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Electronic Effects in Aromatic Metal Carbonyl Complexes. II. Infrared and Proton Magnetic Resonance Spectra of Substituted Benzoic Methyl Ester Tricarbonylchromium Derivatives

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The carbonyl stretching frequencies and the proton chemical shifts of chromium tricarbonyl complexes of substituted benzoic esters have been measured in order to determine the electronic effects in these complexes. The over-all influence of a Cr(CO)₃ group on the organic ligand is found to be strongly electron withdrawing. Its ability to accommodate large charge changes (back donation of electrons when they are needed) produces a buffering of the transmission of electrons among substituents of the benzene ring. The proton magnetic resonance spectra are reasonably interpreted on the basis that the withdrawing effect occurs through the π orbitals of the benzene ring. Mesomeric donation of electrons from lone-pair-containing substituents is increased by complex formation. This phenomenon is compensated by an enhanced inductive back donation and affects the electron properties of the aromatic ring in a rather unique way.

Introduction

The nature of the bonding in metal-arene sandwich compounds and arene-metal carbonyl complexes has been investigated in several ways. A comparison between the chemical reactivity of substituted aromatic derivatives bonded to a chromium tricarbonyl group and of the uncomplexed compounds showed an association between strong electron-accepting power² and back-donating ability³ of the metal-containing moiety to the arene ligand. Some synthetic applications are given by Nicholls and Whiting.⁴

More specific observations are possible with the help of infrared and proton magnetic resonance spectra than by the comparison of reactivities. The infrared absorption of the carbonyl groups is sensitive to the transmission of electronic effects from a substituent of the arene ligand through the metal to the carbonyl groups. Fischer⁵ has made such studies on a number of arene-metal tricarbonyl compounds, which were extended by Brown and Raju.⁶ The influence of the metal moiety on the properties of the organic ligand can be studied by means of proton magnetic resonance and infrared spectra. Thus Humphrey found several changes in C-H and C-C stretching and bending vibrations caused by the bonding between the benzene nucleus and the chromium atom.⁷ Ring proton chemical shifts produced by complex formation between chromium tricarbonyl and several substituted aromatic derivatives have also been reported.^{8,9} Although the results have been obtained for rather complicated ligands, a general upfield shift for ring protons was established.

We report here the results of such a spectroscopic

study of a series of chromium tricarbonyl complexes of substituted benzoic esters. The study of the rates of hydrolysis of these esters was reported in a previous paper.^{2b}

Complexing a substituted benzoic ester to a chromium tricarbonyl group results in a perturbation of the properties of both moieties. This perturbation could manifest itself mainly in three ways: (1) influence of the ligand on the chromium tricarbonyl group; (2) influence of the chromium tricarbonyl on the benzoic ester properties; (3) perturbation of the transmission of electronic effects within the benzene nucleus. In order to be able to analyze these three phenomena, measurements of the infrared spectra and proton magnetic resonances were, if possible, performed under the same conditions for both the free-ligand organic derivatives and the corresponding chromium tricarbonyl complexes.

Experimental Section

The preparation of the compounds has been reported previously.^{2b}

The infrared spectra were measured on a Perkin-Elmer Model 521 grating spectrophotometer. The built-in absorbance scale was used for convenient measurement of the intensities. The spectral slit width over the range of the carbonyl stretching bands was about 1.5 cm⁻¹. Each spectrum was individually calibrated with carbon monoxide or water vapor. The frequencies are therefore accurate to ± 1 cm⁻¹. The absorbance scale was checked from time to time with precision rotating sectors (obtained from Research and Industrial Instruments Co., London). The compounds were dissolved in carbon tetrachloride under exclusion of oxygen. Some of the solutions were light sensitive and had to be protected by a silicon filter from the visible part of the radiation of the infrared light source. The cell lengths b were 0.1 or 1 mm, according to the solubilities of the compounds, and the concentrations c were adjusted to give $1/cb$ values of 2000 (for the ester carbonyl bands) and of 10,000 (for the metal carbonyl stretching bands). The areas under the bands were determined by cutting out and weighing or with an electronic integrator directly fitted to the spectrometer. No corrections for the extended wings or the limited resolution of the spectrometer were applied. The experimental error of the intensities is probably $\pm 15\%$, mainly due to the rather low chemi-

(1) Author to whom inquiries should be sent at the Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106.

