabilization of the α-carbonium centres by coordinated arenes make an exception. It has been shown [16] that the rate of hydrolysis of benzyl and benzhydryl chlorides coordinated with the $Cr(CO)_3$ group is respectively 10^5 and 10^3 times that of hydrolysis of the corresponding non-coordinated compounds. This tendency was later confirmed [17] when it was found by spectroscopy that thermodynamic stability of benzyl cations coordinated with a $Cr(CO)_3$ group exceeds that of the non-coordinated compounds. It is known that for the aromatic series usually there is a correlation between the stabilisation of the α-carbonium centre by the aromatic nucleus and the activity of such a nucleus in electrophilic substitution. In particular it has been found [18] that the values of σ_{p^+} estimated from the rate constants of the solvolysis of *para*-substituted cumyl chlorides provide a good description of the reactivity of the respective substituted benzenes: in the electrophilic substitution. An alternative picture is observed upon coordination of the arenes with the $Cr(CO)_3$ group: the reactivity towards the electrophilic substitution reactions decreases [4 - 9] while the stabilization of the α-carbonium centre increases. In order to investigate in more detail the electronic properties of the π-(tricarbonylchromium)phenyl substituent in a reaction series with strong electron-deficient reaction centres we have launched the study of the kinetics of S_N1 solvolysis (90% aqueous acetone) of cumyl chlorides coordinated to the $Cr(CO)_3$ group. Choice of the model reaction series is determined by the fact that the solvolysis of noncoordinated cumyl chlorides has been studied in detail by Brown and Okamoto and represents the standard reaction set for determining the σ_p^+ substituent constants in the aromatic series [18]. We also determined the σ_p^- Hammett constant for $(CO)_3CrC_6H_5$-group by measuring the apparent dissociation constant of *p*-[π-(tricarbonylchromium)phenyl] benzoic acid.

Experimental

Starting materials

Cumyl chlorides were obtained using previously described syntheses and were used in analytically pure form. The synthesis of arenechromium tricarbonyl complexes was carried out by Nicholls and Whiting's method [1].

Commercial grade acetone was purified by a previously reported method [28], and used 9/1 (v/v) with water.

1. π-(Tricarbonylchromium)cumyl chloride (I)

(a). Synthesis of π-(tricarbonylchromium)cumyl alcohol (Ia)

A solution of 2.2 g (0.01 mole) of $Cr(CO)_6$ and 3.9 g (0.029 mole) of cumyl alcohol in 25 ml of n-heptane and 25 ml of absolute diglyme was refluxed for 16 h. The cooled mixture was filtered over deactivated alumina under an atmosphere of argon. The solvent and unreacted cumyl alcohol were removed in vacuo. The oily residue was crystallized by addition of petroleum ether at −70°. Recrystallization from n-heptane gave 1.1 g (40%) of the lemon-yellow crystalline substance, m.p. 77.5 - 78.5°. (Found: C, 53.21; H, 4.42; Cr, 19.25%. $C_{12}H_{12}O_4Cr$. Calcd.: C, 52.94; H, 4.41; Cr, 19.12%). The PMR-spectrum (CCl_4)* contains the multiplet centred at δ 5.47 ppm (from five protons of the phenyl ring) and a singlet at δ 1.43 ppm (from six equivalent methyl protons).

(b). Synthesis of π-(tricarbonylchromium)cumyl chloride (I)

A stream of dry HCl and argon was bubbled to a solution of 2 g (0.0073 mole) of (Ia) in 20 ml of CH_2Cl_2 for 1 h. The solution was dried over $CaCl_2$, and the solvent evaporated. Recrystallization from hexane gave 1.9 g (90%) of the yellow crystalline substance, which decomposed at 69 - 72°. (Found: C, 48.60; H, 3.93; Cl, 12.16; Cr, 18.12%. $C_{12}H_{11}O_3CrCl$. Calcd.: C, 49.57; H, 3.79; Cl, 12.22; Cr, 17.90%).

