October, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 59, 3079—3084 (1986)* 3079

^{17}O NMR Studies on a Series of Manganese Carbonyl Derivatives with Sn-Mn Bond(s)[1)]

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(Received April 24, 1986)

^{17}O NMR spectra were measured for a series of manganese carbonyl derivatives, $(CH_3)_xCl_{3-x}Sn\text{-}Mn(CO)_{5-y}L_y$ and $(CH_3)_{3-x}Sn[Mn(CO)_{5-y}L_y]_{x+1}$($L=P(OPh)_3$). ^{17}O chemical shifts were correlated with carbonyl stretching frequencies, ^{119}Sn-Mössbauer isomer shifts, and ^{55}Mn NMR chemical shifts. From these correlations, ^{17}O chemical shifts were interpreted in terms of σ- and π-electron acceptance of the tin moieties. It was also clarified that ^{17}O NMR spectroscopy is a direct method to study electronic nature around the oxygen atoms in metal cluster compounds such as $Me_2Sn[Mn(CO)_5]_2$ and $MeSn[Mn(CO)_5]_3$. ^{55}Mn NMR spectra were also measured for some of these compounds to corroborate the ^{17}O NMR results.

The tin atom forms a variety of compounds with transition metals.[2)] Their chemistry has been developed actively by Gorsich, Graham, Clark, Nesmeyanov, and others from the interests to extend the knowledge of "metal-metal bonds," and to look for potential models which emulate metal alloys of relevant metal stoms and/or to find effective new catalysts.[3)] Some series of these compounds have been also the targets of many kinds of spectroscopic studies such as IR, Raman, Mössbauer, NMR, and NQR to elucidate the bonding nature between the tin and transition metal atoms and/or to explore the influence of ligands which are coordinated to the tin and transition metal atoms on the tin-transition metal bonds.[4—7)] We reported similar spectroscpic studies on a series of $R_xX_{3-x}Sn\text{-}Mn(CO)_{5-y}L_y$-type compounds.[8)] In these studies, our attention was mainly focused on the change of the Sn–Mn, Sn–X, and Sn–R bondings as functions of R, X, and L. Variation of electron distribution around the oxygen and carbon atoms is usually investigated by normal coordinate analyses. Although we can get an insight into the bonding nature of the carbonyl groups in terms of C–O and Mn–C stretching force constants from normal coordinate analyses, the information obtained therefrom on the electronic nature of CO groups is somewhat indirect and obscured by introduction of several stretch–stretch interaction force constants to attain better agreement between the observed and calculated frequencies. However, recent technical improvement of NMR spectroscopy, that is, the pulsed FT-NMR technique, has made it possible to obtain ^{17}O NMR spectra of the metal carbonyl derivatives at the naturally abundant ^{17}O-level[9,10)] together with ^{13}C NMR spectra. Direct information on the electron distribution at the oxygen and carbon atoms is available from ^{17}O and ^{13}C NMR data. We have adopted a series of tin-manganese bonded compounds, $R_xCl_{3-x}Sn\text{–}Mn(CO)_{5-y}L_y$ and $R_{3-x}Sn[Mn(CO)_{5-y}L_y]_{x+1}$ for ^{17}O and ^{13}C NMR studies from our renewed interest in these types of compounds and to deepen our understanding on ^{17}O and ^{13}C NMR data by correlating these with other spectroscopic results obtained in the series of previous studies.[8)] During the course of this study, we have found that ^{13}C NMR spectra of CO groups are broad and unresolved for axial and equatorial carbonyls because of the nuclear quadrupole moment of ^{55}Mn, but the ^{17}O NMR spectra are reasonably sharp and clearly resolved for axial and equatorial carbonyls in these compounds. This observation promises that ^{17}O NMR which has recently been expeditiously employed as a structural and bonding prove for metal carbonyl derivatives,[9—11)] is an eligible alternative to ^{13}C NMR for investigating the bonding nature of CO groups and/or structures of these compounds. Kump and Todd reported similar observation during the course of this study.[10f)] We now report ^{17}O NMR spectra of some tin–manganese bonded compounds together with ^{55}Mn NMR data to supplement our previous spectroscopic studies on these compounds and to demonstrate how ^{17}O NMR is instrumental for disclosing the bonding of CO groups in metal carbonyl derivatives in which the nuclear quadrupole moment of the metal atom is greater than 1/2.

