The Infrared Spectra and Normal Coordinate Treatments of X_3M–$Mn(CO)_5$($X=Cl$, Br, and I; $M=Si$, Ge, and Sn). II.[1]

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The infrared absorption spectra (2200—50 cm^{-1}) have been measured for four metal-metal bonded molecules, Cl_3Si–$Mn(CO)_5$, Cl_3Ge–$Mn(CO)_5$, Br_3Ge–$Mn(CO)_5$, and I_3Sn–$Mn(CO)_5$. Vibrational normal coordinate analyses have been made for each of these molecules on the basis of a modified Urey-Bradley force-field. The calculated frequencies agree closely with validly-assigned frequencies. The metal-metal stretching force constant, K(M–Mn), or the F-matrix element, f(M–Mn), varies with the halogen atom, and increases as the electronegativity of X increases. The force constant, K(M–Mn), or f(M–Mn) depends also on the IVb metal atom, and increases in the order of: $K(\text{Si–Mn}) \geqq K(\text{Ge–Mn}) > K(\text{Sn–Mn})$, or $f(\text{Si–Mn}) \geqq f(\text{Ge–Mn}) > f(\text{Sn–Mn})$. However, there is no clear relationship between the electronegativity of M and the K(M–Mn) or (M–Mn). These dependences of K(M–Mn) or f(M–Mn) on X and M are discussed, along with the bonding implications of the M–Mn bonds, on the basis of the sets of the force constants, or the sets of the F-matrix elements, and are interpreted in terms of the predominant σ-bonding framework of the M–Mn bonds.

The nature of metal-metal bonding between a transition metal and a main-Group IV b metal has been studied by a number of spectroscopic techniques, such as IR, NMR, NQR, the Mössbauer effect, *etc.*[1–13]; the common interest of these studies is to clarify the effect of the component-metal atoms or the substituents of the component metal atoms on the nature and/or the strengths of metal–metal bondings in question. Among these techniques, vibrational analyses are quite useful in evaluating the extent of the metal–metal interaction in terms of the force constants. According to a recent report on vibrational analyses by Risen *et al.*,[2b] the metal–metal bond strength in X_3M–$Co(CO)_4$ ($M=Ge$ and Sn, $X=Cl$, Br, and I) increases linearly with the electronegativity of X and the M–Co bond is predominantly σ in character. In Part I of the present series of studies of metal–metal bondings,[1] the present author studied the effect of L on the Sn–Mn bonding nature for L_3Sn–$Mn(CO)_5$ ($L=Cl$, Br, and CH_3) and obtained similar result-that the Sn–Mn strength is strongly affected by the electronegativity of L on the tin atom, and that the π-interaction between the Sn and Mn of Cl_3Sn–$Mn(CO)_5$ is more pronounced than that of $(CH_3)_3Sn$–$Mn(CO)_5$.

The present study was undertaken in order to clarify the effects of the Component IV b metal atom and the electronegativity of the X in X_3M group on the M–Mn bonding nature, and in order to facilitate interpretations of Raman-[14] and IR-[15] intensity studies of a series of X_3M–$Mn(CO)_5$ ($X=Cl$, Br, and I; $M=Si$, Ge, and Sn) compounds by making vibrational analyses.

Experimental

All the compounds were prepared by the methods in the literatures.[16–21] The purity of the samples was checked by elemental analysis and by IR spectra. The infrared spectra in the CO stretching region were measured with a Jasco model IR-G spectrophotometer in a hexane solution, using a NaCl liquid cell (0.1 mm). The spectra were calibrated by making use of gaseous DCl by means of a superposition method. The Nujol mull samples were also examined with a Hitachi EPI-L spectrophotometer and a FIS-3 double-beam vacuum spectrophotometer in the region from 50 to 700 cm^{-1}. The results are summarized in Table 1 and Figs. 1 and 2.

