Journal of Organometallic Chemistry, 92 (1975) 197—205

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

VII*. DETERMINATION OF THE NUCLEOPHILIC AROMATIC CONSTANT OF THE $C_6H_5Cr(CO)_3$ SUBSTITUENT

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(Received January 15th, 1975)

Summary

Ionization constants of p-[π-(tricarbonylchromium)phenyl] phenol in 50% vol. aqueous ethanol, p-[π-(tricarbonylchromium)phenyl] anilinium ion in ethanol/water/acetone (7/2/1), and of their non-coordinated analogues have been obtained. p-[π-(Tricarbonylchromium)phenyl] phenol is shown to be a stronger acid than 4-hydroxybiphenyl and phenol, and p-(π-(tricarbonylchromium)phenyl] aniline is shown to be a weaker base than 4-aminobiphenyl and aniline. Calculated values of σ_p^-, σ_R^-, and $\Delta\sigma_R^-$ for the $(CO)_3CrPh$-substituent revealed its ability, though small, for the direct polar conjugation with a (+R) reaction centre. $\Delta\sigma_R^-$ values characterizing the polarizability of the substituent electron cloud have been found to change upon coordination. The effect of a substituent in monosubstituted biphenyls on the relative distribution of isomers in the Nicholls—Whiting synthesis of chromium tricarbonyl complexes is discussed.

Introduction

Earlier, in a series of reports dealing with the effect of coordination of the $Cr(CO)_3$ group on electronic properties of arene ligand we have shown [1-3] that the total electron-releasing effect of the $C_6H_5Cr(CO)_3$ substituent is determined mainly by its highly positive inductive aromatic constant, while σ values characterizing conjugation ability of a phenyl nucleus do not change markedly upon coordination, even in reactions involving the direct polar conjugation of substituents with a strongly electron-deficient site [3]. This has led to the as-

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* For part VI see ref. 3.

sumption that coordination with the $Cr(CO)_3$ group substantially increases the effective positive charge on the σ-framework of arenes. This assumption was used by Bodner and Todd [4] to elucidate the effect of substituents on ^{13}C shifts in NMR spectra of monosubstituted benzenes, both free and π-bonded to the $Cr(CO)_3$ group, and also by Ceccon et al. [5b, d, e] in studies on elimination of β-phenylethyl derivatives coordinated with the $Cr(CO)_3$ group.

We have now undertaken the study of the ability of the (tricarbonylchromium)phenyl group to enter into direct polar conjugation with a strongly electron-releasing reaction centre posessing a lone electron pair. With this objective in view we have measured ionization constants of *p*-[π-(tricarbonylchromium)phenyl]-phenol and -anilinium ions and used the pK_a and pK_b values obtained to calculate the nucleophilic aromatic constant of the $(CO)_3CrPh$-substituent.

Fischer et al. [6] first discovered that coordination with $Cr(CO)_3$ decreased the basicity of aniline, and increased the acidity of phenol. Later Wu et al. [7,8] systematically studied a series of substituted anilines and phenols, both free and bonded to the $Cr(CO)_3$ group, and found that coordination did not affect the mechanism which transmits electronic effects to the reaction centre.

Experimental

The arenetricarbonylchromium complexes were prepared by Nicholls and Whiting's method [9], and the structures confirmed by elemental analysis, IR, NMR and mass spectra.

Preparation of p-[π-(tricarbonylchromium)phenyl]-N-acetylaniline (Ia)

