757. *Electronic Effects in Organometallic Complexes.*

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The electronic effects due to substituents in complexes of the type $\pi\text{-X}\cdot C_6H_5Cr(CO)_3$ are discussed in terms of simple molecular-orbital theory. It is shown that the degree of charge-transfer to the central metal atom is related to the electron-donating power of X. The theoretical predictions are compared with the observed carbonyl stretching frequencies of these complexes and related solvent effects.

The nature of the bonding in many organometallic systems can be understood in terms of molecular-orbital theory [1] and arises essentially from the interaction of the *s*-, *p*-, and *d*-orbitals of the central metal atom with the π-orbitals of the conjugated system.

The application of such theory [2] to complexes of the type $C_nH_nMY_m$, where $n = 4$—8, M is a transition metal, and Y a ligand, leads to the prediction of increasing charge-transfer from the ring system to the central metal atom as n increases from 4 to 6 within isoelectronic complexes. This result follows from the nature of the interactions between C_nH_n with a ground state $a_1^2e_1^xe_2^y$ ($x = 2$—4, $y = 0$—2) and the metal orbitals under the local symmetry D_n ($n = 4\ldots$); the interactions will be of the type ($a_14s/4p$), ($e_13d/4p$), and (e_23d). The first of these must lead to charge-transfer to the central metal atom since the totally symmetric orbital is always filled; but the extent of charge-transfer in the other two will depend upon x and y. Thus, for a cyclopentadienyl complex ($n = 5$, $x = 3$, $y = 0$) there will be some charge-transfer to the metal, but less than for a benzene complex ($n = 6$, $x = 4$, $y = 0$) since the e_1 interaction in the latter is between a filled π-orbital and empty metal $3d/4p$-hybrids. In both cases there will be back-donation from the metal to the empty e_2-orbitals, but the dominant factor will be the difference in the e_1 class. For complexes in which the ligand Y is carbonyl the extent of charge-transfer is reflected in the carbonyl stretching frequencies; the greater the negative charge on the metal atom M, the greater the transfer to the vacant orbitals of the carbonyl group and hence the lower the C–O stretching frequency. This is illustrated by the sequence: [3] $\pi\text{-}C_5H_5Mn(CO)_3$, $\nu = 2035, 1953$ cm.$^{-1}$; $\pi\text{-}C_6H_6Cr(CO)_3$ (present work), $\nu = 1984, 1916$ cm.$^{-1}$.

In this paper we discuss the transmission of electronic effects due to the substituent X in complexes of the type $\pi\text{-X}\cdot C_6H_5Cr(CO)_3$. The nature of this effect will be considered first in terms of molecular-orbital theory analogous to that of the introductory discussion. The theoretical results will then be compared with experimental evidence from the carbonyl stretching frequencies and from solvent effects upon them.

Molecular-orbital Theory.—As a model for the complex $\pi\text{-X}\cdot C_6H_5Cr(CO)_3$, we assume the structure shown in Fig. 1, in which the plane of the aromatic ring is parallel to the *xy*-plane containing the chromium atom; this structure is known to be correct for the unsubstituted compound.[4]

The three carbonyl groups possess C_{3v} local symmetry, whilst the aromatic component possesses only C_{2v} local symmetry. The σ-orbitals of the $(CO)_3$ group fall, therefore, into the representation $A_1 + E$, and the π-orbitals into $5A_1 + 2B_2$. The symmetry classification of the interaction of these orbitals with the central metal *s*-, *p*-, and *d*-orbitals in the above complex is given in Table 1.

A quantitative estimate of the above interactions is given, first, by the various group overlap integrals and, secondly, by the differences in the Coulomb terms of the respective orbitals. These were evaluated for the above system for two extreme cases in which (*a*) X is assumed to be highly electronegative, *i.e.*, an electron-attracting substitutent

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[1] Cotton and Wilkinson, " Progress in Inorganic Chemistry," Interscience Publ., Inc., New York, 1959, Vol. I, p. 1.

[2] Brown, *J. Inorg. Nuclear Chem.*, 1959, **10**, 39.

[3] Fischer, *Chem. Ber.*, 1960, **93**, 165.

[4] Corradini and Allegra, *J. Amer. Chem. Soc.*, 1959, **81**, 2271.

TABLE 1.

Symmetries of constituent orbitals in complex π-X·$C_6H_5Cr(CO)_3$.

