*Journal of Organometallic Chemistry*, 217 (1981) 315—328
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

# REACTION OF TRIALKYLSTANNYLLITHIUM AND HEXAALKYLDISTANNANE. $^1$H AND $^{119}$Sn NMR STUDIES

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(Recieved March 9th, 1981)

## Summary

The reaction of hexamethyldistannane ($Me_3SnSnMe_3$) with metallic lithium in tetrahydrofuran (THF) has been studied by $^1$H and $^{119}$Sn NMR spectroscopy. All spectra displayed a single peak which moved gradually from the chemical shift of $Me_3SnSnMe_3$ (0.22 ppm in $^1$H NMR and —108.7 ppm in $^{119}$Sn NMR) into those of trimethylstannyllithium ($Me_3SnLi$, —0.37 ppm, —182.7 ppm) in 2 h. A mixture of $Me_3SnSnMe_3$ and $Me_3SnLi$ in THF also showed only a single peak both in the $^1$H and $^{119}$Sn NMR spectra. There was a linear relationship between the chemical shift of the singlet and the amount of lithium per trimethylstannyl group ($Li/Me_3Sn$). The equilibration of the $Me_3Sn$ group between the two species was proposed as a plausible explanation for the apparent equivalency of $Me_3Sn$ and was supported by investigating two mixed alkyl systems. Both the $Me_3SnLi$-$Et_3SnSnEt_3$ and $Et_3SnLi$-$Me_3SnSnMe_3$ systems showed single $Me_3Sn$ and $Et_3Sn$ group resonances each in the NMR spectra. The chemical shift of $Me_3Sn$ vs. ($Li/R_3Sn$) in $^{119}$Sn NMR spectra, however, deviated considerably to higher field from the linear relationship, while that of $Et_3Sn$ shifted to lower field. This can be interpreted in terms of the rapid exchange between $Me_3Sn$ and $Et_3Sn$ in the following two equilibria.

$$Me_3SnLi + Et_3SnSnEt_3 \overset{K_1}{\rightleftharpoons} Et_3SnLi + Me_3SnSnEt_3$$

$$Me_3SnLi + Me_3SnSnEt_3 \overset{K_2}{\rightleftharpoons} Et_3SnLi + Me_3SnSnMe_3$$

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## Introduction

The electron-donating ability of a $\sigma$(Sn—Sn) bond has been clearly shown by oxidative cleavage of hexaalkyldistannanes ($R_3SnSnR_3$) by various $\pi$-electron acceptors [1], and electrophiles such as halogens, oxygen, etc. [2]. On the other hand, studies of the electron acceptor ability of the $\sigma$(Sn—Sn) bond are rather limited. The reactions of $R_3SnSnR_3$ with lithium metal [3,4], alkyllithiums (RLi) [5], Gringard reagents [6] or sodium alkoxides [6] fall into this category. The reaction of $R_3SnSnR_3$ with Li or RLi presents a facile method for the preparation of trialkylstannyllithium ($R_3SnLi$) [3,4,5] in which electron transfer from Li or RLi to the $\sigma$(Sn—Sn) bond is apparently taking place. Although the synthetic utility of $R_3SnLi$ has been widely investigated [7], the very reaction of $R_3SnLi$ with $R_3SnSnR_3$, which takes place essentially in the course of the reaction between $R_3SnSnR_3$ and Li or RLi, appears to have been overlooked. Studies of this reaction by measuring $^{119}Sn$ and $^1H$ NMR spectra and by trapping the trialkylstannyl anion ($R_3Sn^-$) have now demonstrated a rapid scrambling of $R_3Sn$ groups due to nucleophilic attack of $R_3Sn^-$ on $R'_3SnSnR'_3$. The following equilibration has been suggested to be operative.

$$R_3SnLi + R'_3SnSnR'_3 \overset{K}{\rightleftharpoons} R'_3SnLi + R_3SnSnR'_3$$

## Results and discussion

Three methods for the preparation of $Me_3SnLi$ are available in the literature (eq. 1, 2 and 3). The reaction of $Me_3SnX$ with Li metal (eq. 1) [3,4] is considered to be equivalent to that of eq. 2 [3,4], since $Me_3SnSnMe_3$ was shown to be

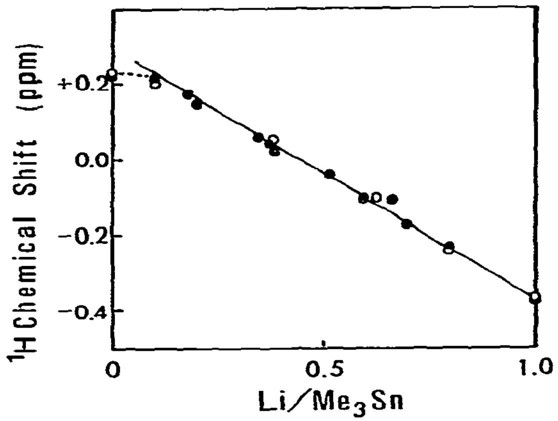
$$Me_3SnX + 2\ Li \rightarrow Me_3SnLi + LiX \quad (1)$$

$$Me_3SnSnMe_3 + 2\ Li \rightarrow 2\ Me_3SnLi \quad (2)$$

$$Me_3SnSnMe_3 + BuLi \rightarrow Me_3SnLi + Me_3SnBu \quad (3)$$

formed initially from $Me_3SnX$ and Li, as described later. Thus, every reaction (eqs. 1—3) is based on the electron-accepting property of the $\sigma$(Sn—Sn) bond.