Spectral Assignments

The molecular structure of Br_3Ge–$Mn(CO)_5$ has been determined by electron-diffraction analysis;[22] its molecular geometry is quite similar to those of $(CH_3)_3Sn$–

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TABLE 1. OBSERVED INFRARED SPECTRA, VIBRATIONAL ASSIGNMENTS, AND CALCULATED FREQUENCIES

Observed frequency, cm^{-1}	Intensity	Calculated frequency, cm^{-1}	Assignments	Approximate vibrational modes
		Cl_3Si–$Mn(CO)_5$		
2124	w	2123	S_5	CO str.
2036	vs	2036	S_4, S_{19}	CO str.
660	sh	651	S_{13}	MnCO def.
650	vs	648	S_{27}	MnCO def.
		570	S_{28}	MnCO def.
542	m	539	S_{16}	MnCO def.
515 497	m m	507	S_{20}	SiCl str.
460	w	461 459	$S_7 + S_8$ S_{18}	SiCl str. + SiMn str. MnC str.
412	w	411	$S_1 + S_7$	MnC str. + SiCl str.
400	w	403	S_2	MnC str.
291	s	291	$S_8 + S_9$	SiMn str. + ClSiCl def.
201	w			
180	s	188	S_{21}	ClSiCl def.
140	m	144	$S_{10} + S_9$	CMnC, CMnSi def. + ClSiCl def.
120	w	125	$S_{25} + S_{23}$	CMnC, CMnSi def. + CMnC def.
		112	S_{24}	CMnC, CMnSi def.
		85	$S_9 + S_{10}$	ClSiCl def. + CMnC, CMnSi def.
		81	$S_{25} + S_{23}$	CMnC, CMnSi def. + CMnC def.
		Cl_3Ge–$Mn(CO)_5$		
2128	w	2128	S_5	CO str.
2048	vs	2049	S_{19}	CO str.
2038	s	2038	S_4	CO str.
655	sh	654	S_{13}	MnCO def.
633	vs	637	$S_{26} + S_{27}$	MnCO def.
535	vw	539	S_{16}	MnCO def.
451	vs	452	S_{18}	MnC str.
411	vw	410	S_1	MnC str.
398	m	398	S_2	MnC str.
371	vs	373 366	S_{20} S_7	ClGe str.
231	m	231	S_8	GeMn str.
164	m	163	S_{21}	ClGeCl def.
126	m	132	S_9	ClGeCl def.
		125	$S_{23} + S_{25}$	CMnC def.
112	vw	111	S_{24}	CMnC def.
96	vw	91	S_{11}	CMnC, CMnGe def.
		83	S_9	ClGeCl def.
		77	S_{25}	CMnC, CMnGe def.
		Br_3Ge–$Mn(CO)_5$		
2126	w	2126	S_5	CO str.
2047	vs	2047	S_{19}	CO str.
2036	s	2036	S_4	CO str.
655	s	654	S_{13}	MnCO def.
631	vs	634	$S_{26} + S_{27}$	MnCO def.
555	vw, br	562	S_{27}	MnCO def.
535	vw	539	S_{16}	MnCO def.
449	vs	448	S_{18}	MnC str.
		404	S_1	MnC str.
394	vw	396	S_2	MnC str.
373	w			
290	s	292	S_{20}	BrGe str.
275	vs	259	S_7	BrGe str.
190	w	190	S_8	GeMn str.
132	w	125	S_{23}	CMnC def.

Table 1 (continued)

Observed frequency, cm^{-1}	Intensity	Calculated frequency, cm^{-1}	Assignment	Approximate vibrational modes
120	br, vw	120	$S_{10}+S_9$	CMnC, CMnGe def. + BrGeBr def.
		115	$S_{24}+S_{21}$	CMnC, CMnGe def. + BrGeBr def.
98	w	103	S_{21}	BrGeBr def.
		71	S_{25}	CMnC, CMnGe def.
		62	S_9	BrGeBr def.
		$I_3Sn-Mn(CO)_5$		
2117	m	2118	S_5	CO str.
2042	vs	2041	S_{19}	CO str.
2035	s	2035	S_4	CO str.
645	s	647	S_{13}	MnCO def.
630	vs	636	$S_{26}+S_{27}$	MnCO def.
545	w	545	S_{16}	MnCO def.
493	vw			
452	s	452	S_{18}	MnC str.
410	vw	409	S_1	MnC str.
394	m	398	S_2	MnC str.
204	vs	206	S_{20}	ISn str.
192	vs	184	S_7	ISn str.
155	m	155	S_8	SnMn str.
		124	$S_{23}+S_{24}$	CMnC, CMnSn def.
118	m	111	$S_{24}+S_{23}$	CMnC, CMnSn def.
		99	S_9	ISnI def.
		86	S_{21}	ISnI def.
70	m	67	$S_{24}+S_{21}$	CMnC, CMnSn def. + ISnI def.