(2) (a) D. A. Brown and J. R. Raju, *J. Chem. Soc., Sect. A*, 40 (1966); (b) G. Klopman and F. Calderazzo, *Inorg. Chem.*, **6**, 977 (1967).

(3) J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem. (Amsterdam)*, **4**, 324 (1965).

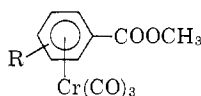
(4) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

(5) R. D. Fischer, *Chem. Ber.*, **93**, 185 (1960).

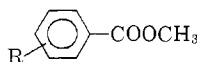
(6) D. A. Brown and J. R. Raju, *J. Chem. Soc., Sect. A*, 1617 (1966).

(7) R. E. Humphrey, *Spectrochim. Acta*, **17**, 93 (1961).

(8) W. Strohmeier and H. Hellmann, *Chem. Ber.*, **97**, 1877 (1964).

TABLE I
 INFRARED ABSORPTION. METAL-CARBONYL STRETCHING VIBRATIONS (CCl₄ SOLUTION)


R	No.	A ₁ band				E band				CO force constants, mdynes/Å	
		ν , cm ⁻¹	ϵ_{\max} , M ⁻¹ cm ⁻¹	10 ⁻³ E, M ⁻¹ cm ⁻²	$\Delta\nu_{1/2}$, cm ⁻¹	ν , cm ⁻¹	ϵ_{\max} , M ⁻¹ cm ⁻¹	10 ⁻³ E, M ⁻¹ cm ⁻²	$\Delta\nu_{1/2}$, cm ⁻¹	k_{CO}	k_i
<i>m</i> -COOCH ₃	1	1997	8000	72	6	1938	4100	110	22	15.48	0.31
<i>p</i> -COOCH ₃	2	1996	7625	55	5	1938	3400	87	22	15.47	0.31
<i>m</i> -Cl	3	1994	5000	50	7	1933	3400	86	22	15.41	0.32
<i>p</i> -Cl	4	1995	6900	49	5	1938	3600	78	19	15.47	0.30
<i>o</i> -Cl	5	1996	7450	63	6	1936	3700	91	21	15.45	0.32
H	6	1990	7250	58	5	1926	3750	93	22	15.32	0.34
<i>m</i> -CH ₃	7	1984	7150	61	6	1920	3650	98	24	15.22	0.34
<i>p</i> -CH ₃	8	1985	8000	65	6	1920	3800	107	25	15.23	0.34
<i>o</i> -CH ₃	9	1984	7200	59	5	1920	3500	93	23	15.22	0.34
<i>p</i> -OCH ₃	10	1983	7400	57	5	1918	3600	99	22	15.20	0.34
<i>o</i> -OCH ₃	11	1984	6800	61	6	1920	3250	107	29	15.22	0.34
<i>p</i> -NH ₂	12	1978	1912	15.11	0.34

 TABLE II
 INFRARED ABSORPTION. ESTER CO STRETCHING BANDS (CCl₄ SOLUTION)


