Contribution from the Union Carbide Corporation Linde Division Research Laboratory Tonawanda, N. Y. U.S.A. PT 1969-2

The Effect of the Metal-Carbon Sigma Bond on C-F Stretching Frequencies in Trifluoromethyl Compounds[1]

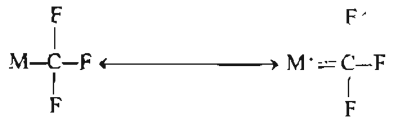
M. P. Johnson

Received Jannuary 21, 1969

The infrared spectra of a wide variety of compounds containing the trifluoromethyl group have been investigated. For a similar series of compounds, XCF_3 [$X = (CH_2)_4Ge$, $(CH_2)_2Sn$, or $(CH_3)_3Pb$; BF_2 or BF_3; or a transition metal], a positive correlation exists between the electron pair affinity of X and the position of the CF_3 stretching frequencies. The data indicate that the carbon-fluorine bond in metal-fluorocarbon compounds is strengthened by increasing the formal oxidation state of the central metal. The effect changes in the carbon-metal sigma bond have upon the strength of the carbon-fluorine bond is discussed.

Introduction

The increased stability of metal-perfluoroalkyl compounds over the corresponding nonfluorinated complexes has received considerable attention.[2] Structural work on metal-perfluoroalkyl complexes has shown that the metal-carbon bond length in these compounds is shorter than the metal-carbon distance in normal alkyl compounds.[3] Several explanations have been put forth to account for this bond shortening: (a) contraction of the metal orbitals due to the high electronegativity of the perfluoroalkyl group;[2a] (b) the contribution of structures involving carbon-fluorine anionic hyperconjungation;[2b]



(c) π-bonding between the metal and CF_3 group.[2c,d] Models b and c are the same in that both involve multiple bonding between the metal and perfluoroalkyl group. Unfortunately, the structural data do not allow one to assess the relative contributions of models a and c to the shortening of the metal-perfluoroalkyl bond.

It has been suggested that the decrease in the carbon-fluorine stretching frequencies in going from ICF_3 to $(CO)_5MnCF_3$ and the differences in CO stretching force constants for $(CO)_5MnBr$ and $(CO)_5MnCF_3$ are consistent with multiple bonding between the metal and trifluoromethyl group.[2d] However, an alternate interpretation of the data from the force constant calculations which does not require π-bonding between the metal and the trifluoromethyl group has been proposed by Graham.[4]

We wish to report some interesting observations on the carbon-fluorine stretching frequencies and discuss the effect of the metal-carbon sigma bond on the position of these frequencies.

Discussion

The CF_3 stretching frequencies for several nontransition metal compounds are collected in Table I.

For the compounds $(CH_3)_3MCF_3$, ($M = Pb$, Sn or Ge) the CF_3 stretching frequencies exhibit an increase with increasing electronegativity of the metal. This increase parallels the increase in the strength of the metal-carbon bond in these compounds.

A striking example of the effect of the electron pair affinity of an acceptor on the CF_3 stretching frequencies can be seen in the compounds F_2BCF_3 and $F_3BCF_3^-$. The former compound shows absorptions attributable to carbon-fluorine stretching vibrations at

Table I. Carbon-Fluorine Stretching Frequencies for Nontransition Metal Compounds Containing the Trifluoromethyl Group

Compound	ν[a]	Ref.	negativity[g]
$(CH_3)_3PbCF_3$	1140, 1070	[b]	1.55
$(CH_3)_3SnCF_3$	1151, 1071	[c]	1.72
$(CH_3)_2GeCF_3$	1194, 1098	[d]	2.02
F_2BCF_3	1190, 1080	[e]	2.01
$(NH_4)F_3BCF_3$	985, 962	[f]	2.01

[a] Frequencies are in cm^{-1}. No definite assignment of the symmetric or asymmetric mode is made by the authors. [b] H. D. Kaesz, J. R. Phillips and F. G. A. Stone, *J. Am. Chem. Soc.*, *82*, 6228 (1960). [c] H. C. Clark and C. J. Wilis, *ibid.*, *82*, 1888 (1960). [d] Quoted by H. C. Clark and J. H. Tsai, *J. Organometal. Chem.*, 7, 515 (1967). [e] See ref. 5. [f] See ref. 6. [g] Electronegativities are those of Allred and Rochow.

---

[1] Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N.J., September 1968.

[2] (a) P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, 1, 143 (1964). (b) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 2, 15 (1964). (c) F. A. Cotton and J. A. McCleverty, *ibid.*, *4*, 490 (1965). (d) F. A. Cotton and R. M. Wing, *ibid.*, 9, 511 (1967).

