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The Infrared Spectra of Pentacarbonyl Fluoroalkylmanganese and -rhenium Complexes in the Carbonyl Stretching Region[1,2a]

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Received September 8, 1964

The carbonyl stretching frequencies of several pentacarbonyl fluoroorganomanganese and -rhenium complexes are reported, as well as those of some of their nonfluorinated analogs. Depending on the nature of the organic groups some of the complexes show four rather than the expected three fundamental CO absorptions. Possible reasons for this, and the splitting of the E modes, are discussed. The various force constants have been calculated.

This paper reports studies on the infrared spectra in the carbonyl stretching region of several recently prepared[1a,3] pentacarbonyl fluoroalkylmanganese and -rhenium complexes. The spectra of some related alkyl and aryl metal carbonyls, measured under identical conditions of high resolution, are also discussed.

A monosubstituted octahedral pentacarbonyl manganese or rhenium complex would have C_{4v} symmetry. Theory[4] predicts four carbonyl stretching frequencies ($2A_1 + E + B_1$). The two A_1 and E vibrations are both infrared and Raman active, the B_1 mode is Raman active only. Studies[5] on the infrared spectra of the compounds $M(CO)_5X$ [M = Mn, Tc, or Re; X = halogen] have essentially confirmed the group theory prediction, but in order to account for relative band intensity differences additional arguments have been invoked.[4,6,7] Moreover, it has been suggested[4] that if in a complex $M(CO)_5L$ [L = organic ligand] the L–M group lacks axial symmetry, all four fundamental vibrations would become infrared active and the degeneracy of the E mode would also be removed. Some indication that this might occur is provided by the reported[8] spectra of $CF_3COMn(CO)_5$ and $C_6H_5CO\text{-}Re(CO)_5$. Besides the three expected carbonyl stretching frequencies, additional bands were listed but no explanation of this phenomenon was advanced. Recently we noted[9] that if the infrared spectra of certain fluoroalkylmanganese pentacarbonyls (*e.g.*, $HCFClCF_2Mn(CO)_5$) having unsymmetrical organic groups were recorded in cyclohexane solution using a grating instrument, a splitting of the E absorption and the simultaneous appearance of the B_1 mode was detectable. This confirmation of Orgel's prediction[4] mentioned above prompted the more comprehensive study described herein.

Experimental

Prior to recording of the infrared spectra, all compounds were resublimed or recrystallized from pentane. Samples were prepared by taking about 1 mg. of complex and dissolving it in 1–5 ml. of solvent. If the solid did not dissolve immediately, the solution was centrifuged for 10–15 min. It was then placed in a 0.1-mm. sodium chloride solution cell and the spectrum obtained with a Perkin-Elmer 237 grating spectrophotometer producing a 0–10 mv. readout connected to an auxiliary Kent recorder having 9-in. chart paper. The latter was calibrated with carbon monoxide absorptions (86 mm. of chart paper corresponded to 100 cm.$^{-1}$); benzene (peak at 2211 cm.$^{-1}$) was used as an external standard. The resolution of the spectrophotometer in the region of interest is $1 \sim 2$ cm.$^{-1}$, while peak positions are accurate to ±1 cm.$^{-1}$ and are the mean of several determinations.

For spectra which showed $2A_1 + E$ modes, approximate force constants were calculated as previously described.[10] For the less symmetrical molecules, with spectra having additional absorptions, force constants were determined using principles discussed elsewhere.[10,11] Two extra force constants were introduced. One of the E vibrations was assumed to be essentially unchanged by the asymmetric side chain while the other was modified either sterically and/or electronically (Figure 1).