The $^1H$ NMR spectrum of $Me_3SnLi$ prepared by eq. 1 showed a singlet at —0.37 ppm [4,8], and that of $Me_3SnSnMe_3$ exhibited a single peak at 0.22 ppm. When a THF solution of $Me_3SnLi$ was added to $Me_3SnSnMe_3$ in various ratios, the $^1H$ NMR spectra of the mixtures displayed a broad single peak assignable to the $Me_3Sn$ protons in every case at a position intermediate between those of $Me_3SnLi$ and $Me_3SnSnMe_3$. There was a linear relationship between the chemical shift of the peak and the amount of lithium in $Me_3SnLi$ per total $Me_3Sn$ groups, (Li/$Me_3Sn$), in solution (Fig. 1). When the ratio of $Me_3SnLi$ was increased, the signal was shifted to higher field. A similar result was obtained in the case of the $^{119}Sn$ NMR spectra of mixtures in various ratios (● points in Fig. 2). The chemical shift of the singlet was correlated to the ratio (Li/$Me_3Sn$), and moved between those of $Me_3SnSnMe_3$ (—108.7 ppm) [9] and $Me_3SnLi$ (—182.7 ppm) [10]. The broad singlet remained unchanged for 2 h at room temperature, and gradually collapsed into several peaks in 20 h.



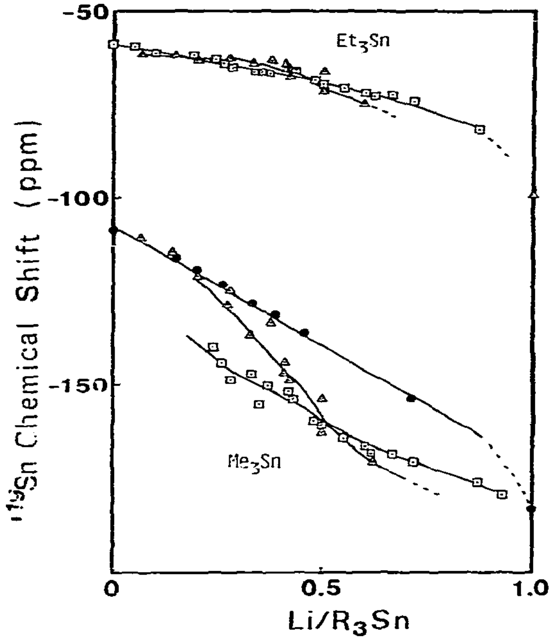


Fig. 1. Plots of the $^1$H NMR chemical shift of $CH_3$ vs. the ratio of Li to $Me_3Sn$ in the system. ● $Me_3SnLi$-$Me_3SnSnMe_3$; ○ BuLi-$Me_3SnSnMe_3$.

Fig. 2. Plots of the $^{119}$Sn NMR chemical shift of $Me_3Sn$ and $Et_3Sn$ groups vs. the ratio of Li to $R_3Sn$ in the system. ● $Me_3SnLi$-$Me_3SnSnMe_3$; □ $Me_3SnLi$-$Et_3SnSnEt_3$; △ $Et_3SnLi$-$Me_3SnSnMe_3$.

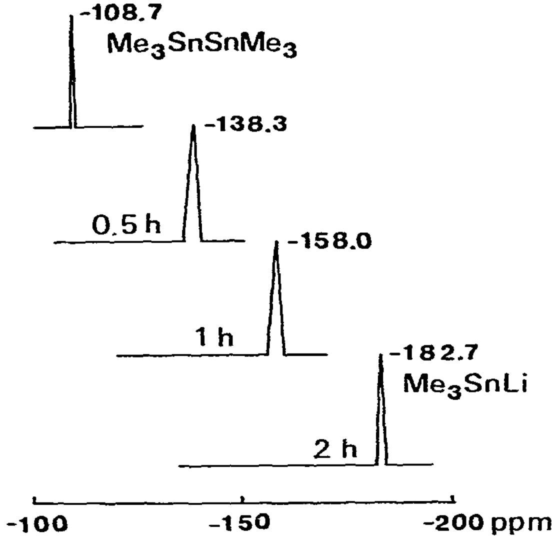


Fig. 3. $^{119}$Sn NMR spectra of the reaction mixture of $Me_3SnSnMe_3$ with Li in THF.

When the reaction of $Me_3SnSnMe_3$ with Li metal (eq. 2) [3,4] was followed by the measurement of the $^1H$ and $^{119}Sn$ NMR spectra, a broad single peak assigned to the $Me_3Sn$ group gradually moved from the position of $Me_3SnSnMe_3$ towards that of $Me_3SnLi$ as the reaction proceeded (Fig. 3). When the reaction of $Me_3SnCl$ with Li metal (eq. 1) was carried out similarly, it was confirmed by the $^{119}Sn$ NMR spectra that $Me_3SnCl$ first was converted to $Me_3SnSnMe_3$ in a few min, which then reacted gradually with Li to form $Me_3SnLi$ in 2 h.

