The Syntheses of $R_3Sn\text{-}Mn(CO)_{5-n}L_n(n=0$ or 1) Compounds and Their ^{119}Sn-Mössbauer and ^1H-NMR Studies

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Seven new compounds with the Sn–Mn bond have been prepared by carbonyl displacement with a weaker π-accepting ligand, L ($L=P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$ for $R_3Sn\text{-}Mn(CO)_5$) or by reaction of the anion $[Mn(CO)_5]^-$ or $[Mn(CO)_4P(C_6H_5)_3]^-$ with R_3SnX ($R=C_2H_5$, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$). A *trans* configuration is deduced for the mono-substituted compounds, $R_3Sn\text{-}Mn(CO)_4L$, on the basis of the infrared spectra in the ν(CO) region. The ^{119}Sn–Mössbauer and IR spectra are measured for sixteen compounds of the $R_3Sn\text{-}Mn(CO)_{5-n}L_n$ type ($R=CH_3$, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, Cl, Br, I; $L=P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$; $n=0$ or 1). Both the Mössbauer-isomer shift and the quadrupole splitting increase with an increase in the length of the alkyl chain attached to the tin atom. The replacement of CO on the manganese atom with the weaker π-accepting ligand, L, has a significant effect on the isomer shift and quadrupole splitting of the tin atom through the σ- and π-interaction between the tin and manganese atoms. An interpretation of the change in the chemical shift of the terminal methyl protons is also given for alkyl derivatives.

The natue of the Sn–Mn bonding and the effect of substituents on the nature of the Sn–Mn bonding have been studied by various kinds of spectroscopic means for a series of compounds, $R_{3-x}X_xSn\text{-}Mn(CO)_{5-n}L_n$.[1-8] It has been reported that not only the substituents attached to the Sn atom but also those attached to the Mn atom can exert significant effects on the Sn–Mn bonding nature. The present study was undertaken in order to provide further evidence for the effect of the substituent attached to the metal atoms on the nature of the Sn–Mn bonding by using ^{119}Sn–Mössbauer and proton NMR spectroscopic techniques. For this purpose, some new compounds with a Sn–Mn bond were synthesized; the effects of weak π-accepting ligands, such as $M(C_6H_5)_3$ (M=P, As, and Sb), on the Sn–Mn bonding in a series of $R_3Sn\text{-}Mn(CO)_4M(C_6H_5)_3$ compounds were also described.

Experimental

Preparation of Compounds. All the reactions were carried out under a nitrogen atmosphere.

Preparation of $R_3Sn\text{-}Mn(CO)_5$ ($R=C_2H_5$, n-C_3H_7, and n-C_4H_9). These compounds were synthesized by a procedure similar to Gorsich's method.[9] A solution containing 20 mmol of R_3SnCl in 50 ml of THF was stirred into a solution of THF containing 20 mmol of $NaMn(CO)_5$. After stirring at room temperature for 3 hr, the precipitates of sodium chloride were separated from the organic phase by centrifuging. The solution was then evaporated under reduced pressure, and traces of the solvent and unreacted trialkyltin chloride were distilled off through a fractionating column. A pale yellow liquid was obtained from the residual yellow oil by fractional distillation under reduced pressure. The boiling points of the products are presented in Table 1, along with the results of carbon and hydrogen analyses.

Preparation of $(C_2H_5)_3Sn\text{-}Mn(CO)_4P(C_6H_5)_3$. 0.86 g (2 mmol) of $Mn(CO)_4P(C_6H_5)_3$ was reduced to $NaMn(CO)_4P(C_6H_5)_3$ in 50 ml of THF by stirring with a 1% sodium amalgam at room temperature.[10] After stirring for 1 hr, the THF solution was decanted into another flask; 0.48 g (2 mmol) of triethyltin chloride in 50 ml of THF was then stirred in. The mixture was stirred at room temperature for 3 hr. The organic phase was separated from fine precipitates of sodium chloride by centrifugation. The orange solution was concentrated under reduced pressure, and some unreacted triethyltin chloride was distilled off at 60 °C (5×10^{-2} mmHg). The residual yellow powder was dissolved into 50 ml of *n*-hexane with refluxing. The hexane solution was then filtered, and the filtrate was concentrated to about 20 ml *in vacuo* to give yellow, needle-like crystals of $(C_2H_5)_3Sn\text{-}Mn(CO)_4P(C_6H_5)_3$ (0.8 g, yield 63%). Recrystallization was effected from the same solvent.