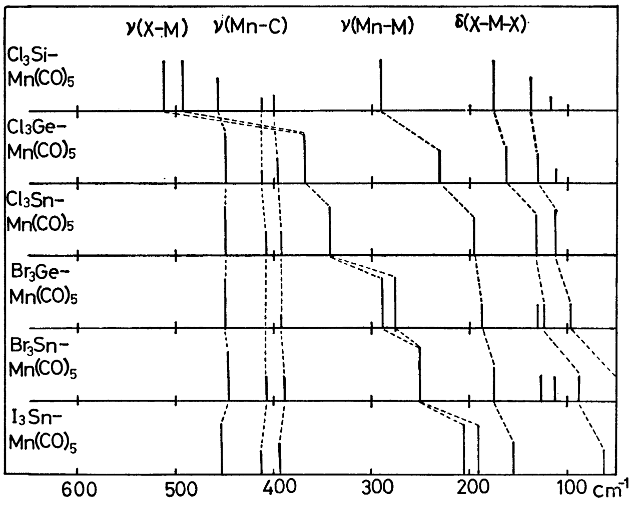

Fig. 1. Correlation diagram of observed ν(X-M), ν(Mn-C), ν(Mn-M), and δ(X-M-X) modes for $X_3M-Mn(CO)_5$.

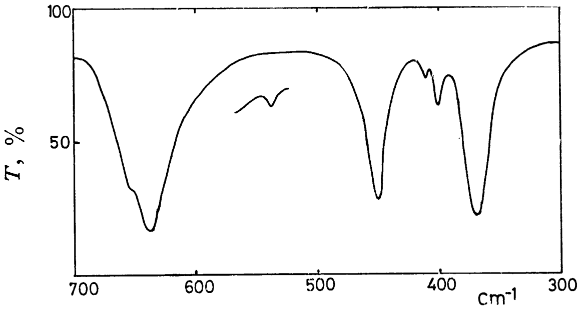

Fig. 2a. Typical spectrum of $X_3M-Mn(CO)_5$: $Cl_3Ge-Mn(CO)_5$.

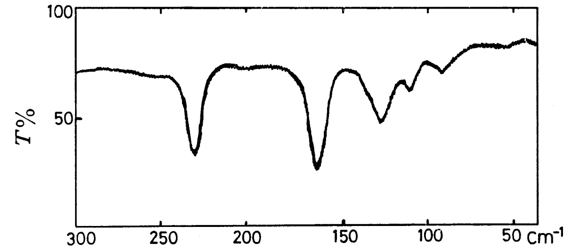

Fig. 2b. Typical spectrum of $X_3M-Mn(CO)_5$: $Cl_3Ge-Mn(CO)_5$.

$Mn(CO)_5$[23] and $(C_6H_5)_3Sn-Mn(CO)_5$[24] (the structures of the latter two compounds were determined by X-ray analyses). According to these reports, the local symmetry around the tin or germanium atom is C_{3v}, while that of the manganese atom is C_{4v}. Similar local symmetries are assumed for $I_3Sn-Mn(CO)_5$, $Cl_3Ge-Mn(CO)_5$, and $Cl_3Si-Mn(CO)_5$ because of the close resemblance of their vibrational spectra and physical and chemical properties to those of $Br_3Ge-Mn(CO)_5$, $(CH_3)_3Sn-Mn(CO)_5$, and $(C_6H_5)_3Sn-Mn(CO)_5$. In the vibrational analysis, these molecules can be regarded as a symmetric-top molecules, and the vibrational representation is $\Gamma_{\mathrm{vib}}=15A_1+2A_2+11E$. This re-

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[24] H. P. Weber and R. F. Bryan, *Acta Crystallogr.*, **22**, 822 (1967).