$X\cdot C_6H_5$ orbitals	Metal orbitals	Ligand orbitals	$X\cdot C_6H_5$ orbitals	Metal orbitals	Ligand orbitals
$1a_1$	$(4s)$		$1b_2$	$3d_{yz}/4p_y$	e_y
	$(4p_z)$	a_1	$2b_2$		
$2a_1$	$(3d_{z^2})$				
$3a_1$	$(3d_{xz})$				
$4a_1$	$(4p_x)$	e_x			
$5a_1$	$3d_{xy}$				
	$3d_{x^2-y^2}$				

(+*E* on Dewar's notation), and (*b*) X is assumed to be highly electropositive, that is, an electron-donating substituent (−*E*). The extent of charge-transfer is then assumed to be the greater the greater is the overlap integral *S* and the smaller the ΔH value; this follows since in all cases we are considering an interaction between a filled orbital and an empty orbital. These cases were obtained by evaluating the molecular orbitals for the molecule C_6H_5X in which the Coulomb term of the heteroatom X and its resonance integral with an adjacent carbon ($2p_\pi$) orbital are given by:

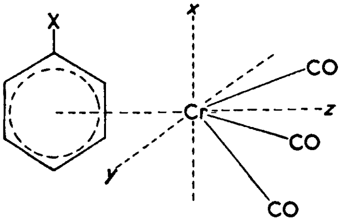

FIG. 1. The complex π-X·$C_6H_5Cr(CO_3)$.

$$H_{XX} = H_{CC} + m\beta_{CC};\ H_{CX} = n\beta_{CC}.$$

The parameters *m* and *n* were assigned the values $m = \pm 2{\cdot}0$ and $n = 1{\cdot}00, 1{\cdot}80$ which cover the two extreme types of substituent. The coefficients of the isolated molecular orbitals were then obtained by standard procedure. The group overlap integrals between these π-orbitals and the various metal orbitals were calculated for the above model in which the Cr–C_i ($i = 1$—6) distance was taken as 2·25 Å,[4] and the Cr–X distance as 3·31 Å; the latter distance is that calculated for the chlorobenzene complex, but since the overlap integrals are relatively insensitive to small differences in this distance the results are generally applicable. The chromium atom was assigned the configuration $3d^44s^2$ and the screening constants of the Slater 3*d*-, 4*s*-, and 4*p*-orbitals were calculated accordingly. The formulæ used for calculating the group overlap integrals were those derived in earlier papers;[5] as an illustration the formula for the overlap integral between a totally symmetric π-orbital and the $4p_z$-orbital of chromium is:

$$S(\psi_1\,4p_z) = \sum_{i=1}^{7} C_i[S_i(2\rho_\sigma\,4p_\sigma)\cos^2\theta_i - S_i(2\rho_\pi\,4p_\pi)\sin^2\theta_i]$$

where C_i is the coefficient of *i*th carbon atom in the given molecular orbital and θ_i the angle between the *Z*-axis and the M–C_i vector. The constituent overlap integrals, *viz.*, $S(2p_\sigma 3d_\sigma)$, $S(2p_\pi 3d_\pi)$, $S(2p_\sigma 4s)$, $S(2p_\sigma 4p_\sigma)$ and $S(2p_\pi 4_\pi)$, were obtained by interpolation from the tables of Jaffé, Leiffer *et al.*, and Brown.[6] The results are given in Table 2. The group overlap integrals involving the $4p_z$- and $3d_{z^2}$-orbitals were found to be small for the complete range of the parameters *m* and *n*. The anti-symmetric orbitals are independent of the substituent and so do not contribute to any difference in electronic effects in the substituted systems. We also give in Table 2, in parentheses, the differences in the

[5] Dunitz and Orgel, *J. Chem. Phys.*, 1955, **23**, 956; Brown, *ibid.*, 1958, **29**, 1086.

[6] Jaffé, *J. Chem. Phys.*, 1953, **21**, 258; Leiffer, Cotton, and Leto, *ibid.*, 1958, **28**, 364; Brown, *ibid.*, 1958, **29**, 1086.

TABLE 2.

Group overlap integrals and Coulomb term differences.

