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VIBRATIONAL SPECTRA AND BONDING IN METAL CARBONYLS
VI. EVIDENCE FOR A π-INTERACTION BETWEEN MANGANESE PENTACARBONYL AND THE PERFLUOROMETHYL GROUP*

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INTRODUCTION

It has been recognized for some time, on the basis of chemical behavior (see *e.g.* refs. 1 and 2, and references therein) that, where transition metal atoms in low formal oxidation states are concerned, metal to perfluoroalkyl bonds are more stable and thus, presumably, thermochemically stronger than metal to alkyl bonds.

It was observed, more or less simultaneously, by King and Bisnette[3] and by Cotton and McCleverty[4] that in several perfluoromethyl compounds of transition metals the C–F stretching frequencies are lower, by the order of 100 cm^{-1}, than the frequencies found in perfluoromethyl halides. Both groups of workers ascribed this (see also ref. 5) to π-interaction involving the filled d_π orbitals of the metal and the empty antibonding C–F orbitals. Detailed formulation can be made either in valence bond[3,5] or molecular orbital[4,5] terms. By either interpretation, it is also to be expected that the C–M bond would be strengthened in rough proportion to the weakening of the C–F bonds.

Structural data showing that the bonds in perfluoroalkyl compounds are short relative to those in the normal alkyl compounds has been provided in several cases[6–10].

The purpose of this paper is to describe in detail an investigation of the infrared spectrum of $CF_3Mn(CO)_5$ in which a calculation of the C–F stretching force constant is made. This provides a semi-quantitative measure of the magnitude of the multiple bonding effect.

EXPERIMENTAL

Gas phase spectra

A cell with a path length of 9.5 cm was used. Rock salt windows were employed from 3000 to 600 cm^{-1} and polyethylene windows from 600 to 250 cm^{-1}. Several small crystals (30–50 mg) of $CF_3Mn(CO)_5$ were placed in the cell prior to evacuation. They were kept from subliming away during evacuation by cooling the small area of the cell wall where they rested with solid CO_2. The spectra were then recorded at the equilibrium vapor pressure after the cell and its contents had come to equilibrium at about 25°. The grating spectrometer used was a Perkin–Elmer Model 521.

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25°. The grating spectrometer used was a Perkin–Elmer Model 521. The uncertainties in the frequencies are believed to be ±2 cm^{-1}.

RESULTS

The spectrum of $CF_3Mn(CO)_5$ has been measured and interpreted in the CO stretching region in considerable detail previously[11]. On the basis of this work, the following assignment of the three infrared-active fundamental bands is well substantiated:

$$A_1^{(2)}: 2135\ \mathrm{cm}^{-1} \quad E: 2042\ \mathrm{cm}^{-1} \quad A_1^{(1)}: 2020\ \mathrm{cm}^{-1}$$

These previous studies have all been done on solutions and the frequencies quoted above were recorded in a hydrocarbon solution.