Table 2. Symmetries of vibrational modes for X_3M-$Mn(CO)_5$ (C_{3v})

CO str. $3A_1 + E$
MnCO def. $3A_1 + A_2 + 3E$
MnC str. $3A_1 + E$
MX str. $A_1 + E$
M-Mn str. A_1
MX_3 def. $A_1 + E$
X-M-Mn def. E
CMnC def. $A_1 + E$
CMnC, C-Mn-M def. $2A_1 + 2E$
Torsion A_2

presentation is spanned by symmetrically complete sets of symmetry coordinates, as is detailed in Table 2 for X_3M-$Mn(CO)_5$ molecules. Among the fifteen symmetry coordinates involving C-O stretching, Mn-C stretching, and Mn-C-O deformation vibrations, three C-O stretching, three Mn-C stretching, and four Mn-C-O deformation vibrations can be expected, on the basis of many studies of $LMn(CO)_5$ compounds and previous work on L_3Sn-$Mn(CO)_5$, to be observed above 390 cm^{-1} for each of these molecules of the C_{4v} local symmetry around the manganese atom. Table 1 and Fig. 1 show that the vibrational spectra of Cl_3Ge-$Mn(CO)_5$, Br_3Ge-$Mn(CO)_5$, and I_3Sn-$Mn(CO)_5$ above 390 cm^{-1} are almost identical with one another, and that they are nearly identical with the spectra reported earlier for Cl_3Sn-$Mn(CO)_5$ and Br_3Sn-$Mn(CO)_5$. Therefore, all the bands observed above 390 cm^{-1} are considered to be mainly due to the vibrations of the $Mn(CO)_5$ moiety, and the same assignments of the observed bands as those given previously for Cl_3Sn-$Mn(CO)_5$ and Br_3Sn-$Mn(CO)_5$ are made for Cl_3Ge-$Mn(CO)_5$, Br_3Ge-$Mn(CO)_5$, and I_3Sn-$Mn(CO)_5$. In the spectral region of 150—390 cm^{-1}, three fundamentals which are mainly M-X (A_1+E) and Mn-M (A_1) stretching vibrations can be expected for Cl_3Ge-$Mn(CO)_5$, Br_3Ge-$Mn(CO)_5$, and I_3Sn-$Mn(CO)_5$. Br_3Ge-$Mn(CO)_5$ and I_3Sn-$Mn(CO)_5$ show broad, intense absorptions at 275 and 192 cm^{-1} respectively, with shoulders occur at frequencies higher by 10—20 cm^{-1} than those of the strong bands; these bands are assignable to the Br-Ge and I-Sn stretching vibrations respectively.[16] The spectrum of Cl_3Ge-$Mn(CO)_5$, however, shows a broad, intense absorption at 371 cm^{-1} which is assignable to Ge-Cl stretching vibrations[2a]; the A_1 and E fundamentals of Ge-Cl stretching modes are expected to be overlapped in this spectrum. The spectra of Cl_3Ge-$Mn(CO)_5$ and I_3Sn-$Mn(CO)_5$ display bands with medium intensities at 231 and 155 cm^{-1} respectively. These bands are assigned mainly to Ge-Mn and Sn-Mn stretching vibrations.[2a,16] The spectrum of Br_3Ge-$Mn(CO)_5$, however, shows a weak bands at 190 cm^{-1}; this absorption is assigned mainly to the Ge-Mn stretching vibration of this molecule. The vibrational modes, which are chiefly the X-M-X deformation vibrations and the skeletal C-Mn-C, M-Mn-C, and X-M-Mn deformations, are expected to occur below 150 cm^{-1} for the Cl_3Ge-$Mn(CO)_5$, Br_3Ge-$Mn(CO)_5$, and I_3Sn-$Mn(CO)_5$ molecules. The X-M-X deformation vibrations of Cl_3Ge-$Mn(CO)_5$ are observed at 164 and 126 cm^{-1}; those of Br_3Ge-$Mn(CO)_5$ are observed at 132, 120, and 98 cm^{-1}, and that of I_3Sn-$Mn(CO)_5$ is observed at 70 cm^{-1}.[2] Most of the skeletal C-Mn-C, M-Mn-C, and X-M-Mn deformation vibrations escape detection for these molecules.