Experimental

Materials. All the syntheses were made under a purified nitrogen atmosphere. The series of $(CH_3)_xCl_{3-x}Sn\text{-}Mn(CO)_5$ compounds, that is $Cl_3Sn\text{-}Mn(CO)_5$ (**1**), $Cl_2(CH_3)Sn\text{-}Mn(CO)_5$ (**2**), $Cl(CH_3)_2Sn\text{–}Mn(CO)_5$ (**3**), and $(CH_3)_3Sn\text{–}Mn(CO)_5$ (**4**) were prepared according to the previous paper.[8b)] Literature methods were employed to obtain $(CH_3)_2Sn[Mn(CO)_5]_2$ (**5**)[12a)] and $CH_3Sn[Mn(CO)_5]_3$ (**6**).[12b)] The syntheses of $(CH_3)_3Sn\text{–}Mn(CO)_4$ L(**7**),[13)] $(CH_3)_2Sn[Mn(CO)_4L]_2$ (**8**),[13)] and $(CH_3)_3Sn\text{–}Mn(CO)_3L_2$ (**9**)[8m)] are described elsewhere.

NMR Measurements. ^{17}O and ^{55}Mn NMR spectra were measured for ca. 1 mol dm^{-3} toluene solutions at ca. 80 °C (**5** and **6**), benzene-*d*$_6$ solutions (**4**, **7**, **8**, and **9**) and chloroform-*d* solutions at 30 °C (**1**, **2**, and **3**) on a Varian FT-80A spectrometer operated at 10.782 and 19.708 MHz respectively with Fourier transform mode for naturally abundant levels (0.037 and 100% for ^{17}O and ^{55}Mn nuclei, respectively). The spectra were recorded using a 10 mm o.d. sample tube.

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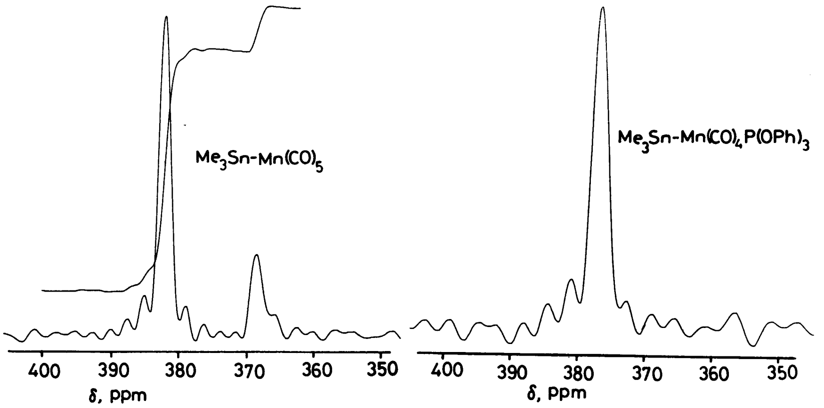
Table 1. ^{17}O and ^{55}Mn NMR Chemical Shifts and Relevant Carbonyl Stretching Frequencies

Compound[a]	$\delta(^{17}O)$/ppm[b] equatorial	axial	$\delta(^{55}Mn)$/ppm[c]	ν(CO)/cm^{-1}
Cl_3Sn-$Mn(CO)_5$ (**1**)	390	383	−2024[d]	2126(A_1^2) 2046(E) 2040(A_1^1)[d]
$Cl_2(CH_3)Sn$-$Mn(CO)_5$ (**2**)	386	380	−2312[d]	2114(A_1^2) 2032(E) 2020(A_1^1)[d]
$Cl(CH_3)_2Sn$-$Mn(CO)_5$ (**3**)	384	373	−2520[d]	2102(A_1^2) 2008(E) 2016(A_1^1)[d]
$(CH_3)_3Sn$-$Mn(CO)_5$ (**4**)	382	369	−2660[d]	2090(A_1^2) 1994(E) 2002(A_1^1)[d]
$(CH_3)_2Sn[Mn(CO)_5]_2$ (**5**)	387	372	−2559	2102(w) 2089(w) 2077(s) 2005(vs) 1980(s, sh)[e]
$CH_3Sn[Mn(CO)_5]_3$ (**6**)	391	376	−2558	2109(w) 2075(s) 2012(s) 1995(vs)[e]
$(CH_3)_3Sn$-$Mn(CO)_4L$ (**7**)	377		−2869[g]	2050(A_1^2) 1956(E)[f]
$(CH_3)_2Sn[Mn(CO)_4L]_2$ (**8**)	380		not observed	2065(vw) 2039(w) 1995(sh) 1075(vs) 1995(sh)[f]
$(CH_3)_3Sn$-$Mn(CO)_3L_2$ (**9**)	367	372	−3458	2019(A_1^2) 1952(E, A_1^1)[f]