Discussion

The carbonyl stretching frequencies of all the compounds studied are given in Table I. The results confirm that with many of the complexes, all of the fundamental CO stretching frequencies are infrared active, and the E type mode is no longer doubly degenerate. Evidently with these compounds the over-all symmetry of the molecules is not as high as C_{4v}. Complexes which show the effect include those with acyl carbonyl groups as substituents, and some of those compounds in which a fluoroalkyl side chain has substituents on the carbon atoms other than fluorine. On the other hand, the more symmetrical compounds like $C_6F_5Mn(CO)_5$ do not show this splitting of the intense E mode and simultaneous appearance of the weak B_1 absorption. In the absence of free rotation about the methyl carbon–metal bond a compound like methylmanganese pentacarbonyl might well show the effect. It would appear that several factors besides the degree of substitution of the side chain determine

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(1) (a) Part XXIX of the series "Chemistry of the Metal Carbonyls." For Part XXVIII, see J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 93 (1965). (b) Also part IX of the series "Spectroscopic Studies on Organometallic Compounds." For Part VIII see E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

(2) (a) We are indebted to the donors of the Petroleum Research Fund, administered through the American Chemical Society, for support of the work described in this paper. (b) Department of Scientific and Industrial Research predoctoral student.

(3) (a) P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, **1**, 511 (1962); (b) J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometal. Chem.*, **2**, 119 (1964).

(4) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

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(6) M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962).

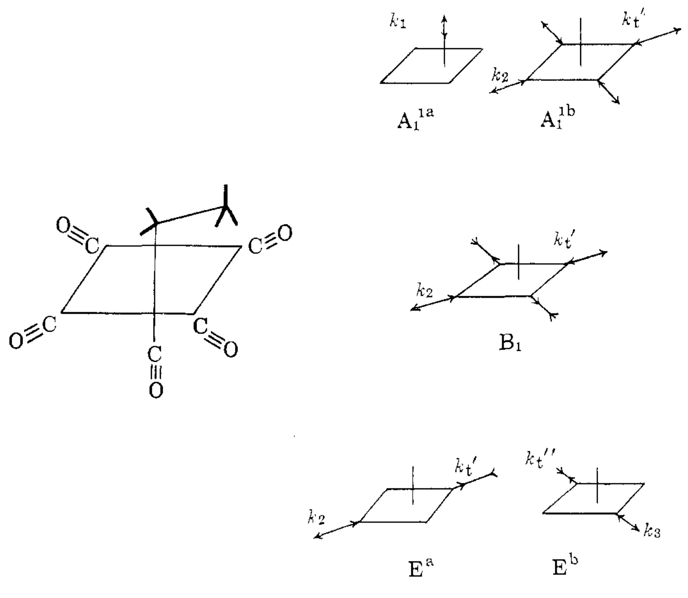
(7) M. A. El-Sayed, *J. Chem. Phys.*, **37**, 680 (1962).

(8) W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, **94**, 862 (1961).

(9) J. B. Wilford and F. G. A. Stone, *J. Organometal. Chem.*, **2**, 371 (1964).

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

(11) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955.



$$\begin{vmatrix} \mu k_1 - \lambda & 2\mu k_c \\ 2\mu k_c & \mu(k_2 + k_t' + 2k_c) - \lambda \end{vmatrix} = 0$$

$$\mu(k_2 + k_t' - 2k_c) - \lambda = 0$$

$$\begin{vmatrix} \mu(k_2 - k_t') - \lambda & 0 \\ 0 & \mu(k_3 - k_t'') - \lambda \end{vmatrix} = 0$$

Figure 1.—Secular equations and related information: (1) to make the equations for the A_1^{1b} mode self-consistent ($k_2 + k_t' = k_3 + k_t''$), (2) the approximations $\frac{1}{2}(k_t' + k_t'') = k_t = 2k_c$ and $\frac{1}{2}(k_t' - k_t'') = k_0$ are used. k_t' and k_t'' are nonequal interaction constants between pairs of *trans* CO groups. Other terms are as defined in ref. 10.

the over-all molecular symmetry, and hence whether additional bands are infrared active or not. Thus the compound $HCF_2CF_2Mn(CO)_5$ shows an E band splitting of 3 cm.$^{-1}$, whereas the apparently less symmetrical side chain in $CH_3CF_2CFClMn(CO)_5$ does not cause this complex to show more than $2A_1 + E$ modes.