As for Cl_3Si-$Mn(CO)_5$, however, the infrared spectrum is quite different from those of X_3Ge-$Mn(CO)_5$ and X_3Sn-$Mn(CO)_5$ in the spectral region above 400 cm^{-1}; that is, only two peaks are observed in the CO stretching region (the E and A_1 (axial) modes are expected to be overlapped) and additional bands with medium intensities are observed at 515 and 497 cm^{-1} in the middle frequency region, besides the Mn-C-O deformation and Mn-C stretching vibrations. According to previous papers on $(CH_3)_nSiCl_{4-n}$[25] and Cl_3Si-$Co(CO)_4$[2a] and the present normal coordinate analysis, these bands are assignable mainly to the Si-Cl stretching vibrations of the E mode (the E mode is supposed to split into two peaks). In the low frequency region, strong bands are observed at 291 and 180 cm^{-1}, and bands with medium to weak intensities are observed at 201, 140, and 120 cm^{-1}. The strong peak at 291 cm^{-1} is assigned mainly to the Si-Mn stretching vibration, while the peaks observed at 180 and 140 cm^{-1} are assigned mainly to $SiCl_3$ deformations.[2a] The bands at 120 cm^{-1} is assigned mainly to C-Mn-C skeletal bending motions, on the basis of the normal coordinate analysis of this molecule.

All the vibrational assignments are presented in Table 1.

Normal Coordinate Analysis

The frequency calculations were carried out on the basis of Wilson's GF matrix method[26] by making use of a modified Urey-Bradley force field.[27] The symmetry and the internal coordinates used were the same as those previously described.[1] The interatomic distances for the $Mn(CO)_5$ moiety used in the calculations were those found in the X-ray analyses of $(CH_3)_3Sn$-$Mn(CO)_5$[23] and $(C_6H_5)_3Sn$-$Mn(CO)_5$.[24] The values of the bond lengths, r(M-X), were taken from the values in Cl_3Si-$Co(CO)_4$,[28] Br_3Ge-$Mn(CO)_5$,[22] and X_4M.[29] The Mn-M bond distances were those found in the structural analyses of Cl_3Si-$Co(CO)_4$,[28] Br_3Ge-$Mn(CO)_5$,[22] and R_3Sn-$Mn(CO)_5$[23,24]: r(Si-Mn) is 2.25 Å, r(Ge-Mn) is 2.44 Å, and r(Sn-Mn) 2.67 Å. Since the trial calculation of Cl_3Sn-$Mn(CO)_5$ revealed that an error of *ca.* 0.17 Å in estimating the r(Sn-Mn) distance causes only negligible changes in the K(Sn-Mn) and other force constants,[30] the use of these metal-metal bond lengths may be

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[25] A. L. Smith, *J. Chem. Phys.*, **21**, 1997 (1953).
[26] E. B. Wilson, *ibid.*, **9**, 76 (1941).
[27] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 759 (1966).
[28] W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, **6**, 1208 (1967).
[29] R. J. H. Clark and C. J. Willis, *ibid.*, **10**, 1118 (1971).
[30] S. Onaka, unpublished data.

seen to provide a better basis for normal coordinate analyses.