a) L denotes triphenyl phosphite, $P(OC_6H_5)_3$. b) Chemical shifts from $H_2{}^{17}O$. c) Chemical shifts from $K^{55}MnO_4$. d) Data from Ref. 8b. e) Data from Ref. 8o. f) C_6H_6 solution; g: doublet with the spacing of 782.2 Hz.



^{17}O NMR Spectra

Fig. 1. ^{17}O NMR spectra of $(CH_3)_3Sn$-$Mn(CO)_5$ in $CDCl_3$ and $(CH_3)_3Sn$-$Mn(CO)_4P(OPh)_3$ in C_6D_6.

Accumulated transients were ca. 5×10^5 (0.02 s acquisition time) for ^{17}O and ca. 10^6 (0.05 s) for ^{55}Mn with 90° pulses. The spectral widths were 8000 Hz both for ^{17}O and ^{55}Mn nuclei and available data points were 323 and 807 for ^{17}O and ^{55}Mn in the time-domain spectra by keeping the Fourier number at 16384. Chemical shifts were measured in parts per million as frequency shifts from synthesizer frequencies, 8.532 and 17.385 MHz respectively for ^{17}O and ^{55}Mn and they were recalculated in the sense that a positive chemical shift designates a resonance to a lower field than that of water oxygen (10.78317 MHz) for ^{17}O, while a positive chemical shift for ^{55}Mn designates a resonance to a higher field than that of potassium permanganate (19.70807 MHz). The ^{17}O NMR spectra of these compounds were reasonably sharp (half band widths of 20—30 Hz). The ^{55}Mn NMR spectra were also sharp for a series of $(CH_3)_xCl_{3-x}Sn$-$Mn(CO)_5$, $(CH_3)_2Sn[Mn(CO)_5]_2$, and $CH_3Sn[Mn(CO)_5]_3$, but the spectra were broad for **7** and **9**. The NMR data are collated in Table 1 together with ν(CO) frequencies.

Spectral Results, Assignment, and Trends

^{17}O NMR Spectra. The compounds **1**—**4** which possess four equatorial and one axial carbonyls show two peaks with relative intensity of 4:1, whereas the compounds **7** and **8** which contain only equatorial carbonyls display one peak (Fig. 1). The stronger peaks of **1**—**4** are assigned to the equatorial carbonyls and the weaker peaks to axial carbonyls. For **5** and **6** which possess two kinds of carbonyl groups, that is, four cis carbonyls and one trans carbonyl for each $Mn(CO)_5$ group with respect to each Sn-Mn bond, we observe two peaks with relative intensity of 4:1; a similar assignment as above is applicable. All the ^{17}O NMR

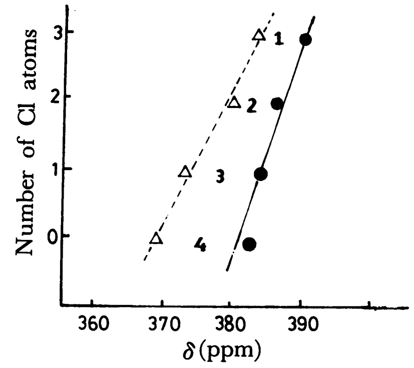
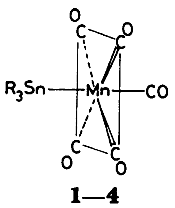
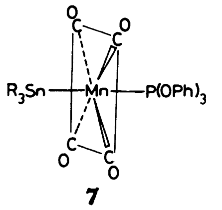


Fig. 2. Plots of ^{17}O chemical shifts vs. the number of the chlorine atoms for $(CH_3)_xCl_{3-x}Sn$-$Mn(CO)_5$.