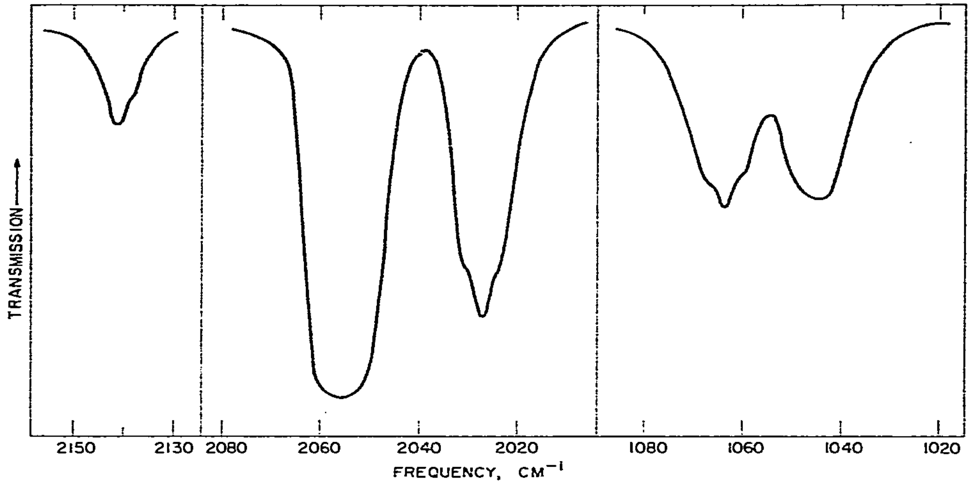

Fig. 1. Portions of the infrared spectrum of gaseous $CF_3Mn(CO)_5$ recorded in a 9.5 cm cell at the equilibrium pressure over the solid compound at about 25°.

The infrared spectrum of the compound has now been recorded in the gas phase. Parts of it are shown in Fig. 1 and numerical values of all the observed gas phase frequencies are listed in Table 1. It is clear in Fig. 1 that two of the CO stretching bands, the highest and lowest, have envelopes which are very similar to each other but different from that of the middle band. This observation may be explained in the following way.

Despite the fact that the $CF_3Mn(CO)_5$ molecule does not actually contain any axis of three-fold or higher symmetry and, therefore, is not a true symmetric top, it is an accidental oblate symmetric top with $I_A = I_B = 903 \neq I_C = 822$ atomic mass units $\times Å^2$. According to Gerhard and Dennison's results[12] a rigid molecule with these moments of inertia should have a fairly sharp Q branch for both the parallel (A_1)-type bands and the perpendicular (E)-type bands. However, it must be remembered that a number of factors, such as anharmonicity of the vibrations, the fact that this molecule does not have rigorous axial symmetry and failure of the rigid rotor approximation[13] in such a complex molecule, will tend to broaden the Q

TABLE 1

OBSERVED FREQUENCIES AND SUGGESTED ASSIGNMENTS IN GASEOUS $CF_3Mn(CO)_5$

Frequency (cm^{-1})	*Band type*[a]	*Assignments*[b]
2142 s	$\parallel$	Sym. str. of radial CO's
2055 s	$\perp$	Degen. str. of radial CO's
2027 s	$\parallel$	Str. of axial CO
1063 m	$\parallel$	Sym. C–F str.
1045 m	$\perp$	Degen. C–F str.
700 vw		Sym. CF_3 def.
665 w		(M–CO wagging modes)
656 m		
~600 m		
579 w		
555 m		Degen. CF_3 def.
543 (sh)		?
443 s		(Mn–C stretches)
~420?		

[a] Only for the first five bands were the band shapes considered indicative of band type, for reasons discussed in the text. [b] Those in parentheses are considered *very* tentative.

branch for perpendicular bands, but not for parallel ones. Thus, bands with spiky centers, like those found at highest and lowest frequencies in the CO stretching region are most likely to be $\parallel$ bands, while a band lacking this feature, as does the middle band in the CO stretching region, should be a $\perp$ band. These conclusions are in complete accord with the assignments made previously, and cited above, and, in fact, provide strong independent support for the assignments.

Turning now to the two C–F stretching bands, at 1063 and 1045 cm^{-1}, it is seen that the former has the same $\parallel$-band appearance as do the $\parallel$-bands in the CO stretching region while the latter one lacks evidence of a pronounced *Q* branch and thus appears to be a $\perp$ band. The conclusion that $\nu(\parallel) > \nu(\perp)$ is valuable since otherwise, by comparison with results for other CF_3X molecules (see Table 2), the opposite assignment would have seemed "obvious". We have thus made the surprising observation that the symmetric C–F stretching mode has changed very little in frequency from the characteristic range for "typical" CF_3X molecules, while the frequency of the mode of *E* symmetry has decreased some 150 cm^{-1}.