Above 400 cm^{-1}, the infrared spectra of these molecules are almost identical with those of Cl_3Sn–$Mn(CO)_5$, Br_3Sn–$Mn(CO)_5$, and $(CH_3)_3Sn$–$Mn(CO)_5$. This agreement is strong evidence that the molecular force fields for the $Mn(CO)_5$ moiety are nearly identical, and so the initial force fields were assumed to be identical with those of L_3Sn–$Mn(CO)_5$ in all the four present molecules. Actually, the calculated frequencies closely agree with the observed frequencies above 400 cm^{-1} throughout the X_3M–$Mn(CO)_5$ series of molecules without causing any serious alterations in that portion of the force-field elements which concern the vibrational modes of the $Mn(CO)_5$ moiety. The initial force constants for the MX_3 groups were taken from the MX_4, LMX_3,[31,32] and X_3Sn–$Mn(CO)_5$[1] molecules, while the reasonable starting values of K(M–Mn) was obtained from the K(Sn–Mn) of Cl_3Sn–$Mn(CO)_5$.[1] The initial force-field elements, such as H(MnMX), F(C···M), F(X···Mn), and Y(M–Mn), were transferred from the force constants of X_3Sn–$Mn(CO)_5$ (X stands for Cl and Br).[1] The force constants were adjusted so as to get the best fit of the calculated frequencies with the observed frequencies, with reference to the Jacobian matrix elements. The numerical calculations were carried out by the use of a HITAC 5020 E of the Computation Center of the University of Tokyo; the programs, BGLZ and LSMB, were set up in the laboratory of Professor Takehiko Shimanouchi.

Results

The final sets of the force constants and the F-matrix elements, f(M–Mn), are presented in Table 3, along with those of Cl_3Sn–$Mn(CO)_5$ and Br_3Sn–$Mn(CO)_5$, which are obtained in a previous work.[1] The symbols and the suffixes have the same meanings as have previously been described.[1]

The eigenvectors obtained show that the vibrational modes associated with the M–Mn stretching vibration are extensively coupled with other vibrational modes, especially with the C–Mn–C deformations, X–M and Mn–C stretching and/or X–M–X deformation vibrations. The purities of the vibrational modes of the M–Mn stretching vibrations are evaluated from the potential energy distribution to the M–Mn stretching coordinate (PED). As is shown in Table 4, the vibrational purities of the M–Mn stretching motions in Cl_3Si–$Mn(CO)_5$ and I_3Sn–$Mn(CO)_5$ are significantly low, and a considerable degree of the contribution of the Cl–Si–Cl deformation and C–Mn–C deformation vibrations to the Si–Mn and Sn–Mn stretching vibrations respectively is observed. The separation of the Mn–M stretching motion from other motions increases in accordance with the increase in the mass of M for Cl_3M–$Mn(CO)_5$, while the purity of the Mn–M

TABLE 3. FORCE CONSTANTS AND F-MATRIX ELEMENT, f(M–Mn), IN md/Å

	Cl_3Si–$Mn(CO)_5$	Cl_3Ge–$Mn(CO)_5$	Cl_3Sn–$Mn(CO)_5$	Br_3Ge–$Mn(CO)_5$	Br_3Sn–$Mn(CO)_5$	I_3Sn–$Mn(CO)_5$
K_a(MnC)	2.0	1.78	1.8	1.78	1.8	1.90
K_e(MnC)	2.32	2.25	2.2	2.22	2.2	2.25
K_a(CO)	16.75	16.85	16.9	16.82	16.85	16.77
K_e(CO)	17.07	17.25	17.23	17.22	17.20	17.09
K(SMMn)	1.30	1.23	1.0	0.85	0.82	0.41
K(MX)	1.85	0.65	1.8	1.52	1.39	1.2
H(XMX)	0.06	0.036	0.06	0.01	0.04	0.01
H(MnMX)	0.02	0.02	0.02	0.02	0.02	0.01
H_e(CMnC)	0.15	0.15	0.15	0.15	0.15	0.15
H_a(CMnC)	0.15	0.15	0.15	0.15	0.15	0.15
H(CMnM)	0.10	0.10	0.10	0.10	0.10	0.10
H_i(MnCO)	0.80	0.80	0.80	0.80	0.80	0.82
H_o(MnCO)	0.85	0.87	0.85	0.88	0.85	0.85
H_a(MnCO)	0.90	0.83	0.86	0.81	0.83	0.80
F(X···X)	0.32	0.32	0.12	0.32	0.12	0.32
F(Mn···X)	0.02	0.02	0.05	0.02	0.05	0.05
F_a(C···C)	0.01	0.01	0.01	0.01	0.01	0.01
F_e(C···C)	0.01	0.01	0.01	0.01	0.01	0.01
F(C···M)	0.01	0.01	0.01	0.01	0.01	0.01
Y(Mn–M)*	0.005	0.005	0.005	0.005	0.005	0.005
P(MC, CO)	0.50	0.50	0.50	0.50	0.50	0.50
P(MC, MC)	0.40	0.40	0.40	0.40	0.40	0.40
P_t(CO, CO)	0.38	0.32	0.30	0.32	0.30	0.30
P_c(CO, CO)	0.17	0.17	0.17	0.17	0.17	0.17
f(M–Mn)	1.36	1.30	1.13	0.91	0.95	0.53