When a hexane solution of BuLi was added to $Me_3SnSnMe_3$ in THF in various ratios (eq. 3) [5], the $^1H$ NMR spectra showed a broad single peak, whose chemical shift was found to be dependent on the ratio of BuLi to $Me_3Sn$ groups, lying on the same straight line as shown in Fig. 1. The $^{119}Sn$ NMR spectrum in this case was not reliable. When 0.2 mol of BuLi was added to 1 mol of $Me_3SnSnMe_3$, the peak of $Me_3SnSnMe_3$ was observed but neither the resonance of $Me_3SnLi$ nor the corresponding peak at an intermediate position between $Me_3SnSnMe_3$ and $Me_3SnLi$ could be detected. In addition, peaks due to $Me_3SnBu$ (-1.1 ppm) [11] and $Me_4Sn$ (0.0 ppm) were observed. When the ratio of BuLi to $Me_3SnSnMe_3$ was greater than 0.6, the peak due to $Me_3SnSnMe_3$ also disappeared and no peaks could be detected. Since the sample for the $^{119}Sn$ NMR measurement was required by the sensitivity to be fairly concentrated, the ratio of the solvent (hexane) of BuLi to THF was larger than that used in the $^1H$ NMR measurement. The insoluble $Me_3SnLi$ thus formed in the mixed solution precipitated, and the corresponding absorption of the $Me_3Sn$ group could not be detected in $^{119}Sn$ NMR spectra.

The reaction of $Et_3SnBr$ with Li metal (eq. 4) [12] also was followed by

$$Et_3SnBr + 2\ Li \rightarrow Et_3SnLi + LiBr \qquad (4)$$

$^{119}Sn$ NMR spectra. After 5 min, all of the $Et_3SnBr$ was converted into $Et_3SnSnEt_3$. As the reaction proceeded, a broad single peak assigned to the $Et_3Sn$ group moved from the position of $Et_3SnSnEt_3$ (—58.8 ppm) [13] toward that of $Et_3SnLi$ (—99.0 ppm).

The reaction of $Et_3SnSnEt_3$ with $Et_3SnLi$ in various ratios gave a similar result to the $Me_3SnLi$-$Me_3SnSnMe_3$ system; i.e. a linear correlation of the chemical shifts of Et vs. the ratio ($Li/Et_3Sn$) as shown in Fig. 4.

In the $^1H$ NMR spectra of $Me_3Sn$-$Et_3Sn$ mixed systems, a broad singlet assigned to Me protons and a quartet and a triplet assigned to the Et protons were observed. The $^1H$ NMR spectrum of an equimolar mixture of $Me_3SnLi$ and $Et_3SnSnEt_3$ displayed a broad singlet at 0.00 ppm, a quartet at 0.94 ppm and a triplet at 1.23 ppm. The resonance of the Me protons (at 0.00 ppm) was found to move to higher field than that at ($Li/Me_3Sn$) = 0.33 on the straight line given by the $Me_3SnLi$-$Me_3SnSnMe_3$ system in Fig. 1.

The chemical shifts of Et protons in the mixed Me-Et system showed shifts to lower field than the values in the $Et_3SnLi$-$Et_3SnSnEt_3$ system in Fig. 4. The spectrum of an equimolar mixture of $Et_3SnLi$ and $Me_3SnSnMe_3$ showed a singlet at 0.08 ppm assigned to the Me protons, a quartet at 0.95 ppm and a triplet at 1.22 ppm assigned to the Et protons. The chemical shift of the Me group deviated slightly from that of Me protons in Fig. 1, and the Et protons were shifted to lower field compared with the Et protons in Fig. 4.

There might be two possible explanations for the above results observed in

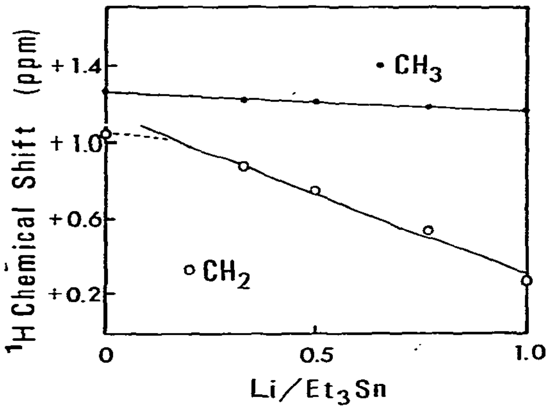


Fig. 4. Plots of the ¹H NMR chemical shifts of $CH_3CH_2$ vs. the ratio of Li to $Et_3Sn$ in the system $Et_3SnLi$-$Et_3SnSnEt_3$.

the ¹H and ¹¹⁹Sn NMR spectra. First, exchange of $R_3Sn$ groups between $R_3SnLi$ and $R'_3SnSnR'_3$ could occur more rapidly than the NMR time scale (eq. 5). Thus each $R_3Sn$ group is equilibrated. Secondly, $R_3Sn$ or $R'_3Sn$ groups

$$R_3SnLi + R'_3SnSnR'_3 \overset{K}{\rightleftharpoons} R'_3SnLi + R_3SnSnR'_3 \tag{5}$$

could be almost equivalent by the formation of a metastable associated trialkylstannyl lithium (I), whose anionic charges are shared by all $R_3Sn$ and $R'_3Sn$ species (eq. 6). The above mechanisms are consistent with the observation that

$$lR_3SnLi + mR'_3SnSnR'_3 \rightarrow \underset{\text{(I)}}{[(R_3Sn)_l(R'_3Sn)_{2m}]^{l-}Li_l^{l+}} \tag{6}$$

the NMR spectra displayed single $Me_3Sn$ and/or $Et_3Sn$ resonances.