R	Parent compounds				Cr(CO) ₃ complexes			
	ν , cm ⁻¹	ϵ_{\max} , M ⁻¹ cm ⁻¹	10 ⁻² E, M ⁻¹ cm ⁻²	$\Delta\nu_{1/2}$, cm ⁻¹	ν , cm ⁻¹	ϵ_{\max} , M ⁻¹ cm ⁻¹	10 ⁻² E, M ⁻¹ cm ⁻²	$\Delta\nu_{1/2}$, cm ⁻¹
<i>m</i> -COOCH ₃	1730	1480	201	13	1732	1260	222	15
<i>p</i> -COOCH ₃	1730	1420	263	14	1735	1390	254	15
<i>m</i> -Cl	1734 ^a	750	112	10	1736	680	128	15
<i>p</i> -Cl	1730	870	134	9	1732	740	127	14
<i>o</i> -Cl	1742	400	123	~31	1738	740	131	15
	1724	250						
H	1729 ^a	860	116	10	1732	740	120	14
<i>m</i> -CH ₃	1727 ^a	850	146	12	1734	640	119	17
<i>p</i> -CH ₃	1727	820	161	13.5	1732	900	155	13
<i>o</i> -CH ₃	1727	630	110	14	1733	670	144	15
<i>p</i> -OCH ₃	1722	690	137	15	1729	770	137	14
<i>o</i> -OCH ₃	1734	400	139	~15	1738	420	157	17
	1714	250						
<i>p</i> -NH ₂	1718	1722

^a These values differ slightly from those given by J. L. Mateos, R. Cotina, and S. Mega, *J. Org. Chem.*, **26**, 2494 (1961).

cal stability of the solutions. The integrated intensities E are given in "practical units"⁹

$$E = \frac{1}{cb} \int_{\nu_1}^{\nu_2} \log \frac{I_0}{I} d\nu$$

where c is in moles per liter, b is in centimeters, and ν is in reciprocal centimeters.

The nuclear magnetic resonance spectra were measured with a DP 60-A Varian instrument using tetramethylsilane (TMS) as internal standard. All compounds were measured in acetone-*d*₆ solution; some also were measured in deuteriochloroform. (Chemical shifts are given as δ values (ppm, from tetramethylsilane (TMS) = 0.)

Results

Infrared Spectra.—The results for the carbonyl stretching modes (frequencies and intensities) of the Cr(CO)₃ group are reported in Table I. All the compounds have two infrared-active stretching vibrations (A₁ + E) for the terminal CO groups, in agreement with the C_{3v} local symmetry of the Cr(CO)₃ moiety.

From these CO stretching frequencies force constants were calculated using the approach proposed by Cotton and Kraihanzel.¹⁰ These force constants are included in Table I.

In order to detect the influence of the chromium tricarbonyl group on the organic part of the complex we have also studied the carbomethoxycarbonyl stretching frequency. The results obtained for the chromium tricarbonyl substituted esters as well as those for the corresponding uncomplexed compounds are given in Table II.

Proton Magnetic Resonance Spectra.—The proton magnetic resonance spectra of the various substituted benzoic ester tricarbonylchromium complexes and those of the corresponding free ligands are reported in Table III.

In a few cases, the spectra were simple enough to be resolved completely and the coupling constants could be determined.¹¹ They are given in Table IV.

(9) K. S. Seshadri and R. N. Jones, *Spectrochim. Acta*, **19**, 1013 (1963).

(10) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

TABLE III
 NMR SPECTRA OF SUBSTITUTED BENZOIC ESTERS AND THEIR CHROMIUM TRICARBONYL COMPLEXES IN HEXADEUTERIOACETONE^a

Substituent	Type of spectrum	Ring protons				Chemical shift, ppm, δ				
		Proton no. (assigned)	Free ligand		Complex		COOCH ₃ protons		Substituent protons	
							Free ligand	Complex	Free ligand	Complex
3-COOCH ₃	AB ₂ X	2	8.60	6.85		3.95	3.93			
		4, 6	8.22	6.57						
		5	7.65	5.75						
4-COOCH ₃	A ₄	2, 3, 5, 6	8.13	6.28		3.92	3.90			
		3-Cl	2	7.92	6.33		3.88	3.93		
			4	7.55	6.02					
4-Cl	AA'XX'	5	7.55	6.02						
		6	7.92	6.02						
		2, 6	7.98-8.13	6.41-6.52		3.88	3.87			
H	(AB) ₂ X	3, 5	7.48-7.63	5.83-5.95						
		2, 6	8.03	6.27		3.87	3.88			
2-CH ₃		3, 5	7.58	5.73						
		4	7.47	5.73						
		3	7.32	5.48		3.83	3.87	2.57	2.52	
		4	7.32	5.93						
		5	7.32	5.48						
3-CH ₃		6	7.90	6.35						
		2	7.83	6.12		3.85	3.88	2.35	2.28	
		4	7.40	5.80						
		5	7.40	5.80						
4-CH ₃	AA'XX'	6	7.83	6.12						
		2, 6	7.88-8.02	6.28-6.40		3.83	3.87	2.40	2.30	
		3, 5	7.27-7.40	5.47-5.58						
2-OCH ₃		3	7.00	5.57		3.82	3.85	3.82	3.80	
		4	7.48	6.05						
		5	7.07	5.18						
		6	7.73	6.33						
4-OCH ₃	AA'XX'	2, 6	7.95-8.10	6.38-6.50		3.83	3.83	3.87	3.83	
		3, 5	6.97-7.12	5.47-5.60						
4-NH ₂	AA'XX'	2, 6	7.72-7.85	6.33-6.45		3.78	3.80	5.13	4.77	
		3, 5	6.65-6.78	5.15-5.27						