m	n	ψ	$S(\psi, 4s)$	$S(\psi, 4p_x)$	$S(\psi, 3d_{xz})$	$S(\psi, 3d_{x^2-y^2})$	$S(\psi, 3d_{xy})$
+2·0	1·0	$1a_1$	0·151 (5·8)	0·146 (8·2)	0·092 (6·5)	—	0·044 (6·5)
−2·0		$1a_1$	0·211 (3·7)	0·026 (6·9)	0·019 (5·0)	—	—
+2·0	1·0	$2a_1$	0·150 (4·4)	0·119 (6·2)	0·032 (4·5)	—	—
−2·0		$2a_1$	0·008 (2·0)	0·258 (4·5)	0·268 (2·7)	0·090 (2·7)	—
+2·0	1·0	$3a_1$	—	0·183 (3·6)	0·238 (1·8)	0·094 (1·8)	—
−2·0		$3a_1$	—	0·007 (−0·2)	0·027 (−2·0)	—	0·161 (−2·0)
+2·0	1·0	$4a_1$	—	—	—	—	0·157 (−2·8)
−2·0		$4a_1$	—	—	—	0·122 (−4·5)	0·040 (−4·5)
+2·0	1·0	$5a_1$	—	—	—	0·132 (−5·1)	—
−2·0		$5a_1$	—	—	—	0·059 (−6·5)	—
+2·0	1·80	$1a$	0·136 (7·4)	0·164 (9·9)	0·113 (8·1)	—	0·054 (8·1)
−2·0		$1a_1$	0·207 (4·7)	0·076 (7·2)	0·063 (5·4)	—	—
+2·0	1·80	$2a_1$	0·164 (3·6)	0·124 (6·1)	0·112 (4·3)	—	—
−2·0		$2a_1$	0·046 (2·50)	0·248 (5·0)	0·251 (3·3)	—	0·078
+2·0	1·80	$3a_1$	—	0·163 (3·0)	0·218 (1·2)	0·060 (1·2)	0·096
−2·0		$3a_1$	—	0·039 (0·52)	0·080 (−1·2)	0·155	0·055
+2·0	1·80	$4a_1$	—	—	—	0·142 (−3·3)	0·051 (−3·3)
−2·0		$4a_1$	—	—	—	0·057 (−4·4)	0·127
+2·0	1·80	$5a_1$	—	—	—	—	0·119 (−5·5)
−2·0		$5a_1$	—	—	—	—	—

Coulomb terms of the π-orbitals and of the chromium orbitals. The latter were obtained from spectroscopic data,[7] and the former by identifying the first ionization potential of benzene with the Coulomb term of the highest filled orbital, $H(e_1e_1)$. The various terms for the two cases of substituents were then obtained from the respective roots by taking the resonance integral β_{CC} as 2·5 ev.[5] This procedure does not, of course, give reliable absolute values for these terms but it should provide a reasonable scale of values.

Consider first the interactions between the filled totally symmetric π-orbitals ($1a_1$—$3a_1$) of C_6H_5X and the empty $4s$-, $4p_x$-, and $3d_{xz}$-orbitals of the chromium atom for the two extreme cases where $m = +2{\cdot}0$ and $-2{\cdot}0$. In the case of the $1a_1$ orbital the interactions with the $4p_x$-orbital will be small in view of the large difference in Coulomb terms. The integral $S(1a_1,4s)$ is greater for $m = -2{\cdot}0$ than for $m = +2{\cdot}0$, whilst the ΔH value is smaller. For the interaction $(1a_1,3d_{xz})$ the integral is smaller, but so is the ΔH value. The predominant interaction is greater then for $m = -2{\cdot}0$ than for $m = +2{\cdot}0$; hence greater charge-transfer will occur from the filled π-orbitals to the empty metal orbitals. Similar arguments apply to the interactions $(2a_1,4p_x)$ and $(2a_1,3d_{xz})$. However, in the case of the $3a_1$-orbital, although the overlap integral is greater for $m = +2{\cdot}0$ than for $m = -2{\cdot}0$,

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[7] Berry, *J. Chem. Phys.*, 1961, **35**, 29.

the ΔH values are of opposite sign, so it is difficult to draw an unambiguous conclusion for this interaction.

Now consider the interaction of the empty $4a_1$- and $5a_1$-orbitals with the filled chromium $3d_{xy}$- and $3d_{x^2-y^2}$-orbitals. For both orbitals the overlap integrals are greater and the ΔH values smaller for $m = +2\cdot0$ than for $m = -2\cdot0$. In other words there will be greater back-donation from the chromium atom to the empty π-orbitals of the C_6H_5X system in the case where $m = +2\cdot0$ than in that where $m = -2\cdot0$. We conclude from these arguments that whatever the direction of net flow of charge in these complexes there will be a greater charge-transfer to the chromium atom for an electron-donating than for an electron-accepting group. We predict, for example, that for complexes containing such strongly electron-attracting groups as nitro a considerable increase in ν(C–O) should occur. To date, such complexes have not been obtained.