[3] (a) R. Mason and D. R. Russel, *Chem. Comm.* 182 (1965). (b) M. R. Churchill, *Inorg. Chem.*, 6, 185 (1967). (c) M. R. Churchill and J. P. Fennessey, *ibid.*, 6, 1213 (1967). (d) M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, 5, 125 (1967). (e) J. B. Wilford and H. M. Powell, *J. Chem. Soc. A*, 2092 (1967).

[4] W. A. G. Graham, *Inorg. Chem.*, *7*, 315 (1968).

1080 and 1190 cm^{-1},[5] while $F_3BCF_3^-$ exhibits CF_3 stretching frequencies at 962 and 985 cm^{-1}.[6] The C–F stretching frequencies in $F_3BCF_3^-$ are the lowest we have encountered in our study of compounds containing the trifluoromethyl group.

The infrared spectra of trifluoromethyl transition metal complexes in the 1000-1100 cm^{-1} region have been collected in Table II. Some comments are necessary concerning the assignment of the CF_3 stretching frequencies.

Table II. Carbon-Fluorine Stretching Frequencies of Trifluoromethyl-Transition Metal Complexes

Compound	νs	νa	$\nu av.$[a]	Ref.
$(CO)_4CoCF_3$	1064	1043	1050	*b*
$(C_6H_5)_3P(CO)_3CoCF_3$	1050	1029	1036	*b*
$(CO)_5MnCF_3$	1053	1018	1030	*c*
$I(CO)_4FeCF_3$	1055		1055	*d*
$[(C_6H_5)_3P]_2IPtCF_3$	1085	1022	1043	*e*
$(C_5H_5)CONiCF_3$	1069	1024	1039	*f*
$[(C_6H_5)_3P]_2IPdCF_3$	1068	1024	1039	*e*
$[(C_6H_5)_3P]_2COClIIrCF_3$	1089	1039, 1019	1048	*e*
$I(C_5H_5)CORhCF_3$	1073	1040	1051	*g*
$I(C_5H_5)COCoCF_3$	1067	1053	1058	*h*
$I(C_5H_5)COCoCF_3$	1067	1053, 1019	1046	*h*

[a] Frequencies in cm^{-1}. The value of νav is weighed according to the degeneracy of the observed bands, νs is symmetric and νa is asymmetric C–F stretch. [b] See ref. 11. [c] See ref. 2b. [d] See ref. 7. [e] This work. [f] D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1752 (1964). [g] J. A. McCleverty and G. Wilkinson, *ibid.*, 4200 (1964). [h] See ref. 8.

The position of the C–F absorptions was readily obtainable from the data in the literature. Two strong bands were observed by most authors in the 1000-1100 cm^{-1} region of the spectra. For $CF_3Fe(CO)_4I$ only one absorption (1055 cm^{-1}) was recorded in this region.[7] The spectrum of $CF_3Ir[P(C_6H_5)_3]_2COClI$ shows absorptions attributable to CF_3 stretching modes at 1019, 1038 and 1089 cm^{-1}. The bands at 1019 and 1038 cm^{-1} probably arise from splitting of the degenerate stretch. The compound $(C_5H_5)CO(CO)(CF_3)I$ exhibits three strong absorptions at 1067, 1053 and 1019 cm^{-1}.[8] The band at 1019 cm^{-1} may be due to the C_5H_5 group since the starting material $(C_5H_5)Co(CO)_2$, shows an absorption at 1018 cm^{-1}.[9] It is possible that the asymmetric CF_3 stretching mode is split into two components due to the low overall symmetry of the molecule. Both possibilities are noted in Table II. We have assumed that the relative position of the symmetric stretching mode does not change within this series of complexes and, in agreement with Cotton[2c] have assigned the higher frequency to the symmetric stretch.[10] The tabulated spectra, except those for $(CO)_4CoCF_3$ and $(C_6H_5)_3P(CO)_3CoCF_3$,[11] were obtained in CS_2 solution.

Table III. Structural Data for Transition Metal Compounds[a]

	<FCαF	^{R}CαF	^{R}M–C
$(C_6H_5)_3P(CO)_3CoC_2F_4H$	102°	1.41Å	1.94Å
$(CO)_4Fe(C_2F_4H)_2$	103.4°	1.379Å	2.068Å
$(C_5H_5)(CO)_3MoC_3F_7$	103.8°	1.399Å	2.288Å
$I(C_5H_5)(CO)RhC_2F_5$	105.8°	1.34Å	2.08Å

[a] See ref. 3.

It can be seen from Table III that there is a positive correlation between the weighted average of the C–F stretching frequencies and the formal oxidation state of the central metal. The data are more clearly summarized in Figure 1 where the weighted average of the frequencies is plotted against the electron affinity for the gaseous metal ion with charge corresponding to the formal oxidation state of the central metal. It appears that the carbon-fluorine bond is strengthened with increasing electron pair affinity of the metal atom. We do not wish to push the correlation in Figure 1 too far since it is certainly a gross approximation to use gas phase ionization potentials to infer relative electron pair affinities of the metal in a complex independent of the other ligands.