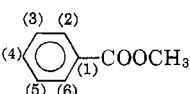
^a The numbering of the ring positions follows the scheme 

 TABLE IV
 COUPLING CONSTANTS FOR SOME *para*-SUBSTITUTED CHROMIUM TRICARBONYL AND FREE BENZOIC ESTERS

Compound	J_{AX} , cps	$J_{AX'}$, cps	$J_{AA'} = J_{XX'}$, cps
Free ligand			
<i>p</i> -NH ₂	8.44	0.26	2.10
<i>p</i> -OCH ₃	8.57	0.43	2.45
<i>p</i> -CH ₃	7.90	0.40	1.90
<i>p</i> -Cl	8.07	0.33	2.10
Complex			
<i>p</i> -OCH ₃	7.31	0.01	2.05
<i>p</i> -CH ₃	6.62	0.08	1.50

Discussion

Infrared Spectra. Cr(CO)₃-Carbonyl Vibrations.—

The frequencies of the carbonyl stretching bands are found to decrease as the electron-donating power of the substituent increases. However there is practically no influence due to the relative position of the substituents within the ring. This conclusion agrees with that of McFarlane and Grim,¹² who found a small decrease in the carbonyl stretching frequency of chromium tricarbonyl polymethoxybenzene complexes with an in-

crease of the number of methoxy groups. The frequencies were, however, independent of the relative positions of the substituents. The same is true for the CO stretching force constants which are derived from these frequencies.

It appears therefore that the decrease in the stretching force constants follows the over-all increase in the π -electron density on the whole aromatic ring rather than at a particular position. This increase in π -electron density enables the chromium atom to transfer electrons into the antibonding orbitals of the CO groups and thus decreases the bond order. A correlation can therefore be expected between the carbonyl stretching force constants and the Hammett σ of the substituent. A general trend of that kind has been shown to hold approximately.^{5,6} In Figure 1, such a correlation was established for our compounds; some other derivatives reported by McFarlane and Grim¹² are also included.

We have reported the correlation with the CO force constants, but almost the same type of correlation can be obtained with the frequencies of the A₁ or the E vibration directly. The total variation of the force constants, including McFarlane and Grim's compounds,¹² are from 15.48 mdynes/Å for chromium tricarbonyl isophthalic dimethyl ester to 14.80 mdynes/

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(12) W. McFarlane and S. O. Grim, *J. Organometal. Chem.* (Amsterdam), **5**, 147 (1966).