4.22 g (0.02 mol) of 4-(acetylamino)biphenyl and 4.1 g (0.02 mol) of $Cr(CO)_6$ in a mixture of heptane and diglyme (30 ml of each) were refluxed in the Strohmeier flask [10] under an inert gas for 20 h, then cooled and filtered. Evaporation of the solvent in vacuo and TLC of the residue (anhydrous Al_2O_3, benzene/EtOAc (3/1), $R_f \approx 0.4$) gave the desired complex. To obtain an analytically pure sample the complex was reprecipitated from acetone with petroleum ether to give 3.5 g (50%) of yellow crystals of Ia, m.p. 171-173°C. (Found: C, 58,38; H, 3.84; Cr, 15.10. $C_{17}H_{13}CrNO_4$ calc.: C, 58.79; H, 3.75; Cr, 14.99%). IR (KBr, cm^{-1}): $\nu(C{\equiv}O)$ 1960, 1880; $\nu(C{=}O)$ 1670; $\nu(N{-}H)$ 3270, 3310. The PMR spectrum (acetone) shows a multiplet centered at 5.95 ppm (aromatic protons of the coordinated ring), a multiplet of the A_2B_2 type centered at 7.75 ppm (aromatic protons of the non-coordinated ring), and a multiplet centered at 9.40 ppm (the amide proton), in the ratio 5/4/1.

Preparation of p-[π-(tricarbonylchromium)phenyl]aniline (I)

3.5 g (0.01 mol) of Ia and 10 g of KOH in 120 ml of 75% ethanol were refluxed for 7 h. under an inert gas. The cooled solution was filtered, diluted with water (250 ml), and extracted with ether (3 × 100 ml). The extract was washed with dilute (1/10) HCl (5 × 60 ml), and the water solution containing the hydrochloride of amine I, after making alkaline with saturated Na_2CO_3 solution, was extracted with ether (4 × 100 ml). The extract was washed with water (3 × 100 ml), dried over $MgSO_4$, and the solvent distilled off in vacuo. Crystallization of the residue from dimethoxyethane/hexane (1/6) gave 1.2 g (38%) of I as yellow crystals, m.p. 156-157°C. To obtain an analytically pure sample the crystals were dried in vacuo at 60°C during 4 h. (Found: C, 58.90; H, 3.68; Cr, 17.07; N, 4.53. $C_{15}H_{11}CrNO_3$ calcd.: C, 59.02; H, 3.61; Cr, 17.05, N, 4.53%). IR (KBr, cm^{-1}): ν(C≡O) 1835, 1880, 1950; ν(N—H) 3380, 3460. The NMR (CH_3CN) shows a multiplet of the A_2B_2C type centered at 5.73 ppm (protons of the coordinated aromatic ring), a quartet of the A_2B_2 type centered at 7.00 ppm (protons of the non-coordinated aromatic ring), and a multiplet centered at 4.35 ppm (amine protons), in the ratio 5/4/2.

Preparation of p-[π-(tricarbonylchromium)phenyl]phenyl acetate (IIa)

2.13 g (0.01 mol) of 4-acetoxybiphenyl and 2.2 g (0.01 mol) of $Cr(CO)_6$ were refluxed in the mixture of heptane (30 ml) and diglyme (30 ml) in a Stromeier flask [10] for 20 h under an inert gas. The product was treated as described for Ia, and the complex isolated by TLC (benzene/petroleum ether (2/1); $R_f = 0.4$). Two recrystallizations from heptane/toluene (2/1) gave 0.4 g (11%) of yellow crystals, m.p. 132-134°C. (Found: C, 58.32; H, 3.42. $C_{17}H_{12}O_5Cr$ calcd.: C, 58.63, H, 3.47%.) IR (KBr, cm^{-1}): ν(C≡O) 1855, 1900, 1965; ν(C=O) 1765. The NMR spectrum (CH_3CN) contained an A_2B_2 system centered at 7.53 ppm (non-coordinated aromatic ring protons), and a multiplet of the A_2B_2C type centered at 5.81 ppm (coordinated aromatic ring protons), in the ratio 4/5. Unreacted 4-acetoxybiphenyl was also isolated by TLC.