* md Å

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31) Y. Kakiuchi, This Bulletin, **26**, 260 (1953).

32) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

Table 4. Potential energy distribution matrix in M–Mn stretching vibration

Approximate vibrational modes	$(PED)_{ij}$					
	Cl_3Si–$Mn(CO)_5$	Cl_3Ge–$Mn(CO)_5$	Cl_3Sn–$Mn(CO)_5$	Br_3Ge–$Mn(CO)_5$	Br_3Sn–$Mn(CO)_5$	I_3Sn–$Mn(CO)_5$
S_1 Mn–C str.	11	13	11	7	8	5
S_7 M–X	16			11	16	4
S_8 M–Mn str.	44	67	68	54	46	36
S_9 X–M–X def.	18	15	5	7		
S_{10} C–Mn–C def.		4	14	12	22	45
S_{13} Mn–C–O def.			4	3	5	9

$$(PED)_{ij} = \frac{(L_{ij})^2 \cdot (F_S)_{ii}}{\lambda_j} \times 100$$

stretching motion decreases with the increase in the mass of X in X_3M, as is expected.

Discussion

The principal objective of the present study is to clarify the variation in the force constants, K(M–Mn), K(Mn–C), K(C–O), and so on, and the F-Matrix elements, f(M–Mn), f(Mn–C), and f(C–O), as the metal atom, M, and the halogen atom, X, are replaced by X_3M–$Mn(CO)_5$ molecules. The effect of the X in the X_3M group on these force constants and on f(M–Mn) is exhibited in Table 3 for X_3Sn–$Mn(CO)_5$ (X stands for Cl, Br, and I) and X_3Ge–$Mn(CO)_5$ (X stands for Cl and Br); the K(M–Mn) and the f(M–Mn) values fall in the order of: chloride>bromide (>iodide). That is, the values of K(M–Mn) and f(M–Mn) increase with the increase in the electronegativity of X; especially for X_3Sn–$Mn(CO)_5$, there is a nearly linear relationship between the K(Sn–Mn) or f(Sn–Mn) values and the electronegativity of X, though the values of K(Mn–C) and K(C–O) or f(Mn–C) and f(C–O) remain almost constant in responce to the change in X.[33] The electron-withdrawing ability of the SnX_3 group is expected to increase in accordance with the increase in the electronegativity difference between halogen and tin atoms. This expectation is substantiated by the previous NQR study of X_3Sn–$Mn(CO)_5$; *i.e.*, the halogen NQR study of X_3Sn–$Mn(CO)_5$ has shown that the ionic character (%) of tin-halogen bonds in X_3Sn–$Mn(CO)_5$ falls in the order of: Sn–Cl>Sn–Br>Sn–I,[6] and a good linear relationship exists, as is shown in Fig. 3, between the f(Sn–Mn) or the K(Sn–Mn) values and the ionic character of the Sn–X bond, thus providing evidence that the electron-withdrawing ability of the SnX_3 group is in the order of: $Cl_3Sn > Br_3Sn > I_3Sn$.

