**507. *Molecular-orbital Theory of Organometallic Compounds.***
Part V.*[1] *Far-infrared Spectra of the Tricarbonylarenechromiums

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The far-infrared spectra of a series of substituted tricarbonylarene-chromiums is discussed in terms of simple molecular-orbital theory developed previously for these molecules. For π-electron substituents $(\pm E)$, the trend in the metal–carbonyl stretching frequency is predicted correctly but inductive substituents show some anomalies. Neither the bending modes nor the ring–metal stretch can be correlated with theory.

In Part III[2] of this Series, we discussed the transmission of electronic effects from a substituent (X) on the arene moiety through the metal atom in complexes of the type π–$XC_6H_5Cr(CO)_3$. The application of simple molecular-orbital theory to such complexes showed that they could be regarded as conjugated systems with transfer of electron density from the substituent to the C–O bond of the terminal carbonyl ligands. In simple resonance terminology, an electron-donating group X will favour the canonical structure (B) in preference to (A) and thus result in a lower carbonyl stretching frequency than that of the unsubstituted compound.

$$\ddot{\underset{\text{(A)}}{X}}\text{–M–C}\!\equiv\!\text{O} \longleftrightarrow \underset{\text{(B)}}{^+X}\text{=M=C=O}^-$$
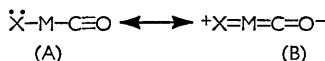
A detailed study[2] of the terminal carbonyl frequencies and of their solvent effects substantiated these arguments. It also follows from the above theory that an electron-donating substituent should not only decrease the carbonyl bond order but also increase the metal–carbonyl bond order and hence increase any related metal–carbon stretching frequency. In view of these theoretical arguments we commenced an investigation of the far-infrared spectra of a series of substituted tricarbonylarenechromiums to test our molecular-orbital predictions.

Table 1 lists the infrared-active modes of the unsubstituted complex in which the frequency numbering is identical with that of Fritz and Manchot.[3] Column three lists

TABLE 1
Infrared-active modes of $C_6H_6Cr(CO)_3$

C_{3v}	$C_6H_6Cr(CO)_3$	C_6H_6–$Cr(CO)_3$	$Cr(CO)_3$	$\delta(CCrC)$	$\delta(CrCO)$	$\nu(CrCO)$	$\nu(CO)$
A_1	10	ν_{21}	4	ν_{26}	ν_{31}	ν_{25}	ν_{29}
E	17	ν_{23}, ν_{24}	5	ν_{28}	ν_{34}, ν_{33}	ν_{27}	ν_{30}

the metal–ring frequencies, ν_{21}, ν_{23}, and ν_{24}. The frequencies associated with the $Cr(CO)_3$ fragment may be considered to be of four types; first, those involving deformation of C–Cr–C angles, $\delta(C$–Cr–$C)$, secondly, those involving deformation of Cr–C–O angles, $\delta(Cr$–C–$O)$, thirdly, those involving metal–carbon bond stretching, $\nu(Cr$–$CO)$, and finally, the carbonyl stretching modes, $\nu(C$–$O)$, which have been discussed in Part III.[2] The

[1] Part IV, D. A. Brown, *J.*, 1963, 4389.
[2] D. A. Brown and H. Sloan, *J.*, 1962, 3849.
[3] H. P. Fritz and J. Manchot, *Spectrochim. Acta*, 1962, **18**, 171.

frequencies observed for these compounds in the region 280—650 cm.$^{-1}$ are given in Table 2 for both Nujol mull and potassium bromide.

TABLE 2
Far-infrared spectra of substituted tricarbonylarenechromiums

$\pi-C_6H_5XCr(CO)_3$

X	ν_{33}, δ(CrCO)	ν_{34}, δ(CrCO)	ν_{25}, ν(Cr–CO)	ν_{21}, ν(Cr–ring)
Cl	638	546	483	300
H	646	540	487	296
Me	645	548	485	298
NH₂	645	538	491	295
p-Tolyl	646	536	489	301

(Measured in KBr discs)

X	ν_{33}, δ(CrCO)	ν_{25}, ν(Cr–CO)	ν_{25}, ν(Cr–CO)	ν_{21}, ν(Cr–ring)
Cl	626	540	478	301
H	634	533	484	297
Me	631	542	483	300
NH₂	634	546	489	297
p-Tolyl	631	531	487	302
NHMe	634	529	487	296
NMe₂	634	537	486	300

(Measured in Nujol mull)