We suggest that important factors responsible for the observed results are: asymmetry of the alkyl side chain, the presence of relatively large chlorine atoms on the β-carbon atoms, the α-carbon–metal distance, and internal rotation about the organic group–metal axis. It is important to realize that some of these factors are necessarily interdependent.

Compounds showing the largest splitting of the E vibrations all have large substituents on the carbon atom β to the metal. The presence of substituents on the α-carbon atom seems to have only a small effect. Thus the splitting for $HCFClCF_2Mn(CO)_5$ is 5 cm.$^{-1}$ while for $HCF_2CFClMn(CO)_5$ it is 2 cm.$^{-1}$. From Figure 1 it can be seen that substituents on the β-carbon atom could interact with one vibration of the four equatorial CO groups while leaving the other E vibration unaffected. The larger the substituents on the β-carbon atom the greater the effect would be. In agreement with this the largest E values are for the benzoyl and perfluorobenzoyl metal carbonyls.

That the α-carbon–metal distance is important is suggested by the fact that only one of the rhenium pentacarbonyls studied shows E band splitting *and* a B_1 mode, and this is the complex $HCCl_2CF_2Re(CO)_5$ with two chlorine atoms in the β-position. The manganese analog $HCCl_2CF_2Mn(CO)_5$ with an E band splitting of 6 cm.$^{-1}$ shows the effect more strongly. This is understandable since rhenium is larger than manganese with the result that in the rhenium compounds the organic group will be further away from the equatorial CO groups and will thus interact less strongly with them.

In comparing the spectra of manganese pentacarbonyls with their rhenium pentacarbonyl analogs it may also be necessary to take into consideration possible variation in the degree of noncoplanarity of the metal atom and the four radial CO groups. An X-ray crystallographic study[12] on the closely related manganese pentacarbonyl hydride has shown that the manganese atom and the four equatorial CO groups are not quite coplanar. Moreover, in manganese carbonyl itself, the equatorial CO groups of the $Mn(CO)_5$ moieties are 4° out of the plane.[13] A recent reexamination of the infrared spectrum of manganese pentacarbonyl hydride is of particular relevance.[14] At low concentrations only two principal bands ($A_1^{1a} + E$) appear, but at higher concentrations the A_1^{1b} mode becomes evident, along with other weaker absorptions. This property has been observed previously in the spectra of manganese and rhenium pentacarbonyl halides where certain of the relative differences in band intensities were attributed to noncoplanarity of the equatorial CO groups and the metal atom.[6] Irrespective of the validity of this explanation for relative differences in band intensities in the halide spectra, it is reasonable to assume that displacement of the metal atom from the plane of the four CO groups in manganese pentacarbonyl hydride or in complexes of the kind listed in Table I will lead to changes in the nature of the π-bonding orbitals and thus to electronic distortions during vibrations. There appears to be an effect which weakly activates the B_1 mode even in manganese pentacarbonyl hydride. Thus in the reported[14] spectrum there is a shoulder at 2044 cm.$^{-1}$ on

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[12] S. J. La Placa, J. A. Ibers, and W. C. Hamilton, *J. Am. Chem. Soc.*, **86**, 2289 (1964); *Inorg. Chem.*, **3**, 1491 (1964).

[13] L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

[14] D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2734 (1964).

TABLE I

OBSERVED CARBONYL STRETCHING MODES FOR FLUOROORGANOMANGANESE AND FLUOROORGANORHENIUM PENTACARBONYLS (CM.$^{-1}$)