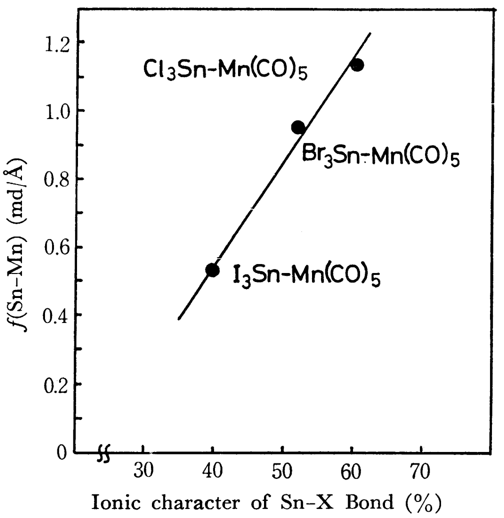

Fig. 3. The relationship between the f(Sn–Mn) and the ionic character of the Sn–X bond.

In the previous work on L_3Sn–$Mn(CO)_5$,[1] the present author has studied the effect of the substituent, L, on the Sn–Mn bonding nature on the basis of the sets of force constants, K(Sn–Mn), K(Mn–C), and K(C–O); he there concluded that the π-interaction between the tin and manganese atoms of $(CH_3)_3Sn$–$Mn(CO)_5$ is weaker than those of X_3Sn–$Mn(CO)_5$ (X=Cl and Br), since not only K(Sn–Mn) but also K(Mn–C) and K(C–O) are changed by the substitution of L from X to CH_3. For the present X_3Sn–$Mn(CO)_5$ and X_3Ge–$Mn(CO)_5$ molecules, it seems that the σ-characters in the Ge–Mn and Sn–Mn bondings predominantly increase with the increase in the electronegativity of X, because the change in X causes no notable amount of variation in K(M–C) and K(C–O) or in f(Mn–C) and f(C–O) in spite of the pronounced dependence of K(M–Mn) or f(M–Mn) on the electronegativity of X (the f(Sn–Mn) of Cl_3Sn–$Mn(CO)_5$ is roughly twice that of I_3Sn–$Mn(CO)_5$). Watters *et al.* have studied X_3M–$Co(CO)_4$ (X=Cl, Br, and I; M=Ge and Sn) by IR and found that the K(Co–M) value decreases monotonously with the decrease in the electronegativity of X, while K(Co–C) and K(C–O) are kept constant.[2b] They have interpreted this similar finding in terms of the difference of the σ-framework of the Co–M bond based on the molecular σ-bonding systems.

Now, let us investigate the effect of M on the M–Mn bondings. As is shown in Table 3, the values of K(M–Mn) or f(M–Mn) increase in accord with the variation in the metal atom, M, from Sn to Si for the corresponding halogen compounds, though the K(Mn–C) and

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[33] As the manner of the changes in f(Mn–C) and f(C–O) toward the substitution of X or M is quite similar to those of K(Mn–C) and K(C–O), the values of f(Mn–C) and the f(C–O) were eliminated from the Table.

K(C–O) or f(Mn–C) and f(C–O) values remain almost constant.[34] However, there is no clear relationship between the electronegativity of M and the force constant, K(M–Mn) or f(Mn–M). By comparing the sets of force constants, K(M–Mn), K(Mn–C), and K(C–O), or the sets of F-matrix elements, f(M–Mn), f(Mn–C), and f(C–O), it can reasonably be concluded, on the basis of above discussions, that the π-characters in the Si–Mn and Ge–Mn bonds are in the same order as that in the Sn–Mn bond, and that the σ-character of the M–Mn bond is, if anything, primarily responsible for the order of M–Mn bond strength, f(Si–Mn)$\geqq f$(Ge–Mn)$>f$(Sn–Mn).

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[34] Although the numerical value of f (Sn–Mn) in Br_3Sn–Mn-$(CO)_5$ is slightly larger than that of Br_3Ge–Mn$(CO)_5$, this difference cannot be regarded as significant.