DISCUSSION

Comparison of our results with those of previous workers [3-5] can be made only for the benzene complex. Agreement is satisfactory for the bands at 634, 533, and 484 cm.$^{-1}$ in Nujol, although these bands appear shifted to higher wavenumbers when measured in potassium bromide, with the magnitude of the shift increasing with wavenumber. However, in both media the relative order with substituent remains unchanged. Fritz and Manchot [3] reported a weak band at 306 cm.$^{-1}$ which they assigned to ν_{28}, δ(C–Cr–C), a deformation mode, and a stronger band at 298 cm.$^{-1}$ which was assigned to ν_{21}, ν(Cr–ring), a metal–ring stretching mode. With the resolving power of our instrument, we observed only the stronger band which we have also listed as ν_{21} in Table 2. As discussed previously,[3,4] the far-infrared spectral region may contain the above four types of vibrational mode. However, we agree with Adams [4] that analogy with the parent hexacarbonyl-chromium suggests that bending modes of the type δ(CCrC) will probably lie below the region under observation and so are not likely to be present in our spectra although, in the absence of a complete normal co-ordinate analysis, any assignment must be regarded as speculative. Fritz and Manchot [3] assigned the band at 484 cm.$^{-1}$ in tricarbonylbenzene-chromium to ν_{26} which involves deformation of the C–Cr–C angles and considered the band at 533 cm.$^{-1}$ to be a stretching metal–carbon mode, that is ν_{25}. However, Adams, again arguing by analogy with the parent hexacarbonylchromium in which all the M–CO stretching frequencies, ν(M–CO), lie below 500 cm.$^{-1}$, suggested that the above assignment is incorrect and that the 484 cm.$^{-1}$ band be assigned to ν_{25}, ν(Cr–CO), the totally-symmetric stretching mode of the Cr–C$_3$ group. Similarly, he assigned the band at 533 cm.$^{-1}$ to ν_{34}, δ(CrCO)e, a doubly-degenerate bending mode. Adams suggested further that the band at 306 cm.$^{-1}$ be assigned to ν_{27}, ν(CrCO)e, the doubly-degenerate metal–carbon stretching frequency.

Examination of Table 2 shows that for all bands, except the 484 band, there is no obvious correlation with the electronic nature of the substituent X. For this band, however, the variation in frequency is of the type predicted by simple molecular-orbital theory. To estimate the theoretical effect quantitatively, we have calculated the variation in the force constants of the C–O bonds, k(C–O), in these complexes by the approximate method due to Cotton.[6] For strict comparison, the carbonyl frequencies measured in potassium

[4] D. M. Adams, *J.*, 1964, 1771.
[5] R. E. Humphrey, *Spectrochim. Acta*, 1961, **17**, 93.
[6] F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702.

bromide by Fischer [7] rather than our own solution values were employed.   Cotton showed that an approximately linear relationship exists between k(C–O) and the C–O bond order, n(C–O), with a slope Δk(C–O)/Δn(C–O) of 6·8 for a large range of carbonyl complexes; the variation of C–O bond order in the tricarbonylarenechromiums with substituent was then calculated taking the unsubstituted compound as reference.   The values are given in column three of Table 3.

TABLE 3

Force constant–bond order changes

X	(C–O) (cm.$^{-1}$)		k(C–O) (mdynes/Å)	n(C–O)	n(M–C)
	A_1	E			
Cl	1977	1886	12·08	+0·02	−0·02
H	1971	1874	11·95	0	0
Me	1961	1871	11·90	−0·01	+0·01
NH$_2$	1946	1864	11·76	−0·03	+0·03

On the assumption of a constant bond order from the metal atoms to ligands in these complexes, the expected change in metal–carbon bond order, n(M–C), is given in column four of Table 3.   Unfortunately, there is insufficient data available to construct a similar force constant–bond order curve for the Cr–C bond but the observed frequencies, ν_{25}, generally follow the trend in bond order, in agreement with the theory outlined above. Some discrepancies seem worthy of comment.   In both media, the values of ν_{25}, ν(Cr–CO), for the toluene and benzene complexes are very close, indicating that the inductive effect of the methyl group is only weakly transmitted across the metal atom.   A similar effect is observed in the values of ν_{25} for the aniline and N-methylaniline complexes.   Essentially the same conclusion may be drawn from our previous measurements of the C–O stretching frequencies in various solvents (Table 3; ref. 2); for example, the totally-symmetric carbonyl stretches for N-methylaniline, NN-dimethylaniline, and toluidine complexes are identical within experimental error when measured in cyclohexane.   The spectroscopic evidence suggests therefore that π-electron effects are strongly transmitted from the arene moiety across the metal atom in preference to inductive effects.

The lack of correlation between the bands at 634 and 533 cm.$^{-1}$ with the electronic nature of the substituent is confirmation of their assignment to bending modes, δ(CrCO), since no direct correlation between bond order and frequency is to be expected for such modes.   The lack of correlation between the band at 297 cm.$^{-1}$ and substituent effect is disappointing since ν_{21}, ν(Cr–ring), involves a simple metal–ring stretch and should be a measure of the metal–ring bond strength.   This frequency will be affected by both the electronic nature of the substituent and also its mass, and presumably for this reason no simple relationship is observed.

Although molecular-orbital theory has provided a satisfactory account of the transmission of electronic effects through the metal atom in these complexes one should mention one cautionary note.   Most spectral investigations of transition-metal complexes are based upon frequency effects such as are discussed in this Paper but it is very rare that in a complex molecule a frequency may be associated rigorously with one type of bond.   A complete normal-co-ordinate analysis with evaluation of force constants is more reliable and it is to be hoped that with increasing studies of the far-infrared region force constants for metal–ligand bonds will soon become available.

Experimental.—The tricarbonylarenechromiums were prepared as previously [2] and were all of analytical purity.   The spectra were recorded on a Grubb–Parson DB4 double-beam spectrometer for both Nujol mulls and potassium bromide discs.

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[7] R. D. Fischer, *Chem. Ber.*, 1962, **93**, 165.