Preparation of p-[π-(tricarbonylchromium)phenyl]phenol (II)

The solution of a Grignard reagent prepared from 0.6 g (0.025 mol) of Mg and 3.5 g (0.025 mol) of CH_3I in 30 ml of absolute ether was added at room temperature over 0.5 h to 100 ml of a solution of 0.7 g (0.002 mol) of IIa in an ether/benzene mixture (3/2). After mixing for another 1 h the solution was decomposed with dilute (1/20) HCl, extracted with ether (3 × 50 ml), the extract washed with water (3 × 50 ml), and dried over $MgSO_4$. Evaporation of the solvent and crystallization from benzene/heptane (3/1) afforded 0.5 g (83%) of II, as yellow crystals, m.p. 140°C. (Found: C, 58.88; H, 3.10. $C_{15}H_{15}CrO_4$ calcd.: C, 58.82; H, 3.27%). IR (KBr, cm^{-1}): ν(C≡O) 1820, 1855, 1890; ν(O—H) 3530. The NMR spectrum (CH_3CN) consisted of a quartet of the A_2B_2 type centered at 6.93 ppm (non-coordinated aromatic ring protons), and a multiplet of the A_2B_2C type centered at 5.63 ppm (coordinated aromatic ring protons), in the ratio 4/5.

pH measurements in amine and phenol solutions

The pH measurements were carried out on a LPU-01 pH meter with a glass electrode. The flowing silver chloride electrode was used as reference electrode. Titrations were carried out at 25 ± 0.1°C under nitrogen.

The CO_2-free alkaline ethanol solutions were prepared by dissolving a fixed amount of Na in absolute ethanol, and subsequent dilution with an equal amount of water.

The K_a values for phenols were calculated according to the formula:

$$K_a = \frac{[H^+] \cdot \{[Na^+] + [H^+] - (K_w/[H^+])\}}{M - \{[Na^+] + [H^+] - (K_w/[H^+])\}}$$

TABLE 1

EFFECT OF SUBSTITUENTS ON THE YIELDS OF ARENETRICARBONYLCHROMIUM COMPLEXES AND ON THE RATIO A[p-$C_6H_5C_6H_4R(CO)_3$]/B[$(CO)_3CrC_6H_5C_6H_4R$-p] IN THE REACTION OF MONOSUBSTITUTED BIPHENYLS WITH $Cr(CO)_6$

R	Total yield (%)	B (%)	A (%)	$\sigma_p{}^e$	$\sigma_I{}^e$	$\sigma_R{}^e$
H	34.5			0	0	0
NH_2	[a]	0	100	−0.66	0.10	−0.76
CH_3	30	X[b]	30−X	−0.170	−0.311	−0.05
$NHCOCH_3$	50	100	0	−0.01	+0.28	−0.27
$C(CH_3)_2OH$	23	0	100	−0.01[d]	+0.10[d]	−0.11[d]
F		100	0	+0.062	+0.52	−0.46
Br		100	0	+0.232	+0.45	−0.22
$OCOCH_3$	12	100	0	+0.31	+0.39	−0.08
$COOCH_3$[c]	28	92	8	+0.44	+0.30	+0.15
$COCH_3$[c]	16	67	33	+0.509	+0.28	+0.22
NO_2	0			+0.778	+0.63	+0.15

[a] Not isolated, formation of A confirmed by NMR. [b] From ref. 14. The A/B ratio not determined. [c] The Rausch synthesis [16] from $(NH_3)_3Cr(CO)_3$ in dioxane gave the same isomer ratio. [d] For CH_2OH. [e] From ref. 17.

TABLE 2

IONIZATION CONSTANTS OF SUBSTITUTED ANILINIUM IONS

Compound	pK_b (In 80% ethanol)	K_b	pK_b (In ethanol/water/acetone)	K_b
p-Toluidine	10.94	1.15 10^{-11}	11.02	9.48 10^{-12}
Aniline	11.51	3.10 10^{-12}	11.55	2.82 10^{-12}
4-Aminobiphenyl	11.74	1.84 10^{-12}	11.78	1.64 10^{-12}
I			12.16	6.93 10^{-13}
p-Bromoaniline	12.25	5.59 10^{-13}	12.33	4.70 10^{-13}