In an attempt to differentiate between the two possibilities, the reaction of $Me_3SnLi$ with $Me_3SnSnMe_3$ was conducted at −70°C. The ¹H NMR spectrum of the mixture displayed only a single peak even at this temperature. Neither broadening nor collapse of the single peak was observed at −70°C. Dilution of the sample by the addition of THF did not cause any change in the ¹H and ¹¹⁹Sn NMR spectra even at −95°C. If the equilibrium (eq. 5) is operative in the mixture, the exchange rate must be very fast even at −95°C.

The ¹¹⁹Sn NMR spectra of mixtures of $R_3SnLi$ and $R'_3SnSnR'_3$ in various ratios were measured at −20°C within 10 min. Every ¹¹⁹Sn NMR spectrum of the $Me_3SnLi$-$Et_3SnSnEt_3$ and $Et_3SnLi$-$Me_3SnSnMe_3$ systems displayed two singlets assigned to $Me_3Sn$ and $Et_3Sn$ groups. The correlation of the chemical shift to the ratio ($Li/R_3Sn$) is shown in Fig. 2. A deviation of the chemical shift of the $Me_3Sn$ group from the straight line in the $Me_3SnLi$-$Me_3SnSnMe_3$ system to higher field was found. When the ratio ($Li/R_3Sn$) was less than 0.50, the extent of the deviation in the $Me_3SnLi$-$Et_3SnSnEt_3$ system was larger than that in the $Et_3SnLi$-$Me_3SnSnMe_3$ system. When the ratio ($Li/R_3Sn$) was greater than 0.50, the deviation was smaller in the former system than that in the latter.

The two curves in both system crossed at (Li/$R_3Sn$) = 0.50. On the other hand, the chemical shift of the $Et_3Sn$ group shifted to lower field to a similar degree in both systems. If a rapid equilibration occurs, two successive equilibria (eqs. 7, 8) could be considered in both systems. When some values are allotted to

$$Me_3SnLi + Et_3SnSnEt_3 \overset{K_1}{\rightleftharpoons} Et_3SnLi + Me_3SnSnEt_3 \tag{7}$$

$$Me_3SnLi + Me_3SnSnEt_3 \overset{K_2}{\rightleftharpoons} Et_3SnLi + Me_3SnSnMe_3 \tag{8}$$

the equilibrium constants, $K_1$ and $K_2$, the ratio of the molar concentration of each component can be calculated from eqs. 9 and 10. Then, we are able to predict the chemical shifts of the $Me_3Sn$ and $Et_3Sn$ groups by the weighted means

$$K_1 = \frac{[Et_3SnLi][Me_3SnSnEt_3]}{[Me_3SnLi][Et_3SnSnEt_3]} \tag{9}$$

$$K_2 = \frac{[Et_3SnLi][Me_3SnSnMe_3]}{[Me_3SnLi][Me_3SnSnEt_3]} \tag{10}$$

of each chemical shift of the components (see Appendix). Empirical optimization of $K_1$ and $K_2$ with respect to chemical shifts gave the combination of $K_1$ = 0.5 and $K_2$ = 0.2 which reproduced the observed curves (Fig. 5). When the ratio (Li/$R_3Sn$) is less than 0.5, the calculated values of the $Me_3Sn$ group in the $Me_3SnLi$-$Et_3SnSnEt_3$ system shift to higher field than the other. In the case of (Li/$R_3Sn$) > 0.5, the calculated chemical shifts of $Me_3Sn$ group in the former

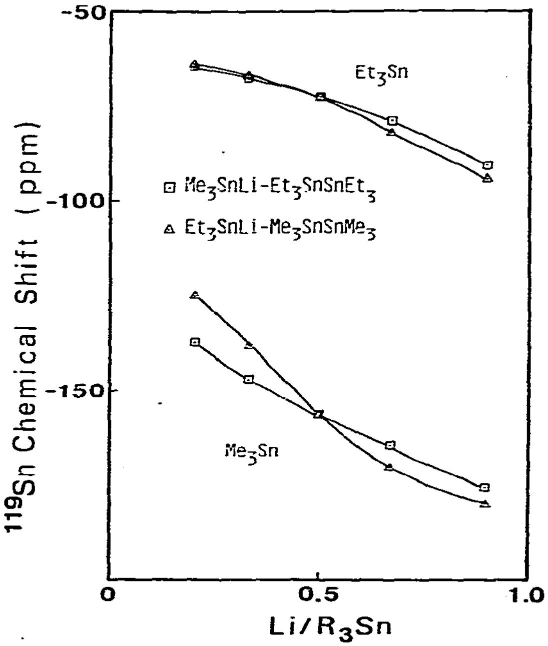


Fig. 5. Plots of the calculated chemical shifts ($K_1$ = 0.5, $K_2$ = 0.2 in eqs. 7 and 8) of $^{119}Sn$ vs. Li/$R_3Sn$.