2. *p-[π-(Tricarbonylchromium)phenyl] cumyl chloride (III)*

(a). Methyl p-[π-(tricarbonylchromium)phenyl] benzoate (IIIa)

A solution of 5.5 g (0.025 mole) of $Cr(CO)_6$ and 5.3 g of methyl 4-phenylbenzoate in 50 ml of heptane/diglyme (1/1) mixture was refluxed for 18 h. The reaction mixture was treated as in 1(a). After removal of the solvent the mixture was separated by means of thin layer chromatography (TLC) on anhydrous alumina using benzene/petroleum ether (2/1). The first substance eluted with R_f 0.66 is the mixture of starting ligand and complex, p-(C_6H_5)-$C_6H_4COOCH_3Cr(CO)_3$ which has a $Cr(CO)_3$ group in the substituted ring (IIIb), the second substance with R_f 0.50 was (IIIa).

Crystallization of (IIIa) from the mixture heptane/dimethoxyethane (10/1) gave 2.3 g (26%) of the yellow crystalline substance, m.p. 167 - 168°. (Found: C, 58.85; H, 3.56; Cr, 14.89%. $C_{17}H_{12}O_5Cr$. Calcd.: C, 58.63; H, 3.47; Cr, 14.93%). The NMR spectrum (CH_3CN) consists of a multiplet of A_2B_2 type centred at δ 7.78 ppm (from four protons of the noncoordinated ring) and a multiplet with two maxima at δ 5.87 and 5.52 ppm (from five protons of phenyl nucleus) and a singlet at δ 3.82 ppm (from three methyl protons). The signal intensities are in the ratio 4/5/3.

(IIIb) was purified on alumina column under the inert atmosphere. The unreacted ligand was separated with petroleum ether. (IIIb) was eluted with benzene/petroleum ether (1/3). Yield 0.20 g (2.3%). Orange crystals, m.p. 106 - 107° (heptane). (Found: C, 58.72; H, 3.56; Cr, 15.13. $C_{17}H_{12}O_5Cr$ calcd.: C, 58.63; H, 3.47; Cr, 14.93%).

The NMR spectrum (CH_3CN) consists of a multiplet centred at δ 7.45 ppm (from five protons of the noncoordinated phenyl nucleus) and a multiplet of the A_2B_2 type at δ 5.84 ppm (from four protons of the coordinated phenyl ring). The ratio of signal intensities is 5/4.

(b). Synthesis of p-[π-(tricarbonylchromium)phenyl] cumyl alcohol (IIIc)

To a solution of 4.6 g (0.013 mol) of (IIIa) in 40 ml of THF and 35 ml of

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*The PMR-spectra were taken on Perkin - Elmer R12 instrument with HMDS as internal standard.

ether, the Grignard reagent (obtained from 1.21 g (0.05 g-a) Mg and 7.1 g (0.05 mol) of CH_3I in 25 ml of ether) was added dropwise at 25° for 1 h. The mixture was stirred for other 1/2 h. The colour changed from red to yellow. After decomposing the reaction mixture and solvent removal the oily residue was crystallized by addition of petroleum ether at −70°. The substance was recrystallized from heptane/toluene (4/1) and had a m.p. of 104 - 105°. Yield 3.4 g (74%). (Found: C, 62.40; H, 4.72%. $C_{18}H_{16}O_4Cr$. Calcd.: C, 62.07; H, 4.60%)*.

(c). Synthesis of p-[π-(tricarbonylchromium)phenyl]cumyl chloride (III)

The substance was prepared from 1.04 g (0.003 mole) of (IIIc) by method 1(b). After solvent removal the oily residue was crystallized by addition of petroleum ether to the solution of the substance in ether at −70°. Yield 1.0 g (90%), decomposed at 80°. (IIIc) is sensitive to light and moisture. (Found: C, 58.91; H, 4.45; Cl, 9.10; Cr, 14.19. $C_{18}H_{15}O_3CrCl$ calcd.: C, 58.93; H, 4.09; Cl, 9.67; Cr, 14.18%.