TABLE 3

IONIZATION CONSTANTS OF SUBSTITUTED PHENOLS

Compound	pK_a (In 50% ethanol)	K_a
p-Cresol	11.73	1.86 10^{-12}
Phenol	11.36	4.36 10^{-12}
4-Hydroxybiphenyl	11.04	9.10 10^{-12}
p-Chlorophenol	10.59	2.57 10^{-11}
II	10.49	3.24 10^{-11}

TABLE 4

σ-VALUES

Substituent	σ_I	σ_p^-	σ_R^-	$\Delta\sigma_R^-$
$Cr(CO)_3Ph$	0.21	0.29	0.08	0.14
Ph	0.09	0.09	0.00	0.10

where M = molar concentration of the phenol, K_w = ion product of the solvent (for 50% ethanol, $K_w = 1.82 \times 10^{-15}$).

The basicity constants of the amines were calculated according to the formula:

$$K_b = \frac{K_w\{[\mathrm{Cl}^-] - [\mathrm{H}^+] + (K_w/[\mathrm{H}^+])\}}{[\mathrm{H}^+]\{M - \{[\mathrm{Cl}^-] - [\mathrm{H}^+] + (K_w/[\mathrm{H}^+])\}}$$

where M = molar concentration of the amine, K_w = ion product of the solvent (for 80% ethanol, $K_w = 2.14 \times 10^{-16}$).

Measurement of acidities of phenols

2.5×10^{-4} mole of a phenol was dissolved in 50 ml of 50% vol. ethanol and titrated with 0.0406 *N* NaOH. The pK_a values were determined by separate titrations corresponding to three degrees of neutralization: 25, 50, and 75%. The electrodes were calibrated using tetraborate buffer solution (pH 9.24). The pK_a and K_a values for *p*-substituted phenols are given in Table 3.

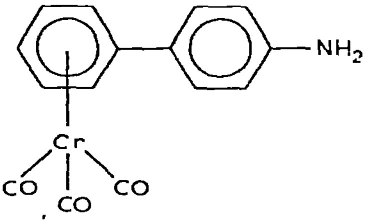
Measurement of basicity constants of amine

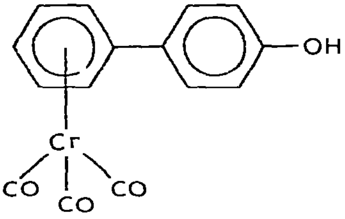
The pH values of partially neutralized (25, 50, 75%) amine solutions (5×10^{-3} *M*) were measured in a mixture of ethanol/water/acetone (7/2/1). 0.1 *M* HCl was used for neutralization. The electrodes were calibrated with bisphthalate buffer solution (pH 4.00). The data obtained are collected in Table 2.

Results and discussion

Synthesis of the p-phenyl-substituted-phenol and -aniline

We had to prepare biphenyltricarbonylchromium derivatives with strongly electron-releasing groups (OH, NH_2 etc.) substituted on the non-coordinated benzene ring:



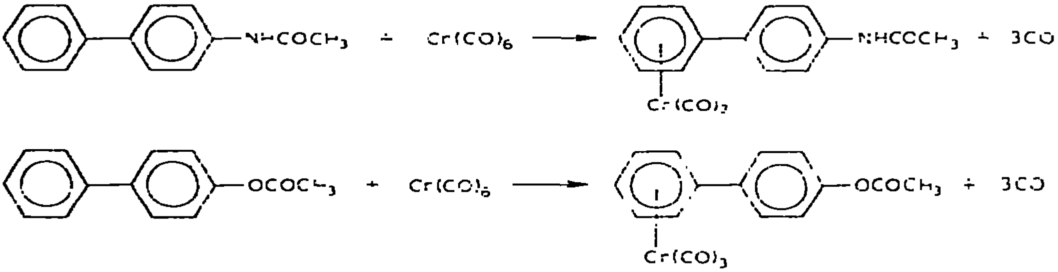


Under the Nicholls and Whiting reaction conditions one may expect two isomeric π-complexes of monosubstituted biphenyls with the $Cr(CO)_3$ group. Available data [13, 14] and our own previous studies [3] indicate that an acceptor substituent in biphenyl directs coordination completely or predominantly to the unsubstituted ring, while with a weak donor (e.g., CH_3) a non-specified mixture of isomers is formed [14]. Thus, the electronic properties of substituents in phenyl rings seem to affect the coordination of the $Cr(CO)_3$ group. It was shown, however, that the presence of 2-hydroxypropyl, a weaker donor than CH_3, in the biphenyl molecule unexpectedly directed coordination completely to the substituted ring [3]. Thus, one would expect that isomers with

$Cr(CO)_3$ in the substituted ring would be obtained if 4-amino- and 4-hydroxy-biphenyls were employed in the synthesis. We have proved this to be the case, at least with 4-aminobiphenyl.

We also attempted the synthesis of complex I from 4-nitrobiphenyl, but this, similarly to nitrobenzene, oxidises $Cr(CO)_6$ under these reaction conditions*.

To obtain complexes I and II we acetylated amino and hydroxy groups in the corresponding *p*-substituted biphenyls, which resulted in an essential weakening of donor properties of the substituents. From these acetylated compounds the corresponding chromium tricarbonyl complexes were prepared.



NMR spectra show that the $Cr(CO)_3$ group is coordinated with the unsubstituted phenyl ring.

Deacetylation by usual methods (with a Grignard reagent, or with water and alkali) led to [*p*-phenyl(tricarbonylchromium)]-phenol and -aniline.

In Table 1 all the available data on the reactions of substituted biphenyls with chromium carbonyl are summarized. In the last column σ-values [17] characterizing electronic effects of corresponding substituents are given. The total yield of the complexes varies over a wide range: from 10 to 60%, the yield of π-complexes from substituted biphenyls being, as a rule, lower than the yield of those from unsubstituted ones. Though indeed, very strongly electron-releasing substituents (NH_2) direct the reaction to the formation of only the isomer A, to relate unambiguously the electronic properties of substituents with the direction of the reaction does not seem possible. This may be attributed to the fact that under the rigid conditions of the Nicholls—Whiting reaction of $Cr(CO)_6$ with substituted biphenyls at least 5 different routes are conceived.

Besides, at elevated temperatures interconversion of isomers A and B is possible. These factors make determination of the effect of substituents on the direction of the reaction impossible at present.

Determination of apparent pK_a values of substituted phenols and amines

Thermodynamic constants of ionization of substituted phenols and anilines measured in standard conditions (in water or 50% ethanol, at 25°) are frequently used to estimate electronic effects of substituents [18]. If, however,