TABLE 1

TREATMENTS OF THE MIXTURES OF $R_3SnLi$ AND $R'_3SnSnR'_3$ WITH $R''X$. GLC ANALYSES (MOLAR RATIO)

| System | $Li/R_3Sn$ | $R''X$ | $Me_3SnR$ | $Me_3SnSnMe_3$ | $Me_3SnSnEt_3$ | $Et_3SnR$ | $Et_3SnSnEt_3$ |
|---|---|---|---|---|---|---|---|
| $Me_3SnLi$-$Et_3SnSnEt_3$ | 0.33 | a | 31 | 4 | 18 | 20 | 27 |
| | | b | 25 | 5 | 24 | 10 | 36 |
| | | Calcd. [c] | 26 | 4 | 13 | 24 | 31 |
| | 0.50 | a | 43 | 4 | 15 | 23 | 14 |
| | | b | 42 | 1 | 30 | 9 | 18 |
| | | Calcd. [c] | 43 | 7 | 14 | 23 | 15 |
| $Et_3SnLi$-$Me_3SnSnMe_3$ | 0.33 | a | 39 | 15 | 27 | 7 | 12 |
| | | b | 35 | 17 | 32 | 5 | 11 |
| | | Calcd. [c] | 41 | 19 | 22 | 9 | 10 |
| | 0.50 | a | 38 | 8 | 16 | 23 | 14 |
| | | b | 45 | 5 | 22 | 11 | 16 |
| | | Calcd. [c] | 43 | 5 | 14 | 24 | 15 |

[a] $Me_3SiCl$. [b] $PhCH_2Cl$. [c] $K_1 = 0.50$, $K_2 = 0.20$ in eqs. 7 and 8.

were at slightly lower field than the latter. The two curves crossed at $(Li/R_3Sn) = 0.50$. This is consistent with observation in both systems. The calculated chemical shifts of the $Et_3Sn$ group also were close to the observed one. The deviation in the mixed alkyl systems from the straight line can be interpreted by the sequence of equilibria (eqs. 7, 8), where $K_1$ and $K_2$ are 0.5 and 0.2, respectively.

The above equilibration has been supported also by the quantitative analysis of all components in the mixtures. Both $Me_3SnLi$ and $Et_3SnLi$ were trapped by reaction with trimethylchlorosilane ($Me_3SiCl$) or benzyl chloride ($PhCH_2Cl$) at −20°C (to give $R_3SnSiMe_3$ or $R_3SnCH_2Ph$), while $R_3SnSnR_3$ was inert toward $Me_3SiCl$ and $PhCH_2Cl$. Equimolar mixtures of $R_3SnLi$ and $R'_3SnSnR'_3$ (R = Me, R' = Et, and R = Et, R' = Me, $Li/R_3Sn = 0.33$), and mixtures of two molar equivalents of $R_3SnLi$ and one of $R'_3SnSnR'_3$ ($Li/R_3Sn = 0.50$) were treated with these reagents, and the reaction mixtures were subjected to GLC analysis. The molar ratio of each compound was compared with the value of each component calculated from eqs. 7 and 8 (Table 1). The molar ratio determined by the treatment with $Me_3SiCl$ was close to the calculated one in each case, but the experiments with $PhCH_2Cl$ did not give satisfactory results. When a mixture of 2 mol of $Me_3SnLi$ and 1 mol of $Et_3SnSnEt_3$ ($Li/R_3Sn = 0.50$) was treated with $Me_3SiCl$, the molar distribution of each product coincided fairly well not only with the calculated one but also with the result from the $Et_3SnLi$-$Me_3SnSnMe_3$ (2 : 1) system. In the case of $(Li/R_3Sn) = 0.50$, the similar distribution of each compound in both systems corresponds to the crossing of the two curves at $(Li/R_3Sn) = 0.50$ in Fig. 2.

The $^{119}Sn$ NMR data and the molar distribution determined with $Me_3SiCl$ might support the presence of two kinds of equilibria (eqs. 7, 8), whose equilibrium constants, $K_1$ and $K_2$, are about 0.5 and 0.2, respectively. Although the possibility of the existence of the associated trialkylstannyl anion (I) cannot be rigorously excluded, we conclude that most of the results described herein can be rationalized in terms of such equilibration.

## Experimental

All reactions were carried out under a nitrogen atmosphere. $^1H$ NMR spectra were obtained on a JEOL-JNM-C60HL spectrometer (60 MHz) and a Varian-EM390 (90 MHz). $^{119}Sn$ NMR spectra were measured in the pulse Fourier transform mode using a Varian-FT80A spectrometer (29.66 MHz) and a JEOL-FX90Q (33.41 MHz) consisted of 4 K or 8 K data points with spectral width 8000 Hz and aquisition time 0.253 sec. $^1H$ chemical shifts were determined from that of β-methylene protons of THF (1.75 ppm) and are reported as ppm in the TMS scale. $^{119}Sn$ chemical shifts were related to $Me_4Sn$. Gas-liquid chromatography (GLC) was run on a Silicone DC HV column.

$Me_3SnLi$ was prepared as described [3,4,5] by the reaction of $Me_3SnX$ (X = Cl, Br) or $Me_3SnSnMe_3$ with Li metal and of $Me_3SnSnMe_3$ with BuLi. $Et_3SnLi$ was prepared from $Et_3SnBr$ and Li metal [12].

### *Reaction of $Me_3SnLi$ with $Me_3SnSnMe_3$ in various ratios*

A THF solution of $Me_3SnLi$ was prepared by the reaction of $Me_3SnBr$ with Li metal. In a typical reaction, 0.20 mmol of $Me_3SnLi$ in 0.40 ml of THF was added by means of syringe to 65.0 mg (0.20 mmol) of $Me_3SnSnMe_3$ at room temperature in a $^1H$ NMR tube of 5 mm o.d. The reactions were carried out using various ratios of $Me_3SnLi$ to $Me_3SnSnMe_3$. The samples for $^{119}Sn$ NMR spectra were prepared by the successive addition of 98.3 mg (0.30 mmol) portions of $Me_3SnSnMe_3$ to 1.5 mmol of $Me_3SnLi$ in 1.5 ml of THF in a sample tube of 10 mm o.d. The $^1H$ and $^{119}Sn$ NMR spectra of these samples showed a broad single peak in every case. The chemical shifts of the singlet had a linear relationship against $Li/Me_3Sn$ in both $^1H$ and $^{119}Sn$ NMR spectra as shown in Figs. 1 and 2 (point ●). The NMR spectra were measured within 0.2 h after the addition. The spectra did not change for 2 h.