Preparation of $(CH_3)_3Sn\text{-}Mn(CO)_4P(C_6H_5)_3$ and $(CH_3)_3Sn\text{-}Mn(CO)_4As(C_6H_5)_3$. A mixture of 3.6 g (0.01 mol) of $(CH_3)_3Sn\text{-}Mn(CO)_5$ and 2.6 g (0.01 mol) of $P(C_6H_5)_3$ or 3.06 g (0.01 mol) of $As(C_6H_5)_3$ was heated at about 120 °C for 2 hr. The resulting yellow material was recrystallized from hexane several times to give pale yellow crystals. All the spectral data support the idea that both the products are mono-substituted, although the elemental analysis of the compound prepared from $P(C_6H_5)_3$ gives a little higher carbon content than the value calculated for $(CH_3)_3Sn\text{-}Mn(CO)_4P(C_6H_5)_3$.

Preparation of $(C_6H_5)_3Sn\text{-}Mn(CO)_4Sb(C_6H_5)_3$. A mixture of 1.6 g (3 mmol) of $(C_6H_5)_3Sn\text{-}Mn(CO)_5$ and 1.1 g (3 mmol) of $Sb(C_6H_5)_3$ was heated at about 190 °C for 2 hr. The reaction products were each extracted three times with 25 ml portions of a 2:1 mixture of ethanol and benzene. The extracts were then concentrated to about half the original volume *in vacuo*. Yellow crystals were precipitated on cooling. Recrystallization was effected from the same mixture of solvents.

The analytical data of these new compounds are shown in Table 1, along with some of their physical properties. All the other compounds were prepared by the methods described in Refs. 7 and 9.

Mössbauer Spectra. The ^{119}Sn-Mössbauer spectra were obtained against a $Ba^{119m}SnO_3$ source moving in a constant acceleration mode at room temperature. The sample was used as an absorber and was kept at 79 K in a cryostat. The calibration of the velocity was made as has previously been reported.[1]

NMR Spectra. The NMR data were obtained on dichloromethane solutions of the samples by means of a

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Table 1. Analytical data

Compound	Color	Bp or mp, °C	Found % C	Found % H	Calcd % C	Calcd % H	Yield, %
$(C_2H_5)_3Sn–Mn(CO)_5$	Pale yellow[a]	62 °C at 0.07 mmHg	32.84	3.72	32.96	3.77	68
$(n\text{-}C_3H_7)_3Sn–Mn(CO)_5$	Pale yellow[a]	87 °C at 0.1 mmHg	37.96	4.94	37.96	4.94	36
$(n\text{-}C_4H_9)_3Sn–Mn(CO)_5$	Yellow[a]	99 °C at 0.06 mmHg	42.16	5.66	42.10	5.61	52
$(C_2H_5)_3Sn–Mn(CO)_4P(C_6H_5)_3$	Pale yellow	113.5 °C	54.09	4.79	52.94	4.79	63
$(CH_3)_3Sn–Mn(CO)_4As(C_6H_5)_3$	Pale yellow	164—165 °C	47.29	3.66	47.14	3.80	29
$(C_6H_5)_5Sn–Mn(CO)_4Sb(C_6H_5)_3$	Pale yellow	168—170 °C	55.36	3.34	55.22	3.48	44

a) Liquid at room temperature.