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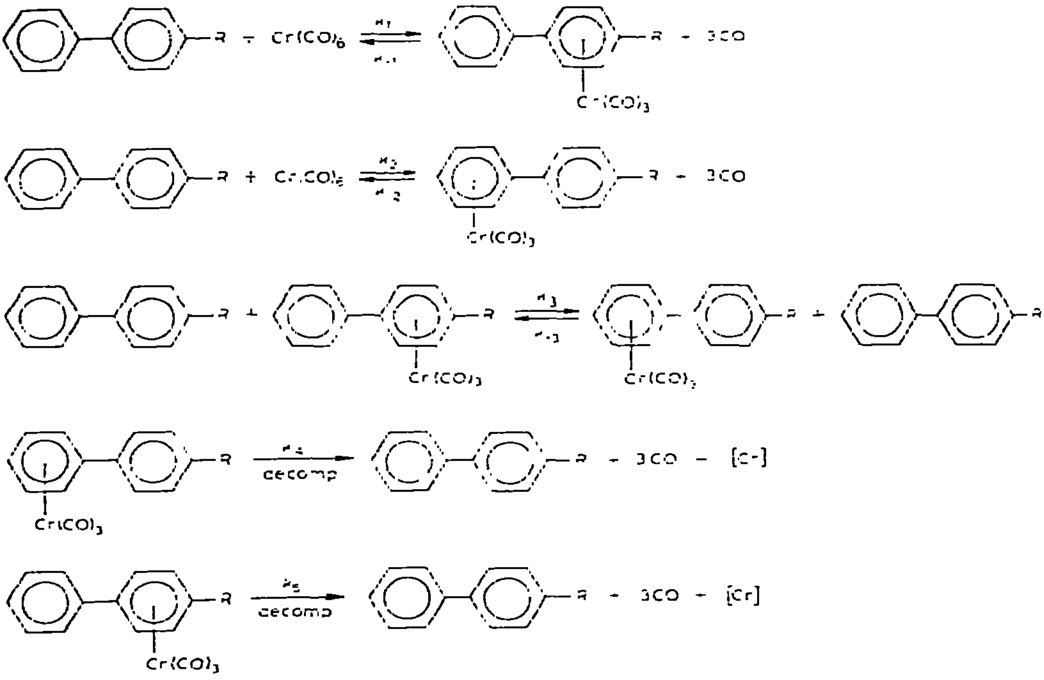
* Attempted synthesis of I from $Cr(CO)_3C_6H_5C_6H_4COOH$ [3] by a classical Curtius method successfully employed for ferrocene and cymanthrene series [15a, b] failed here. (Similarly to Nicholls and Whiting [9], we have not obtained the azide via acid chloride).



the compounds under study are not sufficiently soluble under the standard conditions, one can still measure apparent ionization constants in solvents containing small amounts of water. Provided that certain conditions are met [12, 13], these constants may still be employed to estimate the electronic effects of the substituents. These requirements are: constant ionic strength of solutions through the series, constant frontier potential difference (non-aqueous solvent/aqueous reference electrode), use of the concentration range where roughly linear E—pH dependence is maintained [12]. All these requirements were met in the present study.

Due to the poor solubility of *p*-[π-(tricarbonylchromium)phenyl] aniline (I) in 80% vol. ethanol, the basicity of substituted anilines was measured both in 80% ethanol, and in a mixture of ethanol/water/acetone (7/2/1). The values of K_b and pK_b for the anilines studied are given in Table 2. The closeness of the pK_b values for a series of substituted anilines measured in the solvents mentioned above allows one to estimate the nucleophilic aromatic constant of the $(CO)_3Cr$-C_6H_5 substituent in 80% ethanol*.

The σ_p^- value for $(CO)_3CrC_6H_5$ calculated by this method was +0.17, and that for non-coordinated phenyl was +0.07. To find the constants in the standard conditions we studied the ionization constants of substituted phenols, including *p*-[π-(tricarbonylchromium)phenyl] phenol (II), in 50% vol. ethanol. The data obtained (Table 2) indicate that II is a stronger acid than phenol and

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* To calculate σ_p^- we used the ρ value determined previously by one of us in similar conditions [11].

4-hydroxybiphenyl. The following correlation equation was derived using pK_a values given in a previously published paper [19] and measured in the present study.