The addition of $Me_3SnLi$ to $Me_3SnSnMe_3$ ($Li/Me_3Sn$ = 0.18, 0.35 and 0.52) was conducted at room temperature, and the $^1H$ NMR spectrum in each case showed a singlet at $\delta$ 0.17, 0.06 and −0.03 ppm, respectively, at room temperature. When the $^1H$ NMR spectra of these samples were measured at −30°C and −70°C, a singlet was observed at the same position as at room temperature in every case. The $^{119}Sn$ NMR spectrum of the mixture in the case of ($Li/Me_3Sn$) = 0.90 showed a singlet at −167.8 ppm at 2°C but neither chemical shift nor the form of the peak changed even at −95°C.

When the addition of $Me_3SnLi$ to $Me_3SnSnMe_3$ ($Li/Me_3Sn$ = 0.38 and 0.70) was carried out at −70°C, the $^1H$ NMR spectrum at −70°C exhibited a single peak at 0.01 and −0.18 ppm, respectively. These singlets measured at −70°C had the same chemical shifts as those obtained at room temperature.

### *Reaction of BuLi with $Me_3SnSnMe_3$*

To a solution of 20.0 mg (0.06 mmol) of $Me_3SnSnMe_3$ in 0.25 ml of THF in an NMR tube was added 0.01 ml of a 1.54 *M* hexane solution (0.015 mmol) of BuLi at 0°C. After the measurement of the $^1H$ NMR spectrum of the sample, further successive additions of 0.01 ml (0.015 mmol) portions of BuLi and the measurements of the $^1H$ NMR spectrum of each mixture were carried out. $^1H$ NMR: $\delta$ 0.17 (BuLi = 0.01 ml), 0.03 (BuLi = 0.02 ml), −0.10 (BuLi = 0.03 ml) and −0.37 ppm ($Me_3SnLi$; BuLi = 0.04). The chemical shifts of the broad singlet have a linear relationship against $Li/Me_3Sn$ as shown in Fig. 1 (point o).

### *Reaction of $Me_3SnSnMe_3$ with Li metal*

A solution of 40.0 mg (0.12 mmol) of $Me_3SnSnMe_3$ in 0.4 ml of THF was added to an excess of Li metal dispersion in a $^1H$ NMR tube. The solution turned yellow in a minute. $^1H$ NMR spectrum of the solution measured after 10 min displayed a broad singlet at 0.00 ppm. The $^1H$ NMR spectrum of the solution after 20 min showed a singlet at −0.10 ppm and the spectrum after 25 min gave a singlet at −0.26 ppm. Over the course of 1.5 h the singlet moved to higher field and stopped at the position of $Me_3SnLi$ (−0.37 ppm).

$^{119}Sn$ NMR spectra were measured in more concentrated solution. The mixture of 0.404 g (1.23 mmol) of $Me_3SnSnMe_3$ and excess Li metal in 2 ml of THF showed a singlet at −128.0 ppm after 20 min, at −155.0 ppm after 55 min and at −182.7 ppm ($Me_3SnLi$) after 2 h.

### *Reaction of $Me_3SnCl$ or $Et_3SnBr$ with Li metal*

A solution of 0.418 g (2.10 mmol) of $Me_3SnCl$ in 2 ml of THF was added to an excess of Li metal in an NMR tube. After 5 min, the $^{119}$Sn NMR spectrum of the solution displayed a singlet assigned to $Me_3SnSnMe_3$ at —108.0 ppm. Then the peak moved up to the position of $Me_3SnLi$ in 2 h.

To a solution of 0.595 g (2.0 mmol) of $Et_3SnBr$ in 2 ml of THF was added an excess of Li metal. The $^{119}$Sn NMR spectrum of the mixture, measured after 5 min at —20°C, showed a singlet at —58.8 ppm ($Et_3SnSnEt_3$) which moved gradually to higher field and stopped at the position of $Et_3SnLi$.

*Reaction of $Me_3SnLi$ and $Et_3SnSnEt_3$*

$Me_3SnLi$ was prepared by the reaction of $Me_3SnSnMe_3$ or $Me_3SnCl$ with Li metal at —20°C. To 0.359 g (0.87 mmol) of $Et_3SnSnEt_3$ in 0.5 ml of THF was added 0.1 ml (0.1 mmol) portions of 1 *M* $Me_3SnLi$ solution, and the $^{119}$Sn NMR spectrum of each sample mixed in various ratios ($Li/R_3Sn$) was measured at —20°C. The spectra showed two singlet assigned to $Me_3Sn$ and $Et_3Sn$ in every case. The relation between the chemical shifts of $Me_3Sn$ and $Et_3Sn$ groups and the ratio ($Li/R_3Sn$) was shown in Fig. 2 (point □).

*Reaction of $Et_3SnLi$ and $Me_3SnSnMe_3$*

To a solution of 1 ml (1 mmol) of 1 *M* $Et_3SnLi$ were added 98.3 mg (0.3 mmol) portions of $Me_3SnSnMe_3$. The $^{119}$Sn NMR spectrum of the mixture in each case exhibited two singlets assigned to $Me_3Sn$ and $Et_3Sn$. The relationship of the chemical shift to the ratio ($Li/R_3Sn$) was shown in Fig. 2 (point △).