It should be stressed that neither the chloro- nor the amino-substituent (see below) is directly comparable with the two extreme cases of the above theory. However, similar calculations can be made for the chlorine atom, by taking $m = +2\cdot0$ and allowing for the fact that chlorine utilizes a $3p_\pi$-orbital.[8] The required overlap integrals are available from the above references, save for $S(3p_\pi 4p_\pi)$ which was obtained by interpolation between the values of $S(3p_\pi 3p_\pi)$ and $S(3p_\pi 5p_\pi)$ obtained from the relevant master formulæ. The resultant group overlap integrals are very close to those given in Table 2, and our conclusions are valid, therefore, for the chloro-substituent. Similarly, the case of the amino-group can be simulated by taking $m = +0\cdot20$ and $n = 0\cdot70$.[8] In this case it is found that the interactions for the $1a_1$- and $2a_1$-orbitals lie close to those for $m = -2\cdot0$, $n = 1\cdot0$, that the interaction of the $3a_1$-orbital is very small, and that the interactions of $4a_1$ and $5a_1$ lie close to those for the case where $m = +2\cdot0$ and $n = 1\cdot0$. We conclude, therefore, that the amino-group lies between the two extreme cases of Table 2, but nevertheless that there is greater charge-transfer to the chromium atom than with the chloro-substituent. It is also apparent from Table 2 that the general theory is equally valid for the case where $n = 1\cdot80$ as for that where $n = 1\cdot00$.

The above conclusions based on the molecular-orbital theory of these complexes support a more naïve chemical approach, which considers the complex to be equivalent to a conjugated system. The transmission of electronic effects through such systems containing both π-orbitals and central metal orbitals is then seen to be similar to those observed in simple conjugated molecules.

Comparison with Experiment.—In a complex containing carbonyl groups as simple ligands, any negative charge accumulated on the central metal atom will be dispersed in accordance with the Pauling electroneutrality principle by back-donation to the carbonyl groups. This donation will increase the metal–carbon bond order and lower the carbon–oxygen bond order and hence decrease the carbonyl stretching frequencies. Accordingly, the carbonyl frequencies of a number of substituted complexes π-$X{\cdot}C_6H_5Cr(CO)_3$ were measured in solution and compared with those of the unsubstituted complex and of hexacarbonylchromium. The measurements were made on solutions in cyclohexane, chloroform, carbon tetrachloride, and 1,2-dichloroethane. The bands were in general quite sharp, but a lower frequency was often split for the substituted compounds; the splitting is presumably due to the lifting of the degeneracy in the trigonal $(CO)_3$ grouping in the presence of a substituent (see Fig. 1). Where comparison is available, the results agree well with those of Fischer;[3] the maximum difference is 2 cm.$^{-1}$ and this is probably the limit of accuracy of the measurements. The results are given in Table 3.

It is obvious that, independently of the solvent and of the type of band, the C–O frequencies ν(C–O), lie in the sequence $Cl > H > NH_2 > NMe_2$, which is in agreement with the above theoretical predictions; that is, the greater the electron-donating power of the

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[8] Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5243.

TABLE 3.

Carbonyl frequencies (± 2 cm.$^{-1}$) of $Cr(CO)_6$ and arene–$Cr(CO)_3$ complexes

Solvent	$Cr(CO)_6$	$Cl{\cdot}C_6H_5Cr(CO)_3$	$(C_6H_6)Cr(CO)_3$	$H_2N{\cdot}C_6H_5Cr(CO)_3$	$Me_2N{\cdot}C_6H_5Cr(CO)_3$
C_6H_{12}	1987	1992	1984	1974	1969
		1930, 1926	1916	1902	1895, 1889
CCl_4	1988	1990	1983	1971	1966
		1925, 1923	1910	1895	1887
$CHCl_3$	1984	1985	1977	1965	1959
		1914	1900	1884	1876
$C_2H_4Cl_2$	1982	1980	1972	1959	1956
		1905	1892	1874	1866

substituent, the greater the charge-transfer to the chromium atom and hence the lower the carbonyl frequency. Attention has already been drawn by Fischer[3] to the correlation between the carbonyl stretching frequency and the dipole moment of a complex;[9] this correlation further supports our theory.

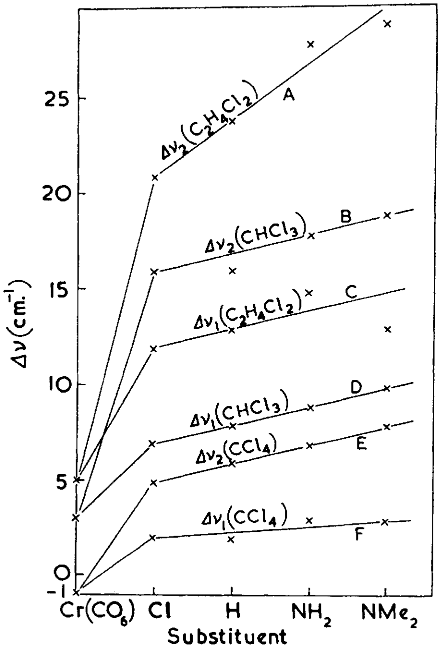

FIG. 2. Solvent effects on C–O frequencies.