$$pK_a = 2.73\ \sigma^- + 11.28$$

$$(n = 13;\ r = 0.999;\ s_{pK_a} = \pm 0.06;\ s_\sigma = \pm 0.02)$$

The σ_p^- values obtained from this equation and the calculated σ_R^- and $\Delta\sigma_R^-$ values for C_6H_5 and $(CO)_3CrC_6H_5$ are given in Table 4; the σ_p^- values show that the $(CO)_3CrC_6H_5$ substituent is a stronger electron-acceptor than free phenyl. Comparison of the Hammet constants σ_p and σ_p^- (or σ_R^- and σ_R) shows the ability of the $(CO)_3CrC_6H_5$ group to enter into direct polar conjugation with a donor reaction centre (+R), although this ability is not very pronounced. The $\Delta\sigma_R^-$ value, characterizing the polarizability of the substituent electron cloud by the donor centre, is changed upon coordination. Following the first paper by Nicholls and Whiting [9] who found the acidity of (tricarbonylchromium)phenylacetic acid to be equal to that of *p*-nitrophenylacetic acid, Bly et al. [25a-d] used the nitro group as a model imitating the electron-releasing effect of the $Cr(CO)_3$ group. In other reaction series this approach seems to have been inadequate; Nicholls and Whiting's pK_a value of *p*-nitrobenzoic acid was lower by about 0.3 than that of the coordinated benzoic acid. Later, tricarbonylchromium phenol [6,8] was shown to be a stronger acid than *p*-nitrophenol [19] by 0.8 pK_a units. Similarly, the activating effect of the $Cr(CO)_3$ group in reactions of nucleophilic substitution in the aromatic ring differs from that of the *p*-nitro group [22]. Discovery by Pettit [23] and Trahanovsky [24] of the high electron-releasing ability of the $Cr(CO)_3$ group at first seemed somewhat surprising, but later their results were confirmed in a number of papers [5a,c, 25a-c]. Ceccon [5c] compared donor and acceptor properties of the $Cr(CO)_3$ group. To define the ability of this group to stabilize or destabilize a reaction centre, its steric effect must be taken into account [5b,c, 22]. Using the present and previous [3] results we attempted a comparative study of the $(CO)_3CrC_6H_5$ group in different reaction series, with RC_6H_4-type substituents. A similar approach has been used by Berliner and Liu [26], who obtained a Hammet σ_p constant for the 4-(3'-nitrophenyl) group of +0.183, which is near to the σ_p value for $(CO)_3CrC_6H_5$ (+0.15). It means that *p*-[π-(tricarbonylchromium)-phenyl]benzoic acid is a somewhat weaker acid than 3'-nitro-4-biphenylcarboxylic acid. Similarly, using Brown's data [27, 28] the electrophilic constant for $(CO)_3CrC_6H_5(\sigma_p^+ = -0.09)$ can be shown to be near to those for 4-(4'-bromo)-phenyl and 4-(3'-bromo)phenyl ($\sigma_p^+ = -0.083$ and -0.093, respectively); thus the ability of $(CO)_3CrC_6H_5$ to stabilize a strongly electron-deficient site is intermediate between the substituted bromophenyls*.

The ability of the $(CO)_3CrC_6H_5$ group to interact with a strongly electron-releasing centre may be estimated using data in refs. 29-31. Comparison with the present data shows that the basicity of I ($\sigma_p^- = +0.17$) is nearly equal to that of 4'-bromo-4-aminobiphenyl ($\sigma_p^- = +0.161$), or of 3'-chloro-4-aminobiphenyl

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* These data indicate that in the absence of direct interaction of the chromium atom with a forming carbonium centre the electron-releasing ability of the coordinated phenyl is normal rather than abnormally high.

($\sigma_p^- = +0.175$), while II ($\sigma_p^- = +0.29$) is a stronger acid than 4′-nitro-4-hydroxybiphenyl ($\sigma_p^- = +0.28$).

On the other hand, among simpler substituents, the $(CO)_3CrC_6H_5$ group is more like halogens rather than the nitro group. Similar to halogens it exhibits a strong electron-releasing inductive effect and a resonance effect strongly dependent in magnitude on the nature of the reaction centre. In this sense the polarizability of the π-electron cloud of the coordinated phenyl is greater than that of the non-coordinated one.

Thus, one of the consequences of the coordination with the $Cr(CO)_3$ group is an increase in polarizability of the π-electron cloud of the phenyl nucleus, with the overall π-charge on the nucleus being nearly constant. In this respect our results and their interpretation are consistent with the Ugo's hypothesis [32] according to which the coordination of unsaturated molecules to transition metals is equivalent to photochemical excitation of the latter.

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