*Treatment of $Me_3SnLi$-$Et_3SnSnEt_3$ system with $Me_3SiCl$ or $PhCH_2Cl$*

Two samples whose ratios ($Li/R_3Sn$) were 0.33 and 0.50, were prepared by the addition of 86.5 mg (0.2 mmol) of $Et_3SnSnEt_3$ to 0.20 ml of 1 *M* $Me_3SnLi$ solution, and by that of 56.0 mg (0.14 mmol) of $Et_3SnSnEt_3$ to 0.28 ml of 1 *M* $Me_3SnLi$ solution. After 10 min, half of each mixture was added to $Me_3SiCl$ at —20°C and was subjected to GLC analysis. The other half of each mixture was treated with $PhCH_2Cl$ at —20°C. The distribution of the products is shown in Table 1.

*Treatment of $Et_3SnLi$-$Me_3SnSnMe_3$ system with $Me_3SiCl$ or $PhCH_2Cl$*

Two solutions of $Et_3SnLi$ (0.17 mmol and 0.30 mmol) were added to 56.0 mg (0.17 mmol) and 49 mg (0.15 mmol) of $Me_3SnSnMe_3$, respectively ($Li/R_3Sn$ = 0.33 and 0.50). After 10 min, half of each mixture was treated with $Me_3SiCl$ at —20°C and was subjected to GLC analysis. The other half of each mixture was treated with $PhCH_2Cl$. The molar ratio of the products is shown in Table 1.

## Appendix

### *Determination of the equilibrium constants $K_1$ and $K_2$. Calculation of the $^{119}$Sn chemical shifts and the distribution of each component*

*a) $Me_3SnLi$-$Et_3SnSnEt_3$ system.* If the ratio of Li (g-atom) to $R_3Sn$ group (mol) is taken as $n$, that is ($Li/R_3Sn$) = $n$, the initially added molar amounts of $Me_3SnLi$ and $Et_3SnSnEt_3$ are presented as $n$ and $(1 — n)/2$, respectively. When the molar amounts of the reacted $Et_3SnSnEt_3$ and the formed $Me_3SnSnMe_3$ are taken as $x$ mol and $y$ mol, respectively, the molar concentration of each component in eqs. 7 and 8 is represented as follows.

$$[\mathrm{Me_3SnLi}] = n - x - y$$

$$[\mathrm{Et_3SnSnEt_3}] = \frac{1-n}{2} - x$$

$$[\mathrm{Me_3SnSnEt_3}] = x - y$$

$$[\mathrm{Et_3SnLi}] = x + y$$

$$[\mathrm{Me_3SnSnMe_3}] = y$$

These are substituted in eqs. 9 and 10 to give two equations (eqs. 11, 12).

$$K_1 = \frac{[\mathrm{Et_3SnLi}][\mathrm{Me_3SnSnEt_3}]}{[\mathrm{Me_3SnLi}][\mathrm{Et_3SnSnEt_3}]} = \frac{(x+y)(x-y)}{(n-x-y)\left(\frac{1-n}{2} - x\right)} \tag{11}$$

$$K_2 = \frac{[\mathrm{Et_3SnLi}][\mathrm{Me_3SnSnMe_3}]}{[\mathrm{Me_3SnLi}][\mathrm{Me_3SnSnEt_3}]} = \frac{(x+y)y}{(n-x-y)(x-y)} \tag{12}$$

If $x$ is eliminated from eqs. 11, 12, a cubic equation for $y$ is obtained (eq. 13),

$$ay^3 + by^2 + cy + d = 0 \tag{13}$$

where $a$—$d$ are presented as follows.

$$a = (4K_2 - K_1)\left(K_1 + \frac{1-K_1}{K_2}\right)$$

$$b = K_1(1 - 2K_2) + K_1(K_1 - 2K_2 - 1)\left(n + \frac{1-n}{2K_2}\right)$$

$$c = \frac{1-n^2}{4} K_1^2 + n^2K_1K_2 - \mathrm{n}(1-n)K_1(K_1 - 2K_2 - 1)$$

$$d = -\frac{n^2(1-n)}{2} K_1K_2$$

Numerical values were substituted into $K_1$ and $K_2$, then $y$ and $x$ were calculated in the case of $n = 0.20, 0.33, 0.50, 0.67, 0.90$ by using an electronic computer. Predicted chemical shifts of $\mathrm{Me_3Sn}$ and $\mathrm{Et_3Sn}$ were calculated by the weighted means of the chemical shift of each component in eqs. 7 and 8 as follows.

$$\delta(\mathrm{Me_3}\mathit{Sn}) = \delta(\mathrm{Me_3}\mathit{Sn}\mathrm{Li})\frac{n-x-y}{n} + \delta(\mathrm{Me_3}\mathit{Sn}\mathrm{SnEt_3})\frac{x-y}{n} + \delta(\mathrm{Me_3}\mathit{SnSn}\mathrm{Me_3})\frac{2y}{n} \tag{14}$$

$$\delta(\mathrm{Et_3}\mathit{Sn}) = \delta(\mathrm{Et_3}\mathit{Sn}\mathrm{Li})\frac{x+y}{1-n} + \delta(\mathrm{Me_3Sn}\mathit{Sn}\mathrm{Et_3})\frac{x-y}{1-n} + \delta(\mathrm{Et_3}\mathit{SnSn}\mathrm{Et_3})\frac{1-n-2x}{1-n} \tag{15}$$