Table 2. Spectral data

Compound	^{119}Sn–Mössbauer data		IR, ν(CO), cm^{-1}			H-HMR data,	
	I.S. (mm/s)	Q.S. (mm/s)	A_1(eq)	E	A_1(ax)	τ(CH) (ppm)[a]	J(^{119}SnCH) Hz
$(CH_3)_3Sn–Mn(CO)_5$	1.33	0.61	2091w	1995vs	2001s[b]	9.50[d]	48.9
$(CH_3)_3Sn–Mn(CO)_4P(C_6H_5)_3$	1.27	0	2035w	1940vs[c]		9.55[d]	~47
$(CH_3)_3Sn–Mn(CO)_4As(C_6H_5)_3$	1.28	0	2034w	1939vs[c]			
$(C_2H_5)_3Sn–Mn(CO)_5$	1.58	0.78	2086w	1989vs	1993s[b]	8.68	~41
$(C_2H_5)_3Sn–Mn(CO)_4P(C_6H_5)_3$	1.44	0.43	2033w	1941vs[c]		8.67	~41
$(n\text{-}C_3H_7)_3Sn–Mn(CO)_5$	1.57	0.85	2086w	1990vs	1994s[b]	8.98	
$(n\text{-}C_4H_9)_3Sn–Mn(CO)_5$	1.51	0.88	2085w	1989vs	1994s[b]	9.05	
$(C_6H_5)_3Sn–Mn(CO)_5$	1.41	0	2095w	2004vs	2004vs[b]		
$(C_6H^5)_3Sn–Mn(CO)_4P(C_6H_5)_3$	1.43	0	2044w	1951vs[c]			
$(C_6H_5)_3Sn–Mn(CO)_4As(C_6H_5)_3$	1.38	0	2045w	1951vs[c]			
$(C_6H_6)_3Sn–Mn(CO)_4Sb(C_6H_5)_3$	1.40	0	2043w	1954vs[c]			
$Cl_3Sn–Mn(CO)_5$	1.68	1.57	2126w	2046vs	2040s[b]		
$Cl_3Sn–Mn(CO)_4P(C_6H_5)_3$	1.72	1.61	2083w	1996vs[c]			
$Cl_3Sn–Mn(CO)_4As(C_6H_5)_3$	1.66	1.74	2081w	1995vs[c]			
$Br_3Sn–Mn(CO)_5$	1.79	1.41[1]	2124w	2045vs	2038s[b]		
$I_3Sn–Mn(CO)_5$	1.92	1.32	2117w	2042vs	2035s[b]		

a) Relative to $Si(CH_3)_4$. b) n-hexane solution. c) $CHCl_3$ solution. d) 0.3 mol solution.

Hitachi-Perkin-Elmer R-20B Spectrometer (60 MHz) at room temperature; the solvent was used as the internal standard. The chemical shift values listed in Table 2 were recalculated with respect to tetramethylsilane (TMS) at an infinite dilution.

IR Spectra. The IR spectra of the CO stretching region were recorded on a JASCO IR-G spectrometer in hexane or chloroform solutions by use of a 0.1 mm KBr liquid cell. The spectra were calibrated by making use of gaseous DCl by means of a superposition method.

All the spectral results are given in Table 2.