1—**4**



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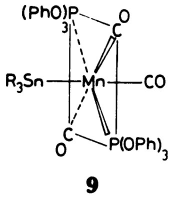

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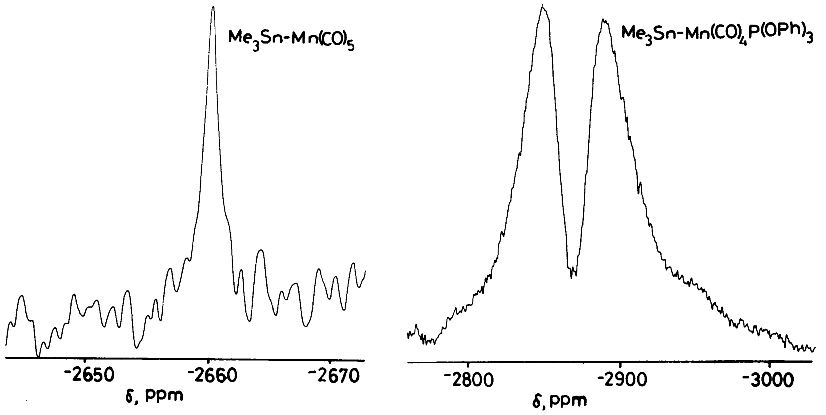

Fig. 3. ^{55}Mn NMR spectra of $(CH_3)_3Sn-Mn(CO)_{5-x}L_x$ in toluene.

signals are reasonably sharp (half-band width=20—40 Hz under these conditions). The spectrum of compound **9** which has two peaks with a relative intensity of 2:1 are overlapped and broad (half-band width=120 Hz), suggesting the presence of a number of conformers and the exchange process thereof. The spectral results is a good example to demonstrate that ^{17}O NMR is superior to IR spectroscopy for polynuclear metal carbonyl derivatives such as **5** and **6** to assess the electron distribution and/or bond order of CO groups; in IR spectra of **5** and **6**, several CO stretching peaks are observed. We are forced to carry out rather a laborious normal coordinate analysis in order to cull information on the electronic nature of CO groups. Attempts were also made to get ^{13}C NMR spectra of CO groups for the present compounds. However, unresolved broad peaks were observed for some of these compounds. For series of $(CH_3)_xCl_{3-x}Sn-Mn(CO)_5$ compounds, the resonances due to axial carbonyl oxygen show monotonous up-field shifts as large as 14 ppm, whereas those of equatorial carbonyls shift 8 ppm to up-field as we replace a chlorine atom with a methyl group (Fig. 2). The observation indicates that the axial carbonyl is more strongly influenced than equatorial carbonyls by this substitution. For a series of $(CH_3)_{3-x}Sn[Mn(CO)_5]_{x+1}$ compounds, **4**, **5**, and **6**, the resonances of the equatorial carbonyl oxygen shifts to downfield quite similarly to those of axial carbonyls with the increase of the number of the manganese carbonyl moiety. For the substitution of carbonyls with triphenyl phosphite(s), the equatorial carbonyls resonate at a higher field with the increase of the triphenyl phosphite ligand(s), while the axial carbonyls are less influenced by this substitution.

^{55}Mn NMR Spectra. In a series of $(CH_3)_{3-x}Sn[Mn(CO)_5]_{x+1}$ compounds, ^{55}Mn chemical shift moves only slightly to lower field and the line width remains almost constant at 27 Hz with the increase of x from 0 to 2. The one-bond Sn-Mn coupling cannot be observed. In contrast, ^{55}Mn NMR spectra exhibit a drastic change as we replace CO with triphenyl phosphite in $(CH_3)_3Sn-Mn(CO)_{5-y}L_y$; (**7**) shows a doublet signal with the separation of 782.2 Hz and the center of this split peaks is at ca. 210 ppm up-field compared with the resonance position of **4** (Fig. 3). For x=2, the signal is very broad ($\Delta\nu_{1/2}$=1340 Hz) and the center is further in the up-field. The observed splitting and broadening are probably due to spin-spin coupling with the phosphorus nucleus, although the ^{31}P NMR of **9** shows a slightly broadened singlet ($\Delta\nu_{1/2}$=31 Hz). It is very often the case that the nucleus with I=1/2 may not show splitting due to coupling but just broadening when coupled with a quadrupolar nucleus which relaxes with fast to intermediate rates.[14] An alternative possibility that this splitting could be derived from the presence of a stereoisomer of **7** where the triphenyl phosphite group occupies a cis position with respecpt to the Sn-Mn bond is rather unlikely, since ^{17}O NMR spectrum of **7** exhibits only one peak. The ^{55}Mn NMR spectra of a series of $(CH_3)_xCl_{3-x}Sn-Mn(CO)_5$ are reported in the previous paper.[8b]