TABLE 2

CALCULATED VALUES OF $x$, $y$ AND CHEMICAL SHIFTS OF $Me_3Sn$ AND $Et_3Sn$ IN THE CASE OF $K_1 = 0.5$, $K_2 = 0.2$

| System | $(Li/R_3Sn) = n$ | $x$ | $y$ | $\delta(Me_3Sn)$ | $\delta(Et_3Sn)$ |
|---|---|---|---|---|---|
| $Me_3SnLi$-$Et_3SnSnEt_3$ | 0.20 | 0.108 | 0.013 | —137.7 | —65.2 |
| | 0.33 | 0.134 | 0.024 | —147.1 | —68.8 |
| | 0.50 | 0.139 | 0.037 | —156.5 | —73.6 |
| | 0.67 | 0.118 | 0.045 | —164.6 | —79.4 |
| | 0.90 | 0.047 | 0.032 | —176.2 | —91.0 |
| $Et_3SnLi$-$Me_3SnSnMe_3$ | 0.20 | 0.155 | 0.027 | —125.4 | —64.5 |
| | 0.33 | 0.206 | 0.064 | —138.4 | —67.4 |
| | 0.50 | 0.213 | 0.111 | —156.5 | —73.6 |
| | 0.67 | 0.159 | 0.118 | —170.7 | —82.6 |
| | 0.90 | 0.050 | 0.047 | —180.5 | —94.7 |

where

$\delta(Me_3\mathit{Sn}Li) = -182.7$ ppm

$\delta(Me_3\mathit{Sn}\mathit{Sn}Me_3) = -108.7$ ppm

$\delta(Me_3\mathit{Sn}SnEt_3) = -108.1$ ppm

$\delta(Me_3Sn\mathit{Sn}Et_3) = -61.8$ ppm

$\delta(Et_3\mathit{Sn}Li) = -99.0$ ppm

$\delta(Et_3\mathit{Sn}\mathit{Sn}Et_3) = -58.8$ ppm

The combination values given to the $K_1$ and $K_2$ were $K_1 = 0.5$, $K_2 = 0.3$, 0.2, 0.1 and $K_1 = 0.6$, $K_2 = 0.3$, 0.2. The case of $K_1 = 0.5$, $K_2 = 0.2$ was shown in Table 2 and Fig. 5 (point □).

*b) $Et_3SnLi$-$Me_3SnSnMe_3$ system.* The molar amount of the reacted $Me_3SnSnMe_3$, $x$, and the molar amount of the formed $Et_3SnSnEt_3$, $y$, were calculated similarly to the system a).

$[Et_3SnLi] = n - x - y$

$[Me_3SnSnMe_3] = \frac{1-n}{2} - x$

$[Me_3SnSnEt_3] = x - y$

$[Me_3SnLi] = x + y$

$[Et_3SnSnEt_3] = y$

$$K_1 = \frac{(n-x-y)(x-y)}{(x+y)y} \tag{16}$$

$$K_2 = \frac{(n-x-y)\left(\frac{1-n}{2} - x\right)}{(x+y)(x-y)} \tag{17}$$

If $x$ is eliminated from eqs. 16 and 17, the following equation (eq. 18) is obtained.

$$ay^3 + by^2 + cy + d = 0 \tag{18}$$

$$a = 4K_1^2 + (K_1 - 1)(K_1/K_2)^2 - (K_1^2 + 4K_1 - 4)K_1/K_2$$

$$b = \left(n + \frac{1-n}{2}K_1\right)(K_1/K_2)^2 - \left(2n + 2 + \frac{1-n}{2}K_1^2\right)K_1/K_2$$

$$c = \left(2n^2 - n + \frac{1-n^2}{4}K_1/K_2\right)K_1/K_2 + n(1-n)(K_1 + 2)$$

$$d = -\frac{1-n}{2}n^2 K_1/K_2$$

Some values were substituted to $K_1$, $K_2$ and $n$, then $x$ and $y$ were calculated similarly to the case in $Me_3SnLi$-$Et_3SnSnEt_3$ system. Chemical shifts of $Me_3Sn$ and $Et_3Sn$ were predicted as follows.

$$\delta(Me_3\mathit{Sn}) = \delta(Me_3\mathit{Sn}Li)\frac{x+y}{1-n} + \delta(Me_3\mathit{Sn}SnEt_3)\frac{x-y}{1-n} + \delta(Me_3\mathit{SnSn}Me_3)\frac{1-n-2x}{1-n} \tag{19}$$

$$\delta(Et_3\mathit{Sn}) = \delta(Et_3\mathit{Sn}Li)\frac{n-x-y}{n} + \delta(Me_3Sn\mathit{Sn}Et_3)\frac{x-y}{n} + \delta(Et_3\mathit{SnSn}Et_3)\frac{2y}{n} \tag{20}$$

The results in the case of $K_1 = 0.5$, $K_2 = 0.2$, were shown in Table 2 and Fig. 5 (point △).

## Acknowledgment

We are deeply indebted to Mr. Kazuhiro Matsushita of JEOL Ltd. for measurement of some of the $^{119}Sn$ NMR spectra. Out thanks are also extended to Dr. T. Imagawa of the Department of Industrial Chemistry, Kyoto University, for stimulating discussions. Finally, Professor J.J. Eisch of the State University of New York at Binghamton is thanked for helpful suggestions and critical reading of the manuscript.

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