3. *p-[π-(Tricarbonylchromium)phenyl] acetophenone (V)*

2.2 g (0.011 mole) of *p*-phenylacetophenone and 6.6 g (0.03 mole) of $Cr(CO)_6$ in 30 ml of absolute diglyme were refluxed for 10 h. The reaction mixture was treated analogously to 1(a). The unreacted *p*-phenylacetophenone was separated by chromatography on an alumina column under an inert atmosphere. Then an orange crystalline substance was eluted which after double crystallization from heptane had a m.p. 108 - 109°. Its elemental, IR and PMR spectral analysis confirmed p-$C_6H_5C_6H_4C(O)CH_3Cr(CO)_3$ (VI) with the $Cr(CO)_3$ group in the phenyl ring of acetophenone. Yield of (VI) was 0.2 g (5.4%). (Found: C, 61.95; H, 3.62; Cr, 15.67%. $C_{17}H_{12}O_4Cr$ calcd.: C, 61.45; H, 3.64; Cr, 15.65%). The PMR spectrum (in CCl_4, TMS as external standard) consists of a multiplet at δ 7.42 ppm (from five protons of the noncoordinated benzene ring), a multiplet of the A_2B_2 type centred at δ 5.82 ppm (from four protons of the coordinated benzene ring) and a singlet at δ 2.38 ppm (from three methyl protons). The ratio of signal intensities was 5/4/3.

(V) was eluted with benzene/heptane (1/5) in the form of yellow crystals. After the double crystallization from heptane/dimethoxyethane (5/1) 0.4 g (10.8%) of (V) was obtained, m.p. 145 - 146°. (Found: C, 61.95; H, 3.69; Cr, 15.75. $C_{17}H_{12}O_4Cr$ calcd.: C, 61.45; H, 3.64; Cr, 15.65%.) The PMR spectrum (CH_3CN) consists of a multiplet of the A_2B_2 type at δ 7.80 ppm (from four protons of the noncoordinated phenyl), multiplet with two maxima at δ 5.89 and 5.47 ppm (from five protons of the coordinated phenyl) and a singlet at δ 2.52 ppm (from three methyl protons). The ratio of signal intensities was 4/5/3.

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* The direct reaction of *p*-phenylcumyl alcohol with $Cr(CO)_6$ gives only the isomer p-$(C_6H_5)C_6H_4$-$C(CH_3)_2OHCr(CO)_3$ with a $Cr(CO)_3$ group in the substituted ring. Yield 23%, m.p. 79 - 80° after double crystallization from heptane. (Found: C, 61.95; H, 4.57; Cr, 15.21%. $C_{18}H_{16}O_4Cr$ calcd.: C, 62.07; H, 4.60; Cr, 14.94%. The NMR spectrum (CH_3CN) consists of a multiplet at δ 7.55 ppm (from five protons of the noncoordinated phenyl ring) and a multiplet of the A_2B_2 type at δ 5.95 ppm (from four protons of the coordinated benzene ring).

4. *p-[π-(Tricarbonylchromium)phenyl] benzoic acid (VII)*

A mixture of 0.22 g (0.0006 mole) of (IIIa), 0.224 g (0.004 mole) of KOH, 0.4 ml of water and 20 ml of methanol was stirred for 48 h at room temperature in darkness. Methanol was removed in vacuo, the residue dissolved in water (100 ml). The unreacted ether was separated by filtration. The aqueous solution was acidified with diluted HCl, which precipitated the orange yellow acid, which was purified via its potassium salt. After the drying, 0.2 g (94.8%) of the orange solid was obtained, which decomposes at 205 - 210°. (Found: C, 57.22; H, 3.03; Cr, 15.75. $C_{16}H_{10}O_5Cr$ calcd.: C, 57.50; H, 3.02; Cr, 15.56%).

Kinetic measurements.

The solvolysis rate constants of the cumyl chlorides were determined by Brown's procedure [18]. Solvolysis of the coordinated chlorides was studied under the identical conditions using the following method: solvent (aqueous acetone) was placed in a 100 ml flask and thermostated, the temperature being maintained with an accuracy of ±0.1°. The sample of complex (I) (0.4 - 0.5 g $\simeq 1.6 \times 10^{-2}$ mole/l) or the sample of complex (III) (usually 0.6 - 0.7 g $\simeq 1.8 \times 10^{-2}$ mole/l) was placed in the flask and the mixture was stirred carefully. After 2 min an aliquot (5 ml) was taken out and poured into 30 ml of dry acetone cooled to a temperature of 10° below that of the reaction mixture. (In the case of (III) the reaction was interrupted by pouring the aliquot into acetone cooled to 0°). The mixture was titrated immediately (zero titration) with NaOH solution. The 5 ml aliquots were taken and treated analogously at fixed intervals. After completion of the run the flask was allowed to stand overnight at room temperature, carefully preserved from light, to obtain a reading for "infinite" time.