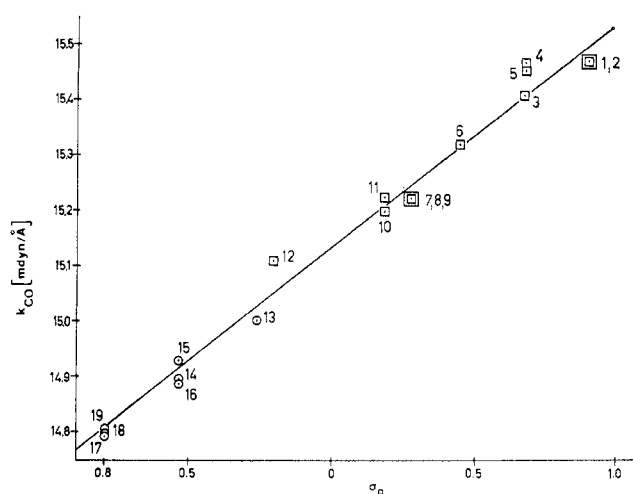


Figure 1.—Hammett plot for the $\text{Cr}(\text{CO})_3$ carbonyl force constants: \square , this work (Table I); \circ , from ref 12: $\text{CH}_3\text{OC}_6\text{H}_5$ (13), *m*-(CH_3O) $_2\text{C}_6\text{H}_4$ (14), *p*-(CH_3O) $_2\text{C}_6\text{H}_4$ (15), *o*-(CH_3O) $_2\text{C}_6\text{H}_4$ (16), 1,2,3-(CH_3O) $_3\text{C}_6\text{H}_3$ (17), 1,2,4-(CH_3O) $_3\text{C}_6\text{H}_3$ (18), 1,3,5-(CH_3O) $_3\text{C}_6\text{H}_3$ (19).

\AA for chromium tricarbonyl 1,2,3-trimethoxybenzene. In order to obtain the correlation of Figure 1, we postulated additivity for the respective electronic effects of the various substituents

$$\sigma_{\text{total}} = \sum_{\text{subst}} \sigma_{\text{subst}}$$

and made use of σ_{para} ¹³ rather than some kind of combination of various σ 's. The reason for this choice is that one wants to represent the over-all effect of the substituents on the π orbitals of the ring, *i.e.*, inductive *plus* mesomeric, and the σ_{para} is probably the best available quantity for this purpose.¹⁴

In spite of these approximations, a very good correlation is obtained. No saturation is produced by the accumulation of substituents as shown by the absence of curvature, suggesting that a large variation of charge can be accommodated by the chromium tricarbonyl moiety. The $\text{Cr}(\text{CO})_3$ group absorbs part of the excess charge created on the ring by electron-donating substituents and thus acts as a sort of charge buffer. The electron-donating or -withdrawing effect of the substituents is therefore partly counterbalanced by the charge withdrawing and the back donation of the chromium tricarbonyl group and results in a decrease of the transmission of electronic effects from one substituent to another on the aromatic ring. This behavior was already found in the saponification of the esters where the Hammett σ decreased from 2.36 for the uncomplexed derivatives to 1.55 for the complexed ones.^{2b}

The intensities of the two infrared-active chromium tricarbonyl bands show rather small variations and it seems difficult to relate them in any systematic way.

Ester-Carbonyl Frequencies.—From Table II it is seen that the frequencies of the complexed species are consistently 1 to 7 wave numbers higher than those of the corresponding parent compounds. (The mean value was taken when there was a doublet.) The

(13) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(14) S. A. Butter and H. C. Beachell, *Inorg. Chem.*, **5**, 1820 (1966).

total spread of the frequencies of the parent compounds and of the chromium tricarbonyl complexes is the same (16 cm^{-1}). The shift toward higher frequencies in going from the parent compounds to the corresponding complexes reflects the over-all electron-withdrawing effect of the $\text{Cr}(\text{CO})_3$ group which is largely preponderant over a possible back donation from the chromium tricarbonyl moiety to the arene ligand.

Although a general trend is followed, no direct correlation between ester carbonyl frequencies and the Hammett σ of the substituents could be found. Nevertheless, such correlation is already very poor for the uncomplexed aromatic derivatives.

The intensities do not seem much influenced by the complex formation although a slight trend toward lower values can be detected.

Proton Magnetic Resonance Spectra.—The chemical shift of the COOCH_3 protons decreases regularly with the electron-donating power of the substituent. No large difference is observed between the complexed and uncomplexed species neither in their general behavior nor in magnitude.