A, $\Delta\nu_2(C_2H_4Cl_2)$. B, $\Delta\nu_2(CHCl_3)$.
C, $\Delta\nu_1(C_2H_4Cl_2)$. D, $\Delta\nu_1(CHCl_3)$.
E, $\Delta\nu_2(CCl_4)$. F, $\Delta\nu_1(CCl_4)$.

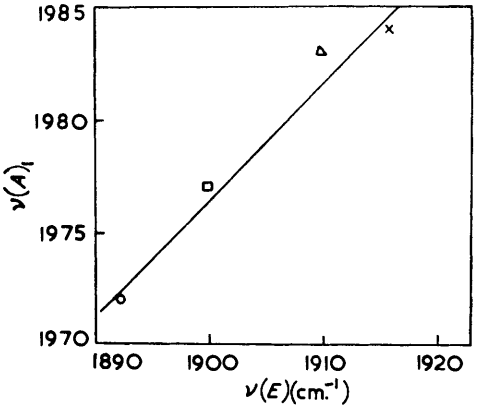

FIG. 3. Relation of carbonyl frequencies.
×, Cyclohexane; △, CCl_4; □, $CHCl_3$;
○, $C_2H_4Cl_2$.

Solvent Effects.—Nyholm and his co-workers[10] drew attention to the effect of solvents upon the carbonyl stretching frequencies of both simple and substituted metal carbonyls. For example, in complexes of the type $MD(CO)_4$, where D is *o*-phenylenebisdimethylarsine, the carbonyl frequency is far more sensitive to the polarity of the solvent than it is with simple carbonyls. The effect was considered as being probably due to a dipole–dipole type of interaction, so that increasing back-donation to a carbonyl group increases the solvent effect. We have used the same criterion to corroborate the charge effects in the complexes considered above, as shown in Table 3.

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[9] Randall and Sutton, *Proc. Chem. Soc.*, 1959, 93.

[10] Barraclough, Lewis, and Nyholm, *J.*, 1961, 2582.

The frequency shifts of the different carbonyl bands for cyclohexane and the other solutions are given in Fig. 2. Although the differences are sometimes within experimental error the same trend is observed for all the frequencies and supports the conclusions based on their absolute positions. It is interesting that the solvent effect is greater for the degenerate than the totally symmetric mode.

It follows, then, that the solvent effect is a useful measure of the charge distribution in these complexes and further supports the theoretical predictions. Direct comparison with the metal carbonyl is not strictly valid, but it is noteworthy that for all the complexes the solvent effect is greater than for the simple carbonyl.

The above results also support a theory of solvent effects proposed by Pullin,[11] according to which the frequencies ν_r and ν_s of two vibrational modes of a molecule in a series of non-polar solvents should be linearly related, since all contributions to them are assumed proportional to a solvent function. This function is closely related to the term $\frac{2(\varepsilon - 1)}{2\varepsilon + 1} \cdot \frac{1}{a^3}$ derived for a model of solute–solvent interactions in which the solute molecule is considered as a point dipole at the centre of a spherical cavity of radius a in a solvent of dielectric constant ε. The plot of $\nu(A_1)$ against $\nu(E)$ in Fig. 3 for the unsubstituted complex supports the argument; the effect of increasing polarity of solvent does not apparently lead to much error in this case. Similar linearity is observed for the substituted complexes.

Experimental.—The tricarbonylarenechromium complexes were prepared by Nicholls and Whiting's method.[12] Deoxygenation of solvents and the use of reaction temperatures below 130° greatly reduced the decomposition of the complex during reaction. The compounds were purified by sublimation or by recrystallization from dry ether. M. p.s agreed with those of the above authors save for the dimethylaniline complex (found 138—139°, instead of 145—146°). Cyclohexane was distilled through a 12 ft. column under nitrogen and the remaining solvents were purified by standard methods.[13] The infrared spectra were measured on a Perkin–Elmer 21 instrument, with lithium fluoride optics, for 10^{-3}—10^{-4}M-solutions.

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[11] Pullin, *Proc. Roy. Soc.*, 1960, *A*, **255**, 39.
[12] Nicholls and Whiting, *J.*, 1959, 551; 1960, 469.
[13] Weissberger, " Techniques of Organic Chemistry," Vol. VII, Interscience Publ., Inc., New York, 1955.