Compound	Solvent	A_1^{1b}	B_1	E^b	E^a	A_1^{1a}	δE
$C_6F_5COMn(CO)_5$	C_6H_{12}	2125	2067	2042	2030	2017	12
$C_6H_5COMn(CO)_5$	C_6H_{12}	2114	2055	2021	2010	2002	11
	C_2Cl_4	2115	2054	2021	2010	2004	11
$C_2F_5COMn(CO)_5$	C_6H_{12}	2130	2069	2041	2036	2023	5
$HCCl_2CF_2Mn(CO)_5$	C_6H_{12}	2131	2072	2043	2037	2013	6
	C_2Cl_4	2132	2072	2042	2036	2013	6
	CCl_4	2133	2073	2042	2036	2014	6
$HCCl_2CF_2Re(CO)_5$	C_6H_{12}	2148	2072	2038	2035	2009	3
	C_2Cl_4	2147	2074	2037		2010	...[a]
	CCl_4	2147	2074	2037		2011	...[a]
	CS_2	...	2072	2033		2007	...[a]
	$CHCl_3$	2148	2077	2036		2014	...[a]
$HCFClCF_2Mn(CO)_5$	C_6H_{12}	2133	2072	2043	2038	2014	5
	C_2Cl_4	2132	2071	2042	2038	2014	4
	CCl_4	2133	2072	2040		2014	...[a]
	CS_2	2130	2071	2039	2035	2013	4
	$CHCl_3$	2134	2075	2040		2020	...[a]
$HCFClCF_2Re(CO)_5$	C_6H_{12}	2147	2076	2038		2011	...[b]
	C_2Cl_4	2147	2075	2037		2011	...[b]
	CS_2	...	2076	2035		2011	...[b]
	$CHCl_3$	2148	2077	2036		2014	...[b]
$HCF_2CFClMn(CO)_5$	C_6H_{12}	2132	2075	2045	2043	2014	2
$CH_3CF_2CFClMn(CO)_5$	C_6H_{12}	2133	...	2043		2011	0
$CH_3CF_2CF_2Mn(CO)_5$	C_6H_{12}	2134	...	2041		2012	0
	Gas phase	2137	...	2054	2052	2021	2
$CH_3CF_2CF_2Re(CO)_5$	C_6H_{12}	2148	...	2038		2008	0
$HCF_2CF_2Mn(CO)_5$	C_6H_{12}	2134	2073	2044	2041	2015	3
$HCF_2CF_2Re(CO)_5$	C_6H_{12}	2148	...	2039		2012	0
$CH_3(CF_2)_4Re(CO)_5$	C_6H_{12}	2150	...	2040		2015	0
$C_6H_5CF_2CF_2Mn(CO)_5$	C_6H_{12}	2130	...	2039		2011	0
$C_6F_5Mn(CO)_5$	C_6H_{12}	2130	...	2042		2011	0
$C_6H_5Mn(CO)_5$	C_6H_{12}	2114	...	2021		1997	0
$CH_3Mn(CO)_5$	C_6H_{12}	2109	...	2010		1989	0
	C_2Cl_4	2110	...	2010		1989	0
	CCl_4	2116	...	2011		1990	0
	CS_2	2109	...	2008		1986	0
	$CHCl_3$	2112	...	2011		1992	0
$CH_3Re(CO)_5$	C_6H_{12}	2125	...	2011		1981	0
	C_2Cl_4	2126	...	2011		1981	0
	CCl_4	2127	...	2012		1980	0
	CS_2	2123	...	2009		1978	0
	$CHCl_3$	2127	...	2013		1970	0

[a] No splitting observable due to broadening of peaks by solvent. [b] This compound may have a finite but nonmeasurable E band splitting.

the band labeled F. Using the force constant 16.93 mdynes/Å. given, the calculated position of the B_1 mode for the hydride is 2046 cm.$^{-1}$.[15] From the foregoing it seems possible that the intensities of the weak B_1 vibrations in the spectra of some of the compounds listed in Table I need not be due entirely to the presence of the organic substituent, except insofar as its asymmetry might induce changes in bonding within the complex leading to distortions. Moreover, in the absence of information to the contrary, there is no reason to assume that methylmanganese or methylrhenium pentacarbonyls have undistorted octahedral structures, or that rotation about the methyl carbon–metal bond is rapid. When the spectra of these two complexes were measured in more concentrated solution than was used to obtain the results given in Table I, very weak bands at 2034 and 2041 cm.$^{-1}$, respectively, appeared. Using force constants (Table II) of 16.8 and 16.9 mdynes/Å., the predicted positions of the B_1 modes for methylmanganese pentacarbonyl and methylrhenium pentacarbonyl are 2037 and 2043 cm.$^{-1}$, respectively, in excellent agreement with the observed weak absorptions.