A large decrease, however, is observed between the chemical shifts of the ring protons of the free ligands and the complexes, as already noticed by other investigators.^{6,8,12} The shift is in the direction opposite to that which one might expect to be caused by the large decrease in electron density in the ring. It is too large to represent a purely electronic modification and appears to be very solvent dependent as shown in Table V. It might therefore be attributed to a structural effect, due to the diamagnetic anisotropy of the chromium tricarbonyl moiety. The chemical shift will also be largely affected by the ease of rotation of the metal moiety and its vibrational state, both functions of the solvation.

An analysis of the chemical shifts of the ring protons in the complexed and uncomplexed species has been made, following the procedure described by Diehl.¹⁵ In this procedure the substituent effects on the chemical shift of each proton are assumed to be additive. Each substituent is characterized by a chemical shift parameter whose value depends on the nature of the substituent and on its position relative to the proton under consideration. The values of these parameters which fit best the results for the two groups of compounds are given in Table VI. The chemical shift for C_6H_6 was taken as 7.27 ppm, and that of $\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3$, as 5.68 ppm. Figure 2 shows a plot of the experimental shifts against the calculated chemical shifts. Using this additivity concept, the assignment of the chemical shifts to the different protons was possible (columns 3, 4, and 5 of Table III).

Although both the free ligands and the complexes are satisfactorily correlated, it is intriguing to find that the substituent effects are markedly different for the two series. In particular, the shift due to the influence of a substituent on a *meta* proton appears always to be negative in the complex even for very strong electron

(15) P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961).

TABLE V
 SOLVENT EFFECT ON CHEMICAL SHIFT (PPM, δ)

Compound	Solvent	COOCH ₃ protons			Ring protons		
		Free ligand	Complex	Δ	Free ligand	Complex	Δ
<i>p</i> -(COOCH ₃) ₂ C ₆ H ₄	Benzene ^a	8.08	5.80	-2.28
	CCl ₄ ^b	3.88	3.92	+0.04	8.08	6.00	-2.08
	Acetone	3.92	3.90	-0.02	8.13	6.28	-1.85
<i>m</i> -CH ₃ C ₆ H ₄ COOCH ₃	CCl ₄ ^b	3.82	3.85	+0.03	7.30-7.80	5.38-5.87	-1.92
	Acetone	3.85	3.88	+0.03	7.40-7.83	5.80-6.12	-1.60
C ₆ H ₆	Benzene ^a	7.27	4.43	-2.84
	CCl ₄ ^b	7.28	5.37	-1.91
	Acetone	7.27	5.68 ^c	-1.59

^a From ref 8. ^b From ref 12. ^c Extrapolated.

 TABLE VI
 CONTRIBUTIONS OF SUBSTITUENTS TO THE
 CHEMICAL SHIFT (PPM) OF THE RING PROTONS

Substituent	Free ligand			Complex		
	<i>ortho</i>	<i>meta</i>	<i>para</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>
COOCH ₃	-0.68	-0.22	-0.23	-0.58	-0.03	-0.22
Cl	-0.03	-0.10	0.03	-0.13	-0.22	0.25
CH ₃	0.13	0.07	0.15	0.17	-0.07	0.18
CH ₃ O	0.40	0.07	0.42	0.17	-0.13	0.53
NH ₂	0.77	0.17	...	0.47	-0.12	...

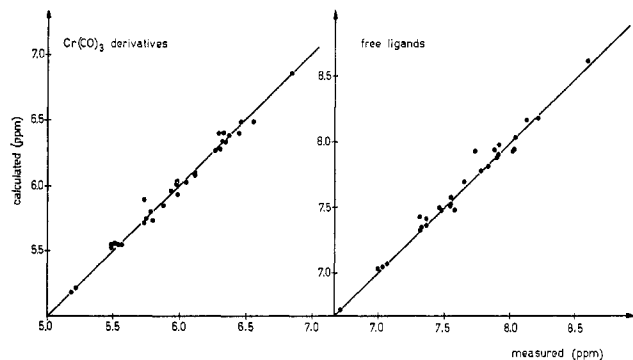


Figure 2.—Proton ring chemical shifts.