Results and Discussion

In a previous paper, it was reported that $(CH_3)_3Sn–Mn(CO)_5$ shows a quadrupole splitting, while $(C_6H_5)_3Sn–Mn(CO)_5$ shows a non-resolved quadrupole splitting.[1] A clearly-resolved quadrupole splitting is observed for the present series of trialkyltin-pentacarbonylmanganese as well. It seems reasonable, therefore, to conclude that a clearly-resolved quadrupole splitting is generally observed for trialkyltin-pentacarbonylmanganese. It was also found that the magnitude of the quadrupole splitting increases in accordance with the length of the alkyl chain and that the isomer shift value of trimethyltin-pentacarbonylmanganese is the lowest among the alkyltin-pentacarbonylmanganese compounds. As the quadrupole splitting of the Mössbauer spectra reflects mainly the p-electron imbalance in the 5p-orbitals of the tin atom, the increase in quadrupole splitting means an increased 5p-electron imbalance around the tin atom in accord with the increase of the length of the alkyl chain. The lowest isomer shift, found in $(CH_3)_3Sn–Mn(CO)_5$, indicates that the compound has the lowest s-electron density around the tin atom among the trialkyltin-pentacarbonylmanganese compounds. The NMR measurements showed that the coupling constant, J(^{119}Sn–C–H) observed for $(C_2H_5)_3Sn–Mn(CO)_5$ is lower than that of $(CH_3)_3Sn–Mn(CO)_5$ (48.9 Hz), indicating a lower s-character of the $Sn–CH_2$ bond in $(C_2H_5)_3Sn–Mn(CO)_5$. It can be concluded on the basis of the results obtained by the rehybridization theory[11,12] that the p-character of the Sn–C bond and the s-character of the Sn–Mn bond for $(C_2H_5)_3Sn–Mn(CO)_5$ are larger than those for $(CH_3)_3Sn–Mn(CO)_5$.

The proton NMR measurements showed that the τ-values of the terminal methyl proton increase in the order of $(C_2H_5)_3Sn–Mn(CO)_5 < (n\text{-}C_3H_7)_3Sn–Mn(CO)_5 < (n\text{-}C_4H_9)_3Sn–Mn(CO)_5 < (CH_3)_3Sn–Mn(CO)_5$, indicating that the methyl protons in $(CH_3)_3Sn–Mn(CO)_5$ are most highly-shielded. Many factors which affect the proton chemical shift have been discussed for some Group IV B alkyl derivatives,[13–16] and it has been

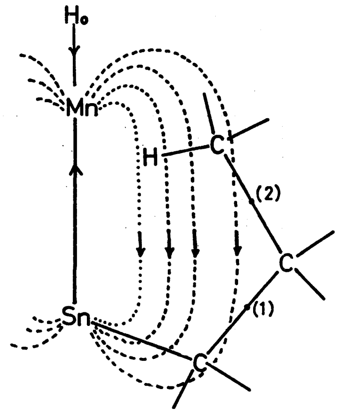

Fig. 1. The magnetic field induced by the applied field H_0 and the closest approach of methyl protons to Sn–Mn bond in $(n\text{-}C_3H_7)_3Sn\text{–}Mn(CO)_5$. (1) and (2) indicate the positions of methyl protons in ethyl and *n*-propyl derivatives, respectively. The terminal methyl protons can contact to Sn–Mn bond by rotating C–C bonds around their axis in the case of *n*-butyl derivative.

concluded that the predominant factor causing a shift to a lower field is the magnetic anisotropy effect for Group 4B ethyl derivatives.13) As for the present series of alkyltin compounds, the magnetic anisotropy effect can account for the lower-field shift of the methyl protons in $(C_2H_5)_3Sn\text{–}Mn(CO)_5$, $(n\text{-}C_3H_7)_3Sn\text{–}Mn(CO)_5$, and $(n\text{-}C_4H_9)_3Sn\text{–}Mn(CO)_5$ as compared to $(CH_3)_3Sn\text{–}Mn(CO)_5$, as is shown in Fig. 1. However, a shift to a higher field in the order of $(C_2H_5)_3Sn\text{–}Mn(CO)_5 < (n\text{-}C_3H_7)_3Sn\text{–}Mn(CO)_5 < (n\text{-}C_4H_9)_3Sn\text{–}Mn(CO)_5$ can be explained neither in terms of the magnetic anisotropy effect nor in terms of the intramolecular van der Waals dispersion forces, since the magnetic anisotropy effect and the intramolecular van der Waals forces cause a lower-field shift. It is possible to consider that the small changes in the s-character of the Sn–Mn bond are the origin of the differences in the $\tau(CH_3)$ values of $(C_2H_5)_3Sn\text{–}Mn(CO)_5$, $(n\text{-}C_3H_7)_3Sn\text{–}Mn(CO)_5$, and $(n\text{-}C_4H_9)_3Sn\text{–}Mn(CO)_5$, since the isomer shift of ^{119}Sn changes in the same order, although such an inductive effect may be estimated to be very small.13) One plausible explanation of this phenomenon is that the high-field shift of the methyl proton resonances going from ethyl to *n*-butyl compounds is due to the direct contact of the terminal methyl protons in $(n\text{-}C_3H_7)_3Sn\text{–}Mn(CO)_5$ and $(n\text{-}C_4H_9)_3Sn\text{–}Mn(CO)_5$ with electrons of the Sn–Mn bonding.13)