It was qualitatively observed that in the rhenium compounds studied the high-frequency A_1^{1b} absorption was very much weaker than the E or A_1^{1a} absorptions. With the manganese complexes relative differences in band intensities are not as great. In this respect the spectra are similar to those of the pentacarbonyl halides.[6]

Because of the known importance of solvents on band widths and frequencies of carbonyl spectra,[16] measurements in the present study were made in several solvents. No significant frequency shifts were found,

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[15] In a private communication, Professor H. D. Kaesz has informed us that the shoulder observed at 2044 cm.$^{-1}$ in his spectrum can be readily resolved into a discrete maximum with slower scan and at higher concentration.

[16] C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2582 (1961).

TABLE II

FORCE CONSTANTS (MDYNES/Å.)[a]

Compound	k_1	k_2	k_3	k_c	k_0
$C_6F_5COMn(CO)_5$	16.39	17.20	17.30	0.257	0.049
$C_6H_5COMn(CO)_5$	15.90	17.01	17.10	0.324	0.044
$HCCl_2CF_2Mn(CO)_5$	16.29	17.32	17.37	0.267	0.025
$C_2F_5COMn(CO)_5$	16.55	17.28	17.32	0.257	0.021
$HCFClCF_2Mn(CO)_5$	16.39	17.32	17.35	0.258	0.017
$HCF_2CF_2Mn(CO)_5$	16.59	17.35	17.37	0.254	0.012
$HCCl_2CF_2Re(CO)_5$	16.43	17.34	17.36	0.295	0.010
$HCF_2CFClMn(CO)_5$	16.32	17.38	17.40	0.258	0.008
$CH_3CF_2CFClMn(CO)_5$	16.45	17.3		0.235	0
$CH_3CF_2CF_2Mn(CO)_5$	16.5	17.3		0.24	0
$CH_3CF_2CF_2Re(CO)_5$	16.45	17.35		0.285	0
$CH_3(CF_2)_4Re(CO)_5$	16.55	17.4		0.285	0
$HCF_2CF_2Re(CO)_5$	16.5	17.35		0.285	0
$HCFClCF_2Re(CO)_5$	16.5	17.35		0.28	0
$C_6H_5CF_2CF_2Mn(CO)_5$	16.45	17.25		0.24	0
$C_6F_5Mn(CO)_5$	16.45	17.3		0.23	0
$C_6H_5Mn(CO)_5$	16.2	17.0		0.24	0
$CH_3Mn(CO)_5$	16.1	16.8		0.25	0
$CH_3Re(CO)_5$	16.05	16.9		0.28	0

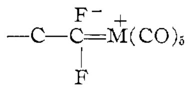
[a] Error in k_0 ±0.005. Error in k_c ±0.01. Error in k_1, k_2, and k_3 ±0.05. Values are calculated from only the carbonyl stretching frequencies and are without anharmonicity corrections. They can thus only be approximate.