donors like NH₂. This behavior was noticed by McFarlane and Grim¹² for the particular case of *p*-dimethoxychromium carbonyl benzene and was tentatively attributed to an enhancement of the inductive effect in the complex *vs.* the mesomeric effect. The observed change of sign was related to the fact that the Hammett σ of *m*-CH₃O is negative whereas that of *p*-CH₃O is positive. This explanation does not hold here since the phenomenon occurs for all substituents. Nevertheless, the large modification occurs mainly for the *meta* position which is less sensitive to mesomeric effects. It might thus still be related to a modification of the ability of the ring to carry inductive effects or alternatively to a modification of the electronegativity of the substituent.

An alternative explanation could be that the change of substituent leads to change in the relative positions of the Cr(CO)₃ group. That this is not likely is shown by the fact that this *meta* effect occurs systematically, irrespective of the relative position of the two substituents. The coupling constants for the *para*-substituted derivatives might have been of significant importance here in order to detect possible deformations of the ring. These coupling constants have been com-

puted for the *para*-substituted compounds and are systematically around 0.14 ± 0.01 ppm for the free ligands (8.5 cps) and 0.12 ± 0.01 ppm for the complexes (7.2 cps). This decrease could be associated with a deformation of the ring. However, since it is rather constant for all substituents, it is more probably due to the strong electron-withdrawing effect of the Cr(CO)₃ group.

Perhaps the best interpretation can be given based on the data of Table VII. In this table the chemical

 TABLE VII
 CHEMICAL SHIFTS (PPM) OF
para-SUBSTITUTED BENZOIC ESTERS

Substituent	Free ligand		Complex	
	H in 3,5 position (<i>ortho</i> to substituent)	H in 2,6 position (<i>meta</i> to substituent)	H in 3,5 position (<i>ortho</i> to substituent)	H in 2,6 position (<i>meta</i> to substituent)
COOCH ₃	8.13	8.13	6.28	6.28
Cl	7.55	8.05	5.89	6.46
CH ₃	7.33	7.94	5.53	6.34
CH ₃ O	7.04	8.02	5.53	6.44
NH ₂	6.71	7.78	5.21	6.39

shifts of the ring protons of the various *para*-substituted benzoic esters and their corresponding chromium tricarbonyl complexes are assembled. It appears that the effect of the different substituents on the chemical shift of the protons in the *ortho* position follows, both for the complexes and the free ligands, the same sequence as the electron-donating power of the substituents. It fits, for example, the Hammett σ_{para} relationship

$$\text{chemical shift: } \text{COOCH}_3 > \text{Cl} > \text{CH}_3 > \text{CH}_3\text{O} > \text{NH}_2$$

$$\sigma_{para}: \quad 0.45 \quad 0.23 \quad -0.17 \quad -0.27 \quad -0.66$$

As already discussed above in relation with the reactivity and infrared spectra, there is a buffering of electronic effects in the complexes. This manifests itself also in the chemical shifts: the total range for the free ligands is 1.42 ppm, and for the complexes, it is decreased to 1.07 ppm. The effect on a *meta* position, although much less pronounced (total range 0.35 ppm), remains, for the free ligand, in reasonable agreement with what one may expect from inductive effects

$$\text{chemical shift: } \text{COOCH}_3 > \text{Cl} > \text{CH}_3\text{O} > \text{CH}_3 > \text{NH}_2$$

$$\sigma_{meta}: \quad 0.37 \quad 0.37 \quad 0.11 \quad -0.07 \quad -0.16$$

However, the behavior of the chromium tricarbonyl complexes here again appears to be drastically modified