Discussion

Correlation of ^{17}O NMR Chemical Shifts with Other Spectroscopic Data. A first attempt was made to correlate the ^{17}O NMR chemical shift values with previously obtained spectral data for **1**—**4**, **7**, and **9**. In Fig. 4 is given the relationship between ^{17}O chemical shifts of axial and equatorial carbonyls and CO stretching frequencies of the carbonyl groups, where A_1^2 mode denotes the symmetric stretching essentially due to equatorial carbonyls and A_1^1 mode denotes the symmetric stretching essentially due to axial carbonyl. It is generally understood that the electron taken up in the part of CO is situated in the antibonding orbital and therefore leads to lowering of the stretching frequencies. Good linear relationship holds for ^{17}O chemical shifts and CO stretching frequencies of A_1^2 mode. For axial carbonyl, however, the plot for **9** deviates conspicuously from the line. Figure 5 shows relationships between ^{17}O chemical shifts and ^{55}Mn chemical shifts for a series of $(CH_3)_xCl_{3-x}Sn-$

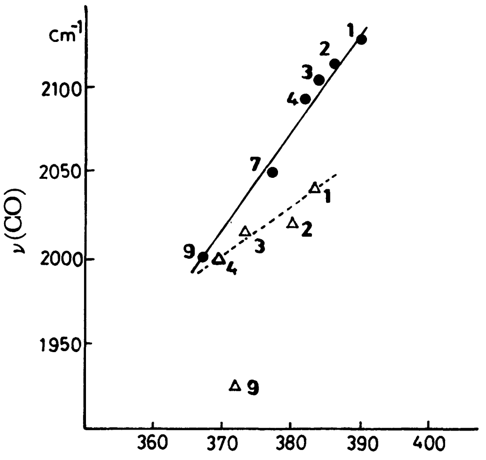

Fig. 4. Correlations of ^{17}O chemical shifts with carbonyl stretching frequencies for $(CH_3)_xCl_{3-x}Sn-Mn(CO)_{5-y}L_y$; ● denotes A_1^2 mode and Δ denotes A_1^1 mode.

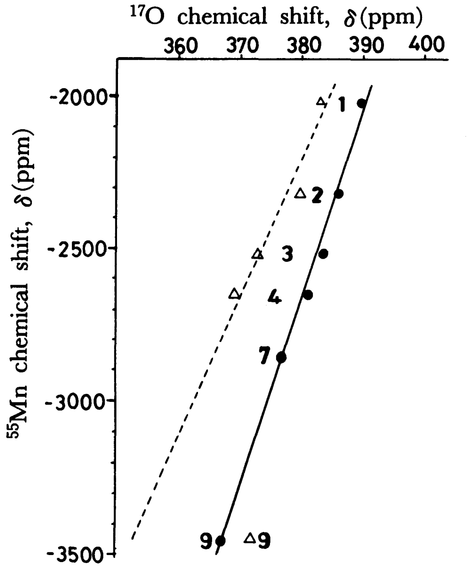

Fig. 5. Relationships between ^{17}O and ^{55}Mn NMR chemical shifts for $(CH_3)_xCl_{3-x}Sn-Mn(CO)_{5-y}L_y$; ● and Δ represent chemical shifts for the equatorial and axial carbonyls, respectively.

$Mn(CO)_{5-y}L_y$ compound. Good linear relationship is observed for equatorial carbonyls, but the plot for axial carbonyl of **9** is far from the line drawn for plots of **1**—**4**. Significant deviation of ^{17}O chemical shift for axial carbonyl of **9** against ν(CO) and ^{55}Mn NMR chemical shift observed in Figs. 4 and 5 leads us to assume that a certain factor other than electronic origin might provoke anomaly of ^{17}O chemical shift of the axial carbonyl in **9**. In Fig. 6, correlation between ^{17}O chemical shifts and ^{119}Sn-Mössbauer isomer shifts is examined for a series of $(CH_3)_xCl_{3-x}Sn-Mn(CO)_5$ and a series of $(CH_3)_{3-x}Sn[Mn(CO)_5]_{x+1}$. ^{17}O chemical shifts move to lower field with the increase of ^{119}Sn isomer shift. Since the increase of ^{119}Sn-Mössbauer isomer shift means s-electron deposit on the tin nucleus,[8a)] the correlation indicates sσ-electron transfer from the manganese carbonyl moiety to the tin atom.