TABLE 2

ASSIGNMENTS OF SOME BANDS FOR $CF_3Mn(CO)_5$ COMPARED WITH ASSIGNMENTS IN OTHER CF_3X MOLECULES

Description	*Symmetry type*[a]	*Frequencies* (cm^{-1})		
		$CF_3Mn(CO)_5$	CF_3I[b]	CF_3Br[b]
C–F str.	a_1	1063	1076	1087
C–F def.	a_1	700	743	762
C–X str.	a_1	(300)[c]	284	348
C–F str.	e	1045	1185	1207
C–F def.	e	555	539	548
C–X bend	e	(270)	260	297

[a] Referred to the assumed local symmetry, C_{3v}, of the CF_3 group. [b] For molecules in gas phase, taken from ref. 14. [c] Not observed. Postulated for use in force constant calculation as explained in text.

The assignment of the bands observed at 700 and 555 cm^{-1} to the symmetric and degenerate CF_3 deformation modes respectively is made solely on the comparison of these frequencies with frequencies similarly assigned in other CF_3X molecules as shown in Table 2.

DISCUSSION

In order to extract a semiquantitative estimate of the extent to which the C–F bonds in $CF_3Mn(CO)_5$ are weakened relative to those in other CF_3X molecules, an approximate normal coordinate analysis, leading to a C–F stretching force constant, was carried out. Since the frequencies of the C–F stretching modes vary relatively little on changing X in the series Cl, Br, I and since I matches the $Mn(CO)_5$ group most closely in mass and in electronegativity, the comparison was made between CF_3I and $CF_3Mn(CO)_5$.

TABLE 3

SYMMETRY COORDINATES FOR THE CF_3X GROUP[a]

$$a_1 \left\{ \begin{array}{l} S_1 = \frac{1}{\sqrt{3}}(\Delta_1+\Delta_2+\Delta_3) \\ S_2 = \frac{1}{\sqrt{6}}(\Delta\alpha_{12}+\Delta\alpha_{13}+\Delta\alpha_{23}-\Delta\beta_1-\Delta\beta_2-\Delta\beta_3) \\ S_3 = \Delta_4 \\ R^b = \frac{1}{\sqrt{6}}(\Delta\alpha_{12}+\Delta\alpha_{13}+\Delta\alpha_{23}+\Delta\beta_1+\Delta\beta_2+\Delta\beta_3) \end{array} \right.$$

$$e \left\{ \begin{array}{l} S_{4a} = \frac{1}{\sqrt{6}}(2\Delta_1-\Delta_2-\Delta_3) \\ S_{4b} = \frac{1}{\sqrt{2}}(\Delta_2-\Delta_3) \\ S_{5a} = \frac{1}{\sqrt{6}}(\Delta\alpha_{12}+\Delta\alpha_{13}-2\Delta\alpha_{23}) \\ S_{5b} = \frac{1}{\sqrt{2}}(\Delta\alpha_{12}-\Delta\alpha_{13}) \\ S_{6a} = \frac{1}{\sqrt{6}}(2\Delta\beta_1-\Delta\beta_2-\Delta\beta_3) \\ S_{6b} = \frac{1}{\sqrt{2}}(\Delta\beta_2-\Delta\beta_3) \end{array} \right.$$

[a] The internal coordinates are defined in the text. [b] R is a redundant coordinate of a_1 symmetry.

Symmetry coordinates (Table 3) were written in the conventional way, employing internal coordinates defined as follows: Δ_1, Δ_2, Δ_3, changes in C–F bond lengths; Δ_4 change in C–X bond length; β_1, β_2, β_3, changes in the X–C–F_i ($i = 1, 2, 3$) angles; α_{12}, α_{23}, α_{13}, changes in the F_i–C–F_j angles. C_{3v} symmetry was assumed. A force field previously described[14] was used. All of the interaction force constants were transferred from the tabulation in ref. 14 except for the C–F stretch–C–F stretch interaction constant k(CF–CF). The latter and the four bending and stretching force constants were varied to obtain the best fit to the observed frequencies. The angle β was taken as 109° in each case.