confirming the nonpolar nature of the CO groups in the compounds. The apparent half-intensity band width[17] was also measured (Table III). For this the $A_1{}^{1a}$ mode was chosen as in most spectra the $A_1{}^{1b}$ absorption was too weak, while the width of the E mode could have been influenced by the nature of the fluoroalkyl side chain even when no splitting could be observed. Thus the E band was broader in the spectra of $HCFClCF_2Re(CO)_5$ and $CH_3CF_2CF_2Mn(CO)_5$ than in the spectra of $CH_3Mn(CO)_5$ and $C_6F_5Mn(CO)_5$. This suggests that splitting of the E band in the first two compounds is finite but too small to be observed, even in cyclohexane solution. It is apparent (Table III) that cyclohexane is the best solvent for observing carbonyl spectra, in agreement with a similar study involving nickel carbonyl.[18] However, when its use is precluded by solubility limitations, tetrachloroethylene is a useful alternative. It was impossible to observe small E band splittings in carbon disulfide or tetrachloroethylene due to broadening of the peaks. Carbon disulfide has similar solvent properties to tetrachloroethylene but its usefulness is reduced by its strong absorption from 2100 to 2200 cm.$^{-1}$. Because the bands are substantially broader in chloroform solution, this solvent is the least satisfactory. No splitting of the modes could be observed, and in many cases the $A_1{}^{1a}$ band appeared only as a shoulder on the low-frequency side of the intense E absorption. Interestingly, the $A_1{}^{1b}$ band, and the B_1 mode if present, could be observed easily in chloroform. This is in agreement with Cotton and Kraihanzel,[10,19] who report B_1 modes in the spectra of $Cr(CO)_5((C_6H_5)_3P)$ and $Mo(CO)_5(py)$. However, no splitting of the E mode was observed and the $A_1{}^{1a}$ mode was partly or completely overlapped by the intense E absorption.

It was also possible to record the gas-phase spectrum of $CH_3CF_2CF_2Mn(CO)_5$ (10-cm. cell) and in this manner a small E band splitting could be detected. The other compounds were not sufficiently volatile for gas-phase spectra to be observed in the usual cells.

Force constant values (Table II) show that $k_1 < k_2$ as required by theory.[10] This is a consequence of the axial CO group being more strongly π-bonded to the metal than the four radial CO groups. It has been suggested that polyfluoroalkyl groups lower the electron density on a transition metal both by inductive attraction[20] and by a small π-acceptor capacity,[21,22] discussed below. These effects have been used to explain the shift to higher frequency of the CO absorptions in fluoroorganometal carbonyls compared with those in organometal carbonyls.[21] In agreement with this, the present study shows that the stretching force constants are higher. The increase in force constants, however, is small, although several times larger than that possible from predicted calculation errors. Of the two distinguishable effects believed responsible for raising the stretching force constants of an $R_FM(CO)_5$ compound, relative to an alkylmetal carbonyl, the inductive is undoubtedly the most important.

If, as suggested by some of the chemistry[20] of fluoroalkylmetal pentacarbonyls, it is assumed that the fluorocarbon groups have a small π-acceptor capacity, *viz.*



$$\text{—C—}\underset{\displaystyle |\atop \displaystyle F}{\overset{F^-}{C}}\text{=}\overset{+}{M}(CO)_5$$

this would tend to decrease slightly the π-bond character of the M–CO axial bond with a commensurate increase in triple bond character of this CO group. This is because of the five carbonyl groups it is the

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(17) S. Walker and H. Straw, "Spectroscopy," Vol. II, Chapman and Hall, London, 1962, p. 137.

(18) G. Bor and L. Marko, *Spectrochim. Acta*, **16**, 1105 (1960).

(19) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(20) P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964), and references cited therein.

(21) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

(22) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

TABLE III

APPARENT HALF-INTENSITY BAND WIDTH OF THE A_1^{1a} MODE (CM.$^{-1}$)

	Solvents				
Compound	C_6H_{12}	C_2Cl_4	CS_2	CCl_4	$CHCl_3$
$HCFClCF_2Mn(CO)_5$	4.8	10.0	9.9	12.2	28
$HCF_2CFClMn(CO)_5$	4.4	...[a]	11.0	...[a]	...[a]
$HCCl_2CF_2Mn(CO)_5$	5.0	9.7	9.1	11.0	...[a]
$HCCl_2CF_2Re(CO)_5$	5.0	11.2	11.1	13.5	28
$HCFClCF_2Re(CO)_5$	4.7	11.7	11.2	...[a]	29
$C_2F_5COMn(CO)_5$	4.4	...[a]	11.1	...[a]	...[a]
$CH_3Mn(CO)_5$	6.2	11.5	11.1	17.0	31
$CH_3Re(CO)_5$	5.6	14.0	13.5	16.2	36

[a] Not measured.