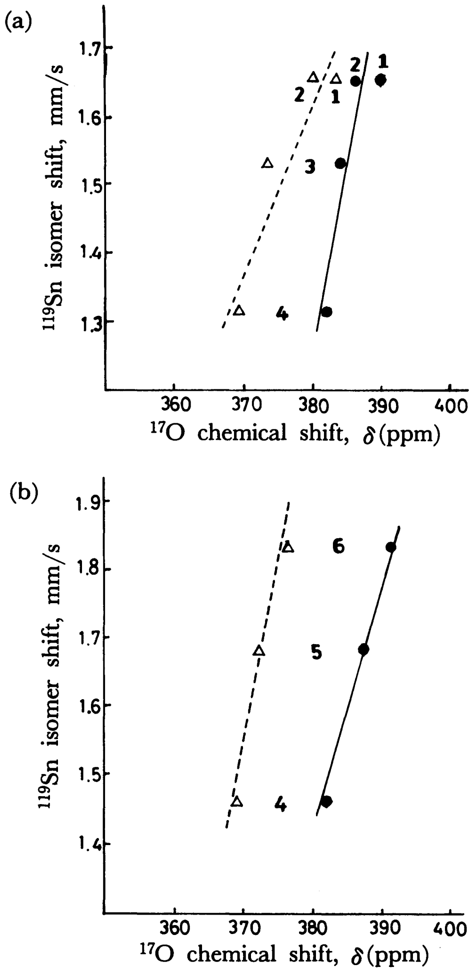

Fig. 6(a): Relationships between ^{17}O NMR chemical shifts and ^{119}Sn-Mössbauer isomer shifts for $(CH_3)_xCl_{3-x}Sn-Mn(CO)_5$. (b): Relationships between ^{17}O NMR chemical shifts and ^{119}Sn-Mössbauer isomer shifts for $(CH_3)_{3-x}Sn[Mn(CO)_5]_{x+1}$; ● represents data for equatorial carbonyls and Δ for axial carbonyls.

Interpretation of ^{17}O Chemical Shifts. The chemical shifts of ^{17}O NMR are dominantly determined by the local paramagnetic contribution to the total screening constant σ.[15,16)] The paramagnetic screening σ_p is expressed by Pople in the form

$$\sigma_p = -\text{const}\langle\Delta E\rangle^{-1}\{\langle r_p^{-3}\rangle(Q_{aa}+Q_{ab})_p\} \quad (1)$$

where ΔE is a mean excitation energy, $\langle r_p^{-3}\rangle$ is the mean inverse cube radius of the valence p-electron, and $(Q_{aa}+Q_{ab})_p$ terms are dependent on the charge imbalance in the ground state valence p-orbitals of the atom **a** and the bond order between the atom **a** and the adjacent atom **b**, respectively. In the previous report from this laboratory,[9b)] it was demonstrated that ^{17}O chemical shift is dominantly determined by the change of electron density through σ-donating and π-accepting ability of the group R for $RMn(CO)_5$-type compounds, that is, Q_{aa} term is operative for

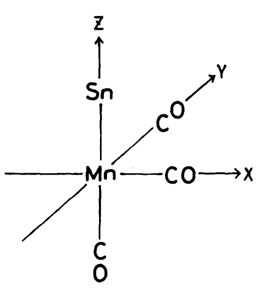

Fig. 7. Coordinate axes for $(CH_3)_xCl_{3-x}$Sn–Mn(CO)$_{5-y}$L$_y$.