In the effect of the replacement of CO on the manganese atom with weaker π-accepting ligands, the most striking feature is shown for $(CH_3)_3Sn\text{–}Mn(CO)_5$ and $(CH_3)_3Sn\text{–}Mn(CO)_4L$ or $(C_2H_5)_3Sn\text{–}Mn(CO)_5$ and $(C_2H_5)_3Sn\text{–}Mn(CO)_4L$ ($L{=}P(C_6H_5)_3$ and/or $As(C_6H_5)_3$). A well-resolved quadrupole splitting is observed for $(CH_3)_3Sn\text{–}Mn(CO)_5$ and $(C_2H_5)_3Sn\text{–}Mn(CO)_5$, whereas a non-resolved spectrum or a slightly-resolved spectrum is observed for the mono-substituted compounds, as is illustrated in Fig. 2. On the other hand, the replacement of CO with L causes a slight change in the isomer shift.

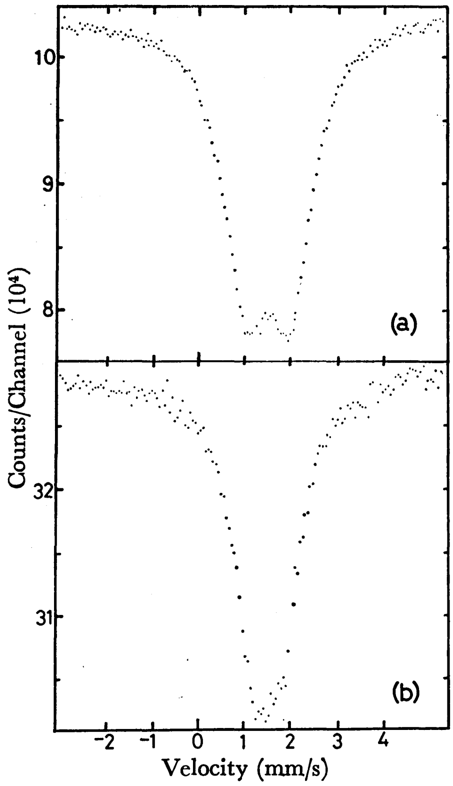

Fig. 2. ^{119}Sn-Mössbauer spectra of (a) $(C_2H_5)_3Sn\text{–}Mn(CO)_5$ and (b) $(C_2H_5)_3Sn\text{–}Mn(CO)_4P(C_6H_5)_3$ both at 78 K.