Titration of the acid with alkali was performed with a LPU-01 device with a glass electrode on the pH scale. The reference electrode was a flowing silver chloride current electrode. The value k_0 was found by extrapolation of the plot of HCl concentration against time to zero time. The values of the rate constants at given moments are found from usual formula:

$$k_t = \frac{2.303}{t} \cdot \log\frac{a-x_0}{a-x_t}$$

TABLE 1
SOLVOLYSIS OF π-(TRICARBONYLCHROMIUM)CUMYL CHLORIDE (I) AT −5° (NaOH = 0.0338 N)

Time (min)	x_t (ml)	$(a-x_t)$ (ml)	% Conversion	$10^4\ k$ (s^{-1})
0	0.30	1.83	14.1	—
3	0.60	1.53	28.1	9.96
6	0.76	1.37	35.8	7.99
10	0.90	1.23	42.3	6.61
15	1.00	1.13	46.9	5.36
25	1.12	1.01	52.6	3.95
∞	2.13		100	
				k_0 10.5

TABLE 2
SOLVOLYSIS OF p-[π-(TRICARBONYLCHROMIUM)PHENYL]CUMYL CHLORIDE (III) AT 25° (NaOH = 0.0224 N)

Time (min)	x_t (ml)	$a-x_t$ (ml)	% Conversion	$10^5 k$ (s^{-1})
0	0.84	4.96	14.5	–
5	1.27	4.53	21.9	30.0
10	1.79	4.01	30.9	36.8
15	2.02	3.78	34.9	30.0
20	2.28	3.52	39.4	28.7
25	2.44	3.34	42.2	26.5
35	2.66	3.14	45.8	21.8
45	2.72	3.08	46.9	17.8
∞	5.80	–	100	–
				k_0 33.4

The error in the constants determined, and the values derived from these data is ± 5% for all investigated compounds except (I), for which error is ± 15% due to the high solvolysis rate. Typical results of kinetic experiments are listed in Tables 1 and 2.

Determination of the acid dissociation constants

The apparent dissociation constants of the acids were measured in 80% (by weight) of the aqueous monomethyl ether of ethylene glycol (methyl cellosolve). The measurements were performed with a "Radiometer" TTT'I G pH meter using an SCE K-401 electrode and G-202 C glass electrode at 25 ± 0.1°C under nitrogen atmosphere, with constant stirring. The samples of compounds (4.8×10^{-3} - 3.7×10^{-3} M) were titrated with 0.108 N NaOH solution in 80 wt.% cellosolve. The pK_a's were corrected on solvent titer [29]. The accuracy of pK_a measurement is to within ± 0.06 units.

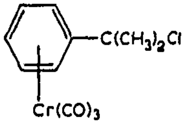
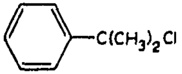
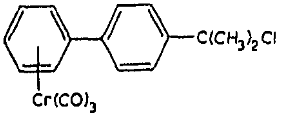
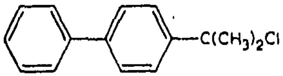
Results and discussion

Using the conditions of Brown and Okamoto [18] we studied the kinetics of solvolysis of π-(tricarbonylchromium)cumyl chloride and p-[π-(tricarbonylchromium)phenyl]cumyl chloride and reproduced their results for the respective noncoordinated ligands. The rate constants of the solvolysis and the activation parameters are given in Table 3.

The values k_0 for the coordinated cumyl chlorides were obtained graphically by extrapolation to zero time, since the rate constant decreases in the course of reaction (see Experimental, Tables 1,2). A similar effect has been observed by Pettit [16] and it is characteristic of S_N1 reactions of the stable carbocations. The theory of this effect was first advanced by Ingold and later developed in detail by Winstein. As seen from Table 3, the π-(tricarbonylchromium)phenyl group stabilizes the α-carbonium centre ($k_{complex}/k_{ligand}$ = 28). The effect, however, is considerably weaker than the stabilization of coordinated benzyl ($k_{complex}/k_{ligand} = 10^5$) and benzhydryl cations ($k_{complex}/k_{ligand} = 10^3$) [16]. The ratio of constants $k_{III}/k_{IV} = 0.40$ is an indication that the $(CO)_3Cr(C_6H_5)$ substituent separated from the reaction centre by the p-phenylene nucleus stabilized the carbonium centre less than the noncoordi-

