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TRANSMISSION OF SUBSTITUENT EFFECTS IN ANILINETRICARBONYLCHROMIUM COMPOUNDS

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SUMMARY

The NMR spectra of several *meta*- and *para*-substituted anilinetricarbonylchromium complexes have been determined in dimethyl sulfoxide. The amine proton chemical shifts plotted *versus* Hammett σ and σ^- values produce a straight line indicating direct resonance interaction between the substituents and the amino nitrogen.

INTRODUCTION

Since the preparation of bis(π-benzene)chromium and benzenetricarbonylchromium there has been considerable interest concerning the nature of the metal–arene bond and the effect of the metal on the electronic character of the benzene ring. Several studies indicate that the $M(CO)_3$ system withdraws electron density from the arene. For example, benzoic acid is a weaker acid than (benzoic acid)tricarbonylchromium[1,2], and aniline is a stronger base than anilinetricarbonylchromium[1]. (Halobenzene)tricarbonylchromium complexes readily undergo nucleophilic substitution, which also indicates reduced electron density in the coordinated benzene ring[2,3].

Klopman and Calderazzo[4] investigated the hydrolyses of several tricarbonylchromium complexes of substituted benzoic acid esters and found a correlation between the Hammett σ values of the substituents and the rates of hydrolysis. Recently the thermodynamic stabilities of several substituted benzyltricarbonylchromium cations were determined[5]. That study indicated a much different interaction of the aromatic π-system with the carbonium ion in the complexed cation than with the free cation. However, recent publications[6,7] suggest that there should be very little change in the π-electron character of the arene upon complexation. Due to these apparent conflicts the present study was undertaken to elucidate the nature of the transmissions of electronic effects in substituted anilinetricarbonylchromium complexes where direct resonance interactions between a substituent and the amino nitrogen should be possible.

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EXPERIMENTAL

Proton NMR spectra were recorded on a Varian A-60 spectrometer, and IR spectra (chloroform solvent) were obtained on a Perkin–Elmer 457 spectrophotometer (standardized by polystyrene). Melting points (decomposition points for most of these complexes) were determined in sealed tubes under nitrogen and are uncorrected. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona.

The tricarbonylchromium complexes of aniline[2], *m*-toluidine[2], *p*-toluidine[2], *m*-(methoxycarbonyl)aniline[8], and *p*-(methoxycarbonyl)aniline[4] were prepared according to literature procedures. The complexes of *m*-anisidine, *p*-anisidine, *m*-chloroaniline, and *p*-chloroaniline were prepared according to the method of Nicholls and Whiting[2]. Recrystallization from butyl ether or benzene/petroleum ether mixtures afforded analytical samples. Pertinent physical properties and analytical data are recorded in Table 1.

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA

$Cr(CO)_3$ compound	M.p. (°C)	Analysis, found (calcd.) (%) C	H	Yield (%)
m-$CH_3OC_6H_4NH_2$	149–151	46.36 (46.33)	3.55 (3.51)	32
p-$CH_3OC_6H_4NH_2$	105–106	46.36 (46.33)	3.39 (3.51)	85
m-$ClC_6H_4NH_2$	145–147	41.07 (41.00)	2.37 (2.30)	29
p-$ClC_6H_4NH_2$	106–107	41.17 (41.00)	2.33 (2.30)	18
p-$CH_3COC_6H_4NH_2$	162–163	48.76 (48.71)	3.12 (3.35)	22

(p-Aminoacetophenone)tricarbonylchromium

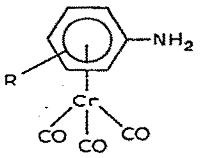
To $Cr(CH_3CN)_3(CO)_3$ prepared from 2.2 g of $Cr(CO)_6$ and acetonitrile[9] was added (under N_2) 1.4 g of *p*-aminoacetophenone in 70 ml of deoxygenated dioxane, and the resultant solution refluxed for 24 h. After cooling to room temperature the mixture was filtered and the solvent removed *in vacuo*. Chromatography on silica gel and elution with benzene followed by methylene chloride produced a bright orange band. Removal of the solvent and crystallization from methylene chloride/petroleum ether produced the desired compound (0.5 g; 22 %) as orange crystals. Melting points and analytical results are recorded in Table 1.