According to the X-ray analysis of $(C_6H_5)_3Sn\text{–}Mn(CO)_4P(C_6H_5)_3$, triphenylphosphine is coordinated to the manganese atom at the *trans* position with regard to the tin atom. The IR spectrum of this compound was checked, and two peaks were found in the CO stretching region (a very weak peak in the higher-energy region and a very strong one in the lower-energy region), as had been expected from its structural symmetry. All the mono-substituted compounds studied here show the same IR pattern in the CO stretching region as that of $(C_6H_5)_3Sn\text{–}Mn(CO)_4P(C_6H_5)_3$. The *trans* configuration may, therefore, be safely concluded to be found in all the substituted compounds. In the *trans* configuration, the tin atom is considered to compete with the ligand, L, to form a π-bonding with d_π-electrons of the manganese atom. Since the π-accepting ability of the ligand, L, is weaker than that of the substituted CO,17) the d_π-electrons of the manganese atom are forced to enter both the vacant 5d orbitals of the tin atom and the remaining CO π-antibonding orbitals, thus influencing the efg around the tin nucleus. The NMR chemical-shift measurements provide other evidence of this interpretation; the methyl proton resonance is observed in a higher magnetic field for $(CH_3)_3Sn\text{–}Mn(CO)_4P(C_6H_5)_3$ than for $(CH_3)_3Sn\text{–}Mn(CO)_5$; *i.e.*, the shielding effect due to electrons around the proton nucleus is greater for $(CH_3)_3Sn\text{–}Mn(CO)_4P(C_6H_5)_3$ than for $(CH_3)_3Sn\text{–}Mn(CO)_5$. It seems reasonable to ascribe this result to the increase in the electron population around the proton nucleus stemming from the increase in the d_π-interaction between the tin and manganese atoms. In contrast to the case of the alkyl drivatives, the quadrupole splitting of $Cl_3Sn-Mn(CO)_4L$ ($L=P(C_6H_5)_3$ and $As(C_6H_5)_3$) is slightly higher than that of the parent compound, $Cl_3Sn-Mn(CO)_5$. A similar contrast is observed in the values of the isomer shift on the comparison of $Cl_3Sn-Mn(CO)_4L$ with $(CH_3)_3Sn-Mn(CO)_4L$ or $(C_2H_5)_3Sn-Mn(CO)_4L$ ($L=P(C_6H_5)_3$, $As(C_6H_5)_3$, and CO). The reversed effect of the substitution of CO with weaker π-accepting ligands on the quadrupole splitting and isomer shift may also be ascribed to the increase of the σ- and π-interaction between the tin and manganese atoms through the substitution. The substitution of X in $X_3Sn-Mn(CO)_5$ increases the isomer shift with a decrease in the quadrupole splitting, whereas the substitution of R in $R_3Sn-Mn(CO)_5$ increases the isomer shift with an increase in quadrupole splitting, as may be seen in Table 2. Recently, Goodman *et al.* and Bancroft *et al.* have determined the sign of the quadrupole coupling constant, e^2qQ, of the tin atom in $Cl_3Sn-Mn(CO)_5$, $(CH_3)_2ClSn-Mn(CO)_5$, and $(CH_3)_3Sn-Mn(CO)_5$ by means of Mössbauer spectroscopy.[18,19] In the case of $Cl_3Sn-Mn(CO)_5$, there was concluded to be an excess of electron density in the p_z, d_{z^2}, d_{xz}, or d_{yz} orbitals because of the positive value of e^2qQ,[18] while an excess of electron density in the p_x, p_y, $d_{x^2-y^2}$, or d_{xy} orbitals was concluded for $(CH_3)_2ClSn-Mn(CO)_5$ and $(CH_3)_3Sn-Mn(CO)_5$ because of the negative value of e^2qQ.[19] As was mentioned above, the replacement of CO with weaker π-accepting ligands will increase the electron density in p_z, d_{xz}, and d_{yz} orbitals of the tin atom in $(CH_3)_3Sn-Mn(CO)_4L$ compared to the parent compound, thus reducing the electron imbalance around the tin atom, whereas the substitution will produce a positive contribution, thus increasing the electron density along the z axis in $Cl_3Sn-Mn(CO)_4L$ and augmenting the electron imbalance around the tin atom.

The fact that the zero quadrupole splitting in $(C_6H_5)_3Sn-Mn(CO)_5$ is not affected by the replacement of CO with L may well be explained in terms of the predominant π-delocalizing effect of the phenyl groups attached to the tin atom, as was described in a previous short communication.[4]

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