TABLE 3

THE RATE CONSTANTS AND ACTIVATION PARAMETERS OF THE SOLVOLYSIS OF CUMYL CHLORIDES

Compound	$10^5 k$ (s^{-1})	Temp (°C)	E_{act} kcal/mole	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ kcal/mole/deg	k_I/k_{II}	k_I/k_{II}
 (I)	360 72 89 100 120 180	+25 −15 −10 − 5 0 + 5	6	6	−50	28	—
 (II)	13	+25	19.5[b]	18.8[b]	−12.5[b]	1	—
 (III)	33.4 17.1 26.3	+25 +15 +20	11	10	−39	2.6	0.40
 (IV)	83.3	+25	18.6[c]	18.0[c]	−12.2[c]	6.4	I

[a] Computed from Arrhenius plot. [b] From ref. 18a k_0 12.6 · 10^{-5} s^{-1}. [c] From ref. 18b k_0 80.6 · 10^{-5} s^{-1}.

nated phenyl does. This agrees with representation of the total electron acceptor effect of the $Cr(CO)_3$ group. The ratio of constants $k_{III}/k_{II} = 2.6$ shows that the $(CO)_3CrC_6H_5$ substituent is, however, a weak donor when substituted into another phenyl ring with direct polar conjugation of the substituent and strongly electron-deficient reaction centres. Analysis of the data in Table 3 shows that the activation parameters of coordinated compounds differ considerably from those of the noncoordinated ones. Low activation enthalpies (specifically in the case of tricarbonylchromiumcumyl chloride) and the high absolute values of the activation entropies have been observed only seldom for the S_N1 type reactions*. This is evidence that a quantitative estimation of the change of electronic properties of the coordinated phenyl in such reactions can not be carried out accurately. Such considerable variation of the activation parameters may result in a change of reaction mechanism involving a different transition state. In the solvolyses investigated, a transition state may involve a carbonium ion, or some other structure stabilized by reversible ring expansion—which is well known for the arene and cycloheptatriene complexes.

The possibility of a different transition state should also be considered in discussing the stabilization mechanism of α- and β-carbonium centres in the transition metal complexes. In spite of a considerable number of the hypotheses [21] the mechanism of stabilization cannot be considered as finally established. Some authors [25] assume that the interaction of p-orbitals of the carbonium ion with the non-bonding metal atomic orbitals and the ring electron delocalization over the vacant p-orbitals of the carbonium ion are equally probable, others [26,27] consider that the direct participation of the metal atom in the stabilization of the carbonium centre is not essential.

In investigating the kinetics of solvolysis of (III) we excluded the possibility of direct interaction between the metal atom and carbonium ion. We were able to confirm that because of the electron-attractive properties of the $Cr(CO)_3$ group the coordinated phenyl is weaker donor than the free one. However the problem is complicated because in spite of a removal of the reaction center from the metal atom the activation parameters are unusual and close to those of (I). Probably in discussing the stabilization mechanism one should account for the fact that the carbonium centre of the complex interacts with electron density at the partially occupied antibonding phenyl orbitals which are more diffuse and readily polarizable.

Determination of the σ_{p^+} and σ_p constants for $(CO)_3CrC_6H_5$ substituent

From the obtained solvolysis constant of (III) we computed the values of δ_p^+ for the $(CO)_3Cr(C_6H_5)$-substituent by Brown's method [18]. The estimated electrophilic aromatic constant —0.09 agrees with the previous observations [4 - 9] that the reactivity of an arene coordinated with $Cr(CO)_3$ group in electrophilic substitution reactions is less than that of the noncoordinated compound. The constant σ_{p^+} of $(CO)_3CrC_6H_5$-substitutent was found in the manner described before [12] using the linear dependence of (CO) frequencies in

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*Known examples are given in refs. 19 and 20. The computed σ values have certain sense only when the isokinetical relation (proportionality of $\Delta H^{\neq}$ and $\Delta S^{\neq}$) holds within the reaction series.

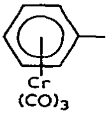
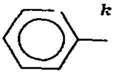
the substituted aromatic ketones XC_6H_4COR and the σ_p+ constants of X substituents. We thus prepared p-[π-(tricarbonylchromium)phenyl] acetophenone (V), and the measured* ν(CO) frequency of 1691.8 cm^{-1} was employed for calculating σ_p+ of $(CO)_3Cr(C_6H_5)$ substituent. The value σ_p+ of +0.04 obtained with such method differs from the value estimated from the solvolysis rates of the respective substituted cumyl chlorides. The deviations are negligible however and probably are determined by specificity of both methods.