and follows the order $\text{Cl} > \text{CH}_3\text{O} > \text{NH}_2 > \text{CH}_3 > \text{COOMe}$. Although the total range is very small (0.18 ppm), it appears that the largest effects are now produced by substituent groups possessing *available lone pairs*. This might suggest that the change in behavior could be due to the strong demand of electrons from the chromium carbonyl moiety. The electrons are coming from the π orbitals of the benzene ring, ultimately from substituent lone pairs, if available. This decrease in electron density in the π orbital of the substituent will then be compensated by an inductive back donation from the σ system of the ring to the substituent. It thus leads to positive charges mainly in the *meta* position but should also affect the *ortho* position. As a matter of fact, an effect of that kind appears and the signal for *ortho* protons is also shifted by complex formation to negative values for all substituents possessing an available lone pair (Table VI)

$$\text{shift} (= \delta_{\text{complex}} - \delta_{\text{free ligand}}) \quad \text{NH}_2 > \text{CH}_3\text{O} > \text{Cl} \\ -0.30 \quad -0.23 \quad -0.10$$

This is compared to a positive shift for the other substituents COOCH_3 (+0.10) and CH_3 (+0.04).

Although this conclusion seems to be supported by experimental facts, it is surprising that such a redistribution of charge density does not affect the reactivity of the ester group as shown by the very good correlation which exists between the rate of saponification of the complexes and their corresponding parent compounds.^{2b} This might however be due, as already noted, to the fact that the *meta* effects appear to be rather small.

Theoretical calculations which take into proper account the effect of the chromium tricarbonyl moiety might clarify these points. Such calculations are now in progress and will be reported in a forthcoming paper.

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Octahedral Metal Carbonyls: Reactions and Bonding. VII. Kinetics of the Substitution Reactions of 2,5-Dithiahexane Complexes of Chromium Hexacarbonyl and Molybdenum Hexacarbonyl¹

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The complexes $(\text{DTH})\text{Cr}(\text{CO})_4$ and $(\text{DTH})\text{Mo}(\text{CO})_4$ ($\text{DTH} = 2,5$ -dithiahexane) react with phosphites with the replacement of the bidentate ligand to yield *cis*- and *trans*-(phosphite)₂ $\text{M}(\text{CO})_4$ complexes according to a second-order rate law. Activation parameters and previous results suggest, however, that the reactions of the two complexes occur substantially through different mechanisms, the Cr reaction proceeding through a preequilibrium step involving the dissociation of one end of the bidentate ligand followed by attack on the resulting five-coordinate species, with the Mo reaction proceeding through the formation of a seven-coordinate intermediate. Reaction rates vary according to the steric nature of the various phosphite ligands employed; the results obtained are compared to those previously obtained for similar systems and are discussed in terms of σ - and π -bonding properties of the bidentate ligands.

Introduction

Recently the emphasis in the study of bonding in octahedral metal carbonyls has shifted from almost exclusive consideration of infrared spectral data to kinetic and mechanistic investigation of their reactions.³ Of particular interest in their implications as to the nature of steric and bonding effects have been the investigations of the kinetics of the reaction of (bidentate)- $\text{M}(\text{CO})_4$ molecules [bidentate = 2,2'-dipyridyl (dipy),⁴

o-phenanthroline (phen) and various substituted phenanthrolines,⁵ and 1,2-diamino-2-methylpropane (dmp),⁵ $\text{M} = \text{Cr}, \text{Mo}, \text{W}$] with various phosphites (L). It was found that derivatives of Cr react according to a first-order rate law

$$\text{rate} = k[(\text{bidentate})\text{Cr}(\text{CO})_4] \quad (1)$$

to give $(\text{L})(\text{bidentate})\text{Cr}(\text{CO})_4$ complexes; the reaction evidently involves dissociation of a carbonyl in the rate-determining step. Mo and W complexes, on the other hand, obey a mixed-order rate law

$$\text{rate} = k_1[(\text{bidentate})\text{M}(\text{CO})_4] + k_2[(\text{bidentate})\text{M}(\text{CO})_4][\text{L}] \quad (2)$$

with the formation of several products for the dipy and dmp derivatives. The exclusive first-order rate de-

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(3) For a brief review of work in this field, see M. Graziani, F. Zingales, and U. Belluco, *Inorg. Chem.*, **6**, 1582 (1967).

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