TABLE IV

PREDICTED POSITION OF THE B_1 MODE[a]

Compound	k_1, mdynes/Å.	k_2, mdynes/Å.	k_c, mdynes/Å.	B_1 predicted, cm.$^{-1}$	B_1 found, cm.$^{-1}$
$HCF_2CF_2Mn(CO)_5$	16.50	17.34	0.24	2071	2073
$HCF_2CFClMn(CO)_5$	16.5	17.34	0.23	2071	2075
$C_2F_5COMn(CO)_5$	16.65	17.26	0.235	2066	2069
$HCFClCF_2Re(CO)_5$	16.5	17.34	0.28	2071	2076
$HCCl_2CF_2Re(CO)_5$	16.45	17.33	0.29	2070	2072

[a] Cyclohexane solution.

axial one which has a π-orbital which would interact the most strongly with the metal d_ϵ orbital required for π-bonding with the organic group. In agreement with this idea, and assuming that the halogen atoms have zero or negligible π-acceptor capacities, a comparison of the force constants k_1 for the fluorocarbon metal carbonyls with those for the metal pentacarbonyl halides[23] shows that the k_1 values are slightly greater for the former compounds, as predicted. The effect is small but is greater than the calculated experimental error. However, k_2 values for the fluorocarbon metal carbonyls are smaller than for the pentacarbonyl chlorides and bromides, but are very similar to those of the iodides. The electronic effects described above would not be expected to produce an observable difference between the various k_2 values. The fact that a very small difference is observed may be related to a relative size factor. The entire effect may be considered as a small perturbation superimposed on the general bonding in $LM(CO)_5$ compounds, which is basically the same whether L is a halogen or a fluorocarbon group.

As reported[6] for the pentacarbonyl halides, the rhenium pentacarbonyls show a greater separation of the two A_1 modes ($\sim$140 cm.$^{-1}$) than do the manganese compounds ($\sim$120 cm.$^{-1}$) (Table I). Interestingly, this is reflected only in higher values of the interaction force constant (k_c). Values of the two stretching force constants are roughly independent of the metal.

For those complexes which show all fundamentals but which have an E band splitting of less than 5 cm.$^{-1}$, force constants were calculated using the mean values of the E frequencies and the two A_1 frequencies. These constants were then used to predict the position of the B_1 fundamental (Table IV), in order to ensure that assignment of these bands was correct.

Finally, it should be noted that E band splitting has been observed with other complexes when their spectra were recorded as mulls or potassium bromide disks. Hieber and Schropp[24] report four peaks for the derivatives $Hg[Mn(CO)_5]_2HgX_2$ [X = halogen]. Abel and co-workers[25] report splitting of the E mode for $Mn(CO)_5I$, but these workers noted that the splitting vanished when solution spectra were recorded. It was considered that the splittings (as large as 20–30 cm.$^{-1}$) were due only to local site asymmetry and were not a fundamental property of the molecules. In the work described in this paper, the splittings were independent both of solvent used and concentration, confirming the effect to be a fundamental property of individual molecules.

Acknowledgment.—We are indebted to Dr. E. W. Abel for valuable discussions.

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[23] From frequencies and assignments made elsewhere force constants (mdynes/Å.) are calculated as follows: $Mn(CO)_5Cl$, k_1 = 16.23, k_2 = 17.49, k_c = 0.22; $Mn(CO)_5Br$, k_1 = 16.24, k_2 = 17.41, k_c = 0.22; $Mn(CO)_5I$, k_1 = 16.28, k_2 = 17.31, k_c = 0.22; $Re(CO)_5Cl$, k_1 = 16.00, k_2 = 17.49, k_c = 0.29; $Re(CO)_5Br$, k_1 = 16.02, k_2 = 17.45, k_c = 0.28; $Re(CO)_5I$, k_1 = 16.07, k_2 = 17.39, k_c = 0.27.

[24] W. Hieber and W. Schropp, *Chem. Ber.*, **93**, 455 (1960).

[25] E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).