The constants other than k(CF) and K(CF–CF) have little value physically due to the uncertainty in assigning the fundamentals other than those due primarily to C–F stretching, though reasonable values were obtained. The only reason for including these lower frequencies and related force constants was to improve the reliability of the k(CF). The reasonable assumption was made that the use of even approximate values for the lower frequencies and the other force constants would lead to better values of k(CF) and k(CF–CF) than could be obtained by setting all other force constants and all frequencies other than the CF stretches equal to zero.

The calculated values of k(CF) and k(CF–CF) are listed in Table 4.

TABLE 4

CALCULATED FORCE CONSTANTS (md./Å.)

k	CF_3I	$CF_3Mn(CO)_5$
k(CF)	5.9	4.6
k(CF–CF)	0.64	0.50

The calculated magnitude of the change in k(CF) from CF_3I to $CF_3Mn(CO)_5$ is sufficiently large that there can be no question that a significant change really occurs even though the actual magnitude may be somewhat in error. Indeed the quantitative reliability of the calculated change might arouse misgivings *not* because it is *too small* to be impressive but because it is rather larger than might be expected. Making the rough assumption, which is probably not seriously in error, that in the bond order range 0–1 the stretching force constant is linearly proportional to bond order, the decrease of k(CF) from 5.9 to 4.6 represents about a 20% decrease in C–F bond orders. Since there are three C–F bonds, this would correspond to a very substantial increase in the F_3C–Mn bond strength. If it is assumed that the gross loss in C–F bond energy must be approximately equalled or exceeded by a gain in F_3C–Mn π-bond energy, we get, using 116 kcal/mole for the normal C–F bond energy, an F_3C –Mn π-bond energy of $\sim$70 kcal/mole, which seems incredibly high.

It is possible that the F_3C–Mn σ bond might be weaker than the H_3C–Mn bond due to the electron-withdrawing effect of the fluorine atoms so that the calculated 70 kcal/mole of π-bond energy would not entirely represent an overall increase in C–Mn bond energy in $CF_3Mn(CO)_5$ over that in $CH_3Mn(CO)_5$. Even so, it does not appear that the foregoing simple analysis or the numerical values involved or both can be taken literally. One can only say that the decrease in k(CF) shows that there is a significant interaction of CF_3 with $Mn(CO)_5$ which weakens the C–F bonds and that the $d_\pi \rightarrow \sigma^*$ mechanism which has previously been proposed is a plausible explanation for this.

Solvent effects

The present study sheds further light on the problem of how solvents influence CO stretching frequencies and hence the important problem of whether comparisons between solution frequencies for different molecules are meaningful. $CF_3Mn(CO)_5$ is now added to the rather short list of carbonyl molecules—other than unsubstituted, mononuclear carbonyls—for which gas phase data are available. Molecules of the $XMn(CO)_5$ type are particularly interesting because they have two kinds of CO groups as well as several different vibrational modes. The data assembled in Table

5 show that the frequency shifts for $CF_3Mn(CO)_5$ from vapor to cyclohexane solution are (*a*) all downward (*b*) all relatively small, but (*c*) not equal, *viz.*, 7, 13 and 7 cm^{-1}. Still, if an average shift of 10 cm^{-1} were assumed for all bands no serious error would be introduced.

Of greater interest is the comparison of the shifts for $CF_3Mn(CO)_5$ with those for the homologous molecule $HMn(CO)_5$. Although the gas phase spectrum of $HMn(CO)_5$ is very complex[15,16] because of rotational structure and could not be assigned when reported, it is possible with the help of the subsequent analysis of the solution spectrum[17] to examine the original traces and identify the band centers of the fundamentals. These gas phase frequencies, together with Huggins and Kaesz' frequencies for cyclohexane solution are also given in Table 5. Again, the shifts are (*a*) all downward, (*b*) relatively small, but (*c*) not equal. However, band for band, they are essentially the same for both compounds. Hence, frequency differences between the two compounds in the gas phase are approximated very closely by the differences measured on cyclohexane solutions.