For determining the Hammett σ_p constant of $(CO)_3CrC_6H_5$ group by the "classical" method we prepared (VII). It was shown, however, that it is impossible to measure the apparent dissociation constant of this acid under the standard conditions in 50% (by volume) aqueous alcohol because of the virtual insolubility of the acid. Thus the pK_a of this acid was determined in 80% (by weight) aqueous methylcellosolve by the method of Simon et al. [29]**. The pK_a value of 6.36 obtained was employed in determining the σ_p Hammett constant of the $(CO)_3CrC_6H_5$ substituent. The correlational equation computed by us using both the pK_a values from ref. 29 and those measured in the present work has the form: $pK_a = 6.61 - 1.68\,\sigma_p$, $n = 17$, $r = 0.983$, $S(pK_a) = \pm 0.12$. The computed σ_p constant for $(CO)_3CrC_6H_5$ group was 0.15, which again suggests the electron-attractive character of π-(tricarbonylchromium)phenyl group relative to the noncoordinated phenyl.

Conclusion

Table 4 lists all the values of σ obtained previously [12,13] and those determined in this work, which specify the electronic effect of π-(tricarbonylchromium)phenyl group. On the basis of the data available we have suggested

TABLE 4
σ VALUES FOR THE $(CO)_3CrC_6H_5$ GROUP AND C_6H_5-GROUP AS SUBSTITUENTS.

Substituent	Experimental σ values obtained from a standard reaction series				Calculated σ values characterizing electron donor conjugation of the substituent			
	σ_i [a]	σ_p^0 [b]	σ_p [c]	σ_p^+ [d]	σ_R^0 [e]	σ_R [g]	σ_R^+ [g]	$\Delta\sigma_R^+$ [h]
	+0.21	+0.26	+0.15	−0.09	−0.04	−0.06	−0.30	−0.24
 [k]	+0.09	0.00	−0.01	−0.179	−0.10	−0.10	−0.27	−0.17

[a] From the ^{19}F NMR of m-$FC_6H_4C_6H_5Cr(CO)_3$ [13]. [b] From dissociation constant of $(CO)_3CrC_6H_5$-CH_2COOH. [c] From dissociation constant of $(CO)_3CrC_6H_5C_6H_4COOH$-p. [d] From the rate constant of solvolysis of $(CO)_3CrC_6H_5C_6H_4C(CH_3)_2Cl$-$p$. [e] $\sigma_R^0 = \sigma_p^0 - \sigma_i$; [f] $\sigma_R = \sigma_p - \sigma_i$; [g] $\sigma_R^+ = \sigma_p^+ - \sigma_i$; [h] $\Delta\sigma_R^+ = \sigma_R^+ - \sigma_R$. [k] From ref. 31.

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[*] Experimental conditions are described in ref. 12.

[**] In order to use the values taken from ref. 29 the selective pK_a measurements were performed for compounds with standard substituents. The agreement of the values with the literature data used for calculation was attained within standard experimental error. E.g. for benzoic acid $pK_a = 6.62$ (6.63, ref. 29).

[12] that the total π-electron density at the bonding and antibonding orbitals of the coordinated phenyl should be approximately constant and equal to that in a noncoordinated ligand. The data obtained in this work are in good agreement with this postulate.

Analysis of σ values determined by different methods shows that the values specifying the conjugative ability of the phenyl substituent ($\sigma_R^0\ \sigma_R$) are practically unchanged upon coordination with the $Cr(CC)_3$ group. In going from one substituent to another the changes of σ_R^0 are proportional to the change of total π charge in the phenyl ring bound to such substituent. Thus the experimental data obtained demonstrate that the total charge on the phenyl changes negligibly when combined with the π-(tricarbonylchromium)phenyl group and the observed differences in reactivity of the free and coordinated phenyl are due to the change of effective positive charge at its σ-core.

However, the problem is still open concerning the effect of coordination on π density redistribution over the bonding and antibonding orbitals, and the effect of the "geometry" (spatial distribution) of π-electron cloud in the arene ligand on the ring π-currents etc. Studies in this field are under way.

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