NMR spectra

The spectra were determined in dimethyl sulfoxide-d_6 solvent with tetramethylsilane as an internal standard. The average concentration was 0.1 g of the complex per 0.5 ml solution. The spectral data are recorded in Table 2.

TABLE 2

SPECTRAL DATA OF SUBSTITUTED ANILINETRICARBONYLCHROMIUM COMPOUNDS



R	NMR				IR
	δ (Aromatic protons) (ppm)		δ (Substituent protons)	$-NH_2$ (Hz)	Metal carbonyl (cm^{-1})
H	5.02 (m, 3H)	5.80 (m, 2H)		345	1962, 1874
m-Cl	5.10 (m, 3H)	5.89 (m, 1H)		364	1972, 1892
p-Cl	5.11 (m, 2H)	6.15 (m, 2H)		356	1969, 1889
m-CH_3	4.92 (m, 3H)	5.73 (m, 1H)	2.15 (s, 3H)	348	1956, 1871
p-CH_3	5.09 (m, 2H)	5.78 (m, 2H)	1.97 (s, 3H)	343	1958, 1872
m-OCH_3	4.97 (m, 3H)	5.83 (m, 1H)	3.67 (s, 3H)	351	1958, 1870
p-OCH_3	5.14 (m, 2H)	5.80 (m, 2H)	3.57 (s, 3H)	330	1959, 1872
m-CO_2CH_3	5.33 (m, 3H)	5.92 (m, 1H)	3.87 (s, 3H)	369	1971, 1891
p-CO_2CH_3	5.15 (m, 2H)	6.35 (m, 2H)	3.78 (s, 3H)	381	1972, 1893
p-$COCH_3$	5.25 (m, 2H)	6.38 (m, 2H)	2.37 (s, 3H)	389	1972, 1894

RESULTS AND DISCUSSION

The complexed anilines are such weak bases that titrimetric determinations of the pK become difficult. Linear relationships between amino proton chemical shifts and Hammett substituent constants have been found to exist in dimethyl sulfoxide (DMSO) and other solvents[10]. Dimethyl sulfoxide is an excellent solvent because the amino proton chemical shift is independent of concentration due to almost exclusive intermolecular hydrogen bonding between the $-NH_2$ group and DMSO. Since results indicate that the amino proton shifts are primarily dependent upon the π-electron density at the amino nitrogen atom[11], the properties of the solvated $-NH_2$ group enable one to observe the effects transmitted from the ring*.

The NMR spectra of the complexed anilines were determined in DMSO-d_6 (Table 2). The spectra were often quite complex with the amino proton absorptions overlapping the aromatic proton absorptions. To clarify the complex spectra, a drop of D_2O was added to the NMR solution. This caused a rapid disappearance of the amino proton absorptions. By obtaining spectra of the same complex at different concentrations, the chemical shifts of the amino protons were shown not to be concentration dependent. It should also be noted that the chemical shifts of some groups ($-CH_3$, $-OCH_3$, $-CO_2CH_3$) are changed only very slightly by coordination to the tricarbonylchromium system[13,14]. This suggests that the systematic shift of the $-NH_2$ absorptions is due to the combined electronic effect of both the substituent and the metal system and not merely that of the metal itself.