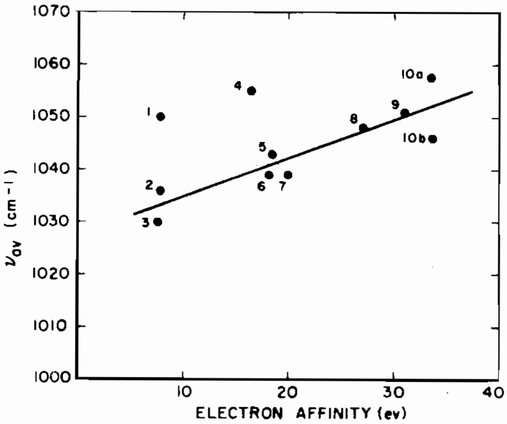


Figure 1. Weighed average of CF_3 stretching frequencies vs. electron affinity of the gaseous metal ion with charge equal to the oxidation state of the metal in the complex. The numbers correspond to the compounds listed in Table II.

Further evidence for changes in the strength of the carbon-fluorine bonds can be obtained by examining the structural data on metal perfluoroalkyl compounds (Table III). Unfortunately, data on compounds containing the trifluoromethyl group are not available; however, the compounds listed contain an M-CF_2X group. Looking at configuration around the α-carbon we note an increase in the FCF angle and a decrease in the C-F bond length with increasing formal oxidation state of the central metal. These changes parallel the changes in frequencies given in Table II.

Shriver has suggested that « for a ligand, LX_n, the L–X force constant will increase upon coordination of L to an electron acceptor if X is significantly more

---

(5) T. D. Parsons, J. M. Self and L. H. Schaad, *J. Am. Chem. Soc.*, 89, 3446 (1967).

(6) R. D. Chambers, H. C. Clark, and C. J. Willis, *ibid.*, 82, 5298 (1960).

(7) R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *ibid.*, 83, 3604 (1961).

(8) R. B. King, P. M. Treichel, and F. G. A. Stone, *ibid.*, 83, 3593 (1961).

(9) H. P. Fritz, *Advan. Organometal. Chem.*, 1, 283 (1964).

(10) Very little change occurs in the correlation given in Figure 1 if the assignments are reversed.

(11) (a) W. Hieber, W. Beck, and E. Linder, *Z. Naturforschg.*, *16b*, 229 (1961). (b) W. Hieber and E. Linder, *Chem. Ber.*, 95, 2042 (1962).

electronegative than L and it will decrease for the converse situation ».[12]

These effects should be most pronounced with the acceptor of the greatest electron pair affinity. Variations in the L–X force constant can be related to changes in the acceptor-ligand σ-bond by considering the electrostatic interaction between the metal and coordinated trifluoromethyl group or the hybridization of the carbon-fluorine bonding orbital.

In an electrostatic model the C–F stretching are related to $\overset{\sigma+}{C}-\overset{\sigma-}{F}$ restoring force. An increase in electron pair affinity of a metal should increase the positive charge on the carbon and lead to a stiffer carbon-fluorine bond. Similarly, an increase in electron pair affinity of an acceptor will tend to increase the p-character of the carbon orbital directed toward the metal.[12,13] This should increase the s-character of the orbitals involved in carbon-fluorine bonding.

During our discussion of the C–F stretching frequencies we have neglected to mention the effect of back π-bonding from the metal to the trifluoromethyl group. The data presented here do not rule out the participation of metal-to-carbon π-bonding. However, the present discussion indicates that cognizance of changes in the metal-carbon σ-bond may be in order.

Experimental Section

The complexes $Pd[P(C_6H_5)_3]_2CF_3I$, $Pt[P(C_6H_5)_3]_2CF_3I$ and $Ir[P(C_6H_5)_3]_2COCF_3ClI$ were prepared by published methods[14,15] and C, H and halogen analysis agreed with the calculated values. The infrared spectra were recorded in CS_2 solution on a Beckman IR 12.

Acknowledgments. The authors would like to thank Drs. J. E. McKeon and D. F. Shriver for helpful discussions and Dr. J. Fisher and Mr. C. R. Green for experimental assistance.

---

(12) D. F. Shriver and M. P. Johnson, *Inorg. Chem.*, *6*, 1265 (1967).

(13) (a) D. F. Heath and J. W. Linnett, *Trans. Faraday Soc.*, *44*, 556 (1948). (b) H. A. Bent, *J. Inorg. and Nucl. Chem.*, *19*, 43 (1961).

(14) D. F. Rosevear and F. G. A. Stone, *J. Chem. Soc. A*, 164 (1968).

(15) J. P. Collman and C. T. Sears, Jr., *Inorg. Chem.* *7*, 27 (1968).