paramagnetic shift of ^{17}O resonance. The series of $(CH_3)_xCl_{3-x}$Sn–Mn(CO)$_5$ type compounds, **1**—**4**, are appropriate to see the electronic effect of the tin moiety on the ^{17}O chemical shift. As is shown in Figs. 2 and 6(a), ^{17}O resonances of carbonyl groups are shifted to a lower field by replacing the methyl group with more electronegative chlorine atom and the trend of the shift is more pronounced for axial carbonyl than for equatorial carbonyls. If we choose coordinate axes as is shown in Fig. 7, the axial carbonyl can exploit two π-orbitals (d_{xz} and d_{yz}) which interact with the π-orbitals of the tin atom, whereas the equatorial carbonyl can utilize one π-orbital (d_{xz} or d_{yz}) for π bondings between carbonyls and manganese atom. From this symmetry consideration, we find that the increase of π-electron withdrawal by the more electronegative tin moiety reduces π-interactions between manganese and equatorial and axial carbonyls and the reduction of this π-interaction should be enhanced for axial carbonyl and σ-electron-withdrawing by the tin moiety reduces electron density of only axial carbonyl. Thus, the change of σ- and π-electron-withdrawing ability of the tin moiety should be more strongly reflected on the change of charge density around the oxygen atom of axial carbonyl than that of equatorial carbonyls. The observed trend of enhanced deshielding of ^{17}O nuclei for axial carbonyl than that for equatorial carbonyls is interpreted in terms of increased σ- and π-electron acceptance of the tin moiety with the increase of the number of chlorine atoms. Similar conclusion was obtained in the previous spectroscopic studies for this series of compounds,[8a–c] but the effect of the substitution is more adequately reflected on the ^{17}O chemical shift than, for instance, on a set of force constants of carbonyl groups; in the previous normal coordinate analyses, the effect of this substitution was enhanced for equatorial carbonyls than for axial carbonyls when the Mn–C and C–O stretching force constants of equatorial and axial carbonyls were compared for **1** and **4**.[8c]

The substitution of CO group(s) with triphenyl phosphite(s) which is a weaker π-accepting ligand than CO affects π-interactions between the tin and manganese atoms and between the remaining CO groups and the manganese atom in a similar manner. When the axial carbonyl is replaced with triphenyl phosphite, the π-interaction between the tin and manganese atoms and between the manganese atom and equatorial carbonyls should be enhanced. When equatorial carbonyls are replaced with triphenyl phosphites, the π-interactions between the manganese atom and axial carbonyl and between the manganese atom and the remaining equatorial carbonyls are increased. However, the π bond order between carbon and oxygen atoms is decreased by synergetic effect for both types of substitution. The change of the π-interaction between the tin and manganese atoms was already discussed in the previous ^{119}Sn-Mössbauer study[8d,81] and the attention is now focused on the ^{17}O chemical shift. By replacing axial and/or equatorial carbonyls with triphenyl phosphite as in the case of **7** and **9**, ^{17}O resonance of equatorial carbonyl shifts to a higher field. This observation is in agreement with our expectation that the π bond order between the carbon and oxygen atoms of the remaining carbonyls is reduced by this substitution and reduction of π bond order should lead to a higher field shift of ^{17}O resonance of equatorial carbonyls in **8** by substituting the triphenyl phosphite for axial carbonyl in **7**. However, ^{17}O chemical shift of the axial carbonyl in **9** shifts slightly to a lower field by this substitution. A plausible explanation of this anomaly is that deshielding effect due to diamagnetic phenyl groups which are arranged just in the position to deshield the axial carbonyl might contribute to a lower field shift to some extent, although exact discussion must wait for further study on ^{17}O chemical shift of similar metal carbonyl derivatives.

For a series of Me$_{3-x}$Sn[Mn(CO)$_5$]$_{x+1}$ compounds, ^{17}O resonances of both equatorial and axial carbonyls shift monotonously to a lower field with the increase of manganese carbonyl moiety. A heuristic treatment of ^{17}O chemical shifts is shown in Fig. 6(b), that is, a plot of ^{17}O chemical shifts versus ^{119}Sn-Mössbauer isomer shifts shows that ^{17}O chemical shift moves to a lower field with the number of the Mn(CO)$_5$ group and/or with the increase of ^{119}Sn-Mössbauer isomer shift. The result indicates that the more electronegnative tin atom accepts more sσ-electron from the manganese carbonyl moieties with the increase of Mn(CO)$_5$ groups[17] and σ-electron term in Eq. 1 is operative for ^{17}O chemical shift for this series of compounds.

The crux of the matter clarified in this study is that ^{17}O NMR spectroscopy is very convenient and useful technique to investigate the change of electron distribution of the carbonyl groups in metal cluster compounds such as **5** and **6**, and ^{17}O chemical shifts reflect σ- and π-electron acceptance of the tin moiety.

References

1) This work was presented at the 29-th Symposium for Coordination Chemistry held by Chem. Soc. Jpn. on October, 1979 in Hamamatsu.

2) N. S. Vyazankin, G. A. Razuvaev, and O. A. Kruglaya,

Organometal. Chem. Rev. (A)., **3**, 323 (1968) and references therein.