When the chemical shifts of the amino protons are plotted *versus* Hammett

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* Similar effects and results have been obtained with substituted phenols[12].

substituent constants (Fig. 1), a straight line is obtained. A much better plot is obtained when σ^- values are used for p-CO_2CH_3 and p-$COCH_3$. This result indicates that shielding of the protons attached to the nitrogen ($+R$ group) are greatly modified by a strong direct resonance interaction with a $-R$ substituent in the *para* position. Since the same effect has been noted in the uncomplexed anilines[10,15], it appears that the π-electron cloud of the complexed benzene ring can function in much the same way as that of an uncomplexed benzene ring in the transmission of resonance effects.

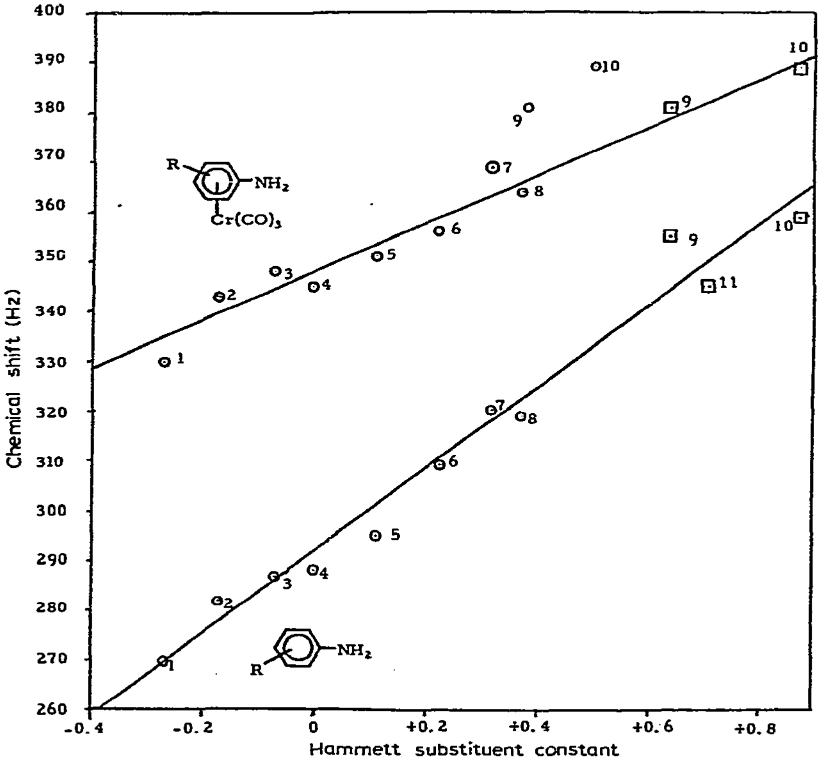

Fig. 1. Plot of chemical shift *vs.* Hammett substituent constants. ⊙ σ values; □ σ^- values. Line for the uncomplexed anilines constructed from information in ref. 10. (1) p-OCH_3; (2) p-CH_3; (3) m-CH_3; (4) H; (5) m-OCH_3; (6) p-Cl; (7) m-CO_2CH_3; (8) m-Cl; (9) p-CO_2CH_3; (10) p-$COCH_3$; (11) m-NO_2.

From Fig. 1, it can be seen that the slope of the plot of the uncomplexed compounds is greater than that of the complexed compounds. This simply indicates that the electron density on nitrogen in the complexed anilines is less sensitive to electronic changes in the aromatic ring induced by the substituents. This can be explained by the presence of the strongly electron-withdrawing tricarbonylchromium group which induces a considerable effective positive charge on the complexed aromatic system[6,7]. This decreased electron density would then act against the removal of charge by a substituent and would diminish any effect caused by the donation of electron density by a substituent.

The transmission of electronic effects from the aromatic ring to the carbon monoxide groups is also seen here. There is a slight but perceptible increase in the carbonyl frequencies (accuracy ±2 cm^{-1}) as the substituent becomes more electron attracting. However, the relative position of the substituent seems to matter very little and the stretching frequencies are best correlated by the use of the Hammett σ_p substituent constants which take into effect both inductive and resonance interactions.

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