TABLE 5

COMPARISON OF GAS AND SOLUTION SPECTRA OF $HMn(CO)_5$ AND $CF_3Mn(CO)_5$

Mode	$\nu[CF_3Mn(CO)_5]$			$\nu[HMn(CO)_5]$			$\nu[CF_3Mn(CO)_5]-\nu[HMn(CO)_5]$	
	Cyclohexane[a]	*Gas*	Δ^b	*Cyclohexane*[c]	*Gas*[d]	Δ^b	*Cyclohexane*	*Gas*
$A_1^{(2)}$	2135	2142	7	2118	2125	7	17	17
E	2042	2055	13	2016	2029	13	26	26
$A_1^{(1)}$	2020	2027	7	2007	2016	9	13	11

[a] From ref. 11. [b] Gas phase frequency minus solution frequency. [c] From ref. 17. [d] From refs. 15 and 16.

Interpretation of CO stretching force constants

If we assume that the frequency differences for any two $XMn(CO)_5$ compounds which would be found in the gas phase are accurately represented by the differences measured on cyclohexane solution, it is then valid to examine and attempt to interpret the differences in the force constants calculated[11] from hydrocarbon solution spectra for $CF_3Mn(CO)_5$ and $BrMn(CO)_5$. These force constants (md./Å), as given in Table 6 of ref. 11, are:

$CF_3Mn(CO)_5$: k_1, 16.58; k_2, 17.34 $BrMn(CO)_5$: k_1, 16.22; k_2, 17.44

The choice of $BrMn(CO)_5$ for comparison with $CF_3Mn(CO)_5$ is based on the similarity of Br to CF_3 in (1) electronegativity, (2) size and (3) mass. Estimates of the electronegativity of CF_3 (and other perfluoroalkyl) groups vary somewhat, but a figure of about 3.3 is indicated[18], which may be compared with a value of about 3.0 for Br. The van der Waals radius of Br is about 1.95 Å while the van der Waals contact radius for CF_3 should be about 0.15 Å larger than that for CH_3, namely about 2.15 Å (see ref. 19 for source material). The masses are 80 (Br) and 69 (CF_3).

It can be seen that k_2 (which pertains to the four equatorial CO groups) is virtually identical in $BrMn(CO)_5$ and $CF_3Mn(CO)_5$; a difference of only 0.1 unit is of borderline significance since an uncertainty of 3 cm^{-1} in the measurement of a frequency leads to an uncertainty of about 0.05 md./Å in the corresponding force constant. However, the k_1's differ quite significantly, *viz.*, by about 0.36 md./Å. These results are in good qualitative accord with the proposed $d_\pi \rightarrow \sigma^*$ process. Any difference in the inductive effects of the groups CF_3 and Br in $CF_3Mn(CO)_5$ and $BrMn(CO)_5$ would be expected to influence both types of CO in the same way. Besides, the difference in the electronegativities of CF_3 and Br is small. However, the type of $d_\pi \rightarrow \sigma^*$ donation proposed should be markedly directional in its effect. The two d_π orbitals from which the CF_3 group is postulated to withdraw electrons are both used in metal–carbon π-bonding to the one CO *trans* to CF_3. Each of these d_π orbitals is shared by two of the equatorial CO groups and, besides, each equatorial CO group interacts with a third d_π orbital which cannot have any π-interaction with the CF_3 group. Hence, the $d_\pi \rightarrow \sigma^*$ interaction should raise k_1 much more than k_2, which is what we observe. A purely inductive effect would be isotropic.

SUMMARY

The infrared spectrum of $CF_3Mn(CO)_5$ has been investigated in the gas phase. The C–F stretching bands are found at 1045 and 1063 cm^{-1} and the shapes of the band envelopes indicate that these are the frequencies of the e and a_1 modes, respectively. Using these and other data, a calculation of the C–F force constants in $CF_3Mn(CO)_5$ and CF_3I was made, the results (in md./Å) being 4.6 and 5.9 respectively. This very substantial reduction in $CF_3Mn(CO)_5$ is attributed to C–F bond weakening by overlap of filled metal d_π orbitals with C–F σ^* antibonding orbitals.

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