3) H. C. Clark and J. H. Tsai, *Inorg. Chem.*, **5**, 1407 (1966).

4) K. L. Watters and W. M. Risen, Jr., *Inorg. Chim. Acta Rev.*, **1969**, 129 and references therein.

5) D. D. Spencer, J. L. Kirsh, and T. L. Brown, *Inorg. Chem.*, **9**, 235 (1970) and references therein.

6) G. M. Bancroft, K. D. Butler, A. T. Rake, and B. Dale, *J. Chem. Soc., Dalton Trans.*, **1972**, 2025 and references therein.

7) D. H. Harris, M. F. Lappert, J. S. Poland, and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, **1975**, 311.

8) a) S. Onaka, Y. Sasaki, and H. Sano, *Bull. Chem. Soc. Jpn.*, **44**, 726 (1971); b) S. Onaka, T. Miyamoto, and Y. Sasaki, *ibid.*, **44**, 1851 (1971); c) S. Onaka, *ibid.*, **44**, 2135 (1971); d) S. Onaka and H. Sano, *ibid.*, **45**, 1271 (1972); e) S. Onaka, *Nippon Kagaku Kaishi*, **1972**, 1978; f) Y. Kume, D. Nakamura, M. Kubo, and S. Onaka, *J. Magn. Reson.*, **10**, 58 (1973); g) S. Onaka, *Bull. Chem. Soc. Jpn.*,**46**, 2444 (1973); h) S. Onaka, *Bull. Nagoya Inst. Tech.*, **1973**, 133; i) S. Onaka, *Nippon Kagaku Kaishi*, **1974**, 255; j) S. Onaka, *J. Inorg. Nucl. Chem.*, **36**, 1721 (1974); k) S. Onaka, *Bull. Chem. Soc. Jpn.*, **48**, 319 (1975); l) S. Onaka and H. Sano, *ibid.*, **48**, 258 (1975); m) S. Onaka, Y. Yoshikawa, and H. Yamatera, *J. Organomet. Chem.*, **157**, 187 (1978); n) S. Onaka, *Chem. Lett.*, **1978**, 1163; o) S. Onaka and N. Furuichi, *J. Organomet. Chem.*, **173**, 77 (1979).

9) a) Y. Kawada, T. Sugawara, and H. Iwamura, *J. Chem. Soc., Chem. Commun.*, **1979**, 291; b) S. Onaka, T. Sugawara, Y. Kawada, and H. Iwamura, *J. Chem. Soc., Dalton Trans.*, **1982**, 257.

10) a) J. P. Hickey, J. R. Wilkinson, and L. J. Todd, *J. Organomet. Chem.*, **179**, 159 (1979); b) J. P. Hickey, I. M. Baibich, I. S. Butler, and L. J. Todd., *Spectrosc. Lett.*, **11**, 671 (1978); c) D. Cozak, I. S. Butler, J. P. Hickey, and L. J. Todd, *J. Magn. Reson.*, **33**, 149 (1979); d) S. Aimer, L. Milone, D. Osella, G. E. Hawkes, and E. W. Randall, *J. Organomet. Chem.*, **178**, 171 (1979); e) R. L. Kump and L. J. Todd, *J. Chem. Soc., Chem. Commun.*, **1980**, 292; f) R. L. Kump and L. J. Todd, *J. Organomet. Chem.*, **194**, C43 (1980).

11) S. Aime, D. Osella, L. Milone, G. E. Hawkes, and E. W. Randall, *J. Am. Chem. Soc.*, **103**, 5920 (1981).

12) a) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2218 (1966); b) A. J. Thompson and W. A. G. Graham, *ibid.*, **6**, 1365 (1967).

13) S. Onaka, Y. Kondo, N. Furuichi, K. Toriumi, and T. Ito, *Bull. Chem. Soc. Jpn.*, **56**, 87 (1983).

14) a) L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **80**, C31 (1974); b) S. Aime, G. Gervasic, L. Milone, and E. Rosenberg, *Transition Metal Chem.*, **1**, 177 (1976).

15) L. O. Anderson and J. Mason, *J. Chem. Soc., Dalton Trans.*, **1974**, 202.

16) K. A. K. Ebraheem and G. A. Webb, *J. Magn. Reson.*, **25**, 399 (1974).

17) C. Whynter and L. Chandler, *Bull. Chem. Soc. Jpn.*, **43**, 2115 (1970).