

Journal of Organometallic Chemistry, 233 (1982) 299—311
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

MECHANISTIC STUDIES ON DECOMPOSITION OF TRIALKYLSTANNYL LITHIUMS

KAZUKO KOBAYASHI (née KUNÔ), MITUYOSI KAWANISI,

*Department of Industrial Chemistry, Faculty of Engineering, Kyôto University,
Sakyô-ku, Kyôto, 606 (Japan)*

TORAZÔ HITOMI and SINPEI KOZIMA *

*Department of Chemistry, School of Liberal Arts & Sciences, Kyôto University,
Sakyô-ku, Kyôto, 606 (Japan)*

(Received December 23rd, 1981; in revised form February 19th, 1982)

Summary

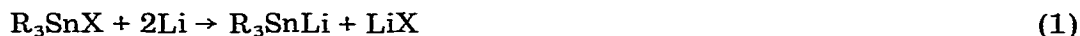
The fast decomposition of trialkylstannyl lithiums, R_3SnLi ($R = Me, Et$ and Bu), in the presence of hexaalkyldistannanes, R_3SnSnR_3 , was observed, and its mechanism was investigated kinetically. Partial dissociation of R_3SnLi into a $(\overline{RLi})(\overline{R_2Sn})$ complex in a solvent cage is suggested to occur in the initial step. The RLi in the complex can be trapped instantaneously by R_3SnSnR_3 to afford R_4Sn and R_3SnLi , and the counterpart R_2Sn : by R_3SnLi giving R_3SnR_2SnLi . The decomposition of R_3SnLi followed first-order kinetics within 3.5 h, corresponding well to the rate of disappearance of R_3SnSnR_3 and of appearance of R_4Sn . The partial dissociation rate constant (k_1) of Me_3SnLi into the complex was determined as $2.0 \times 10^{-3} \text{ min}^{-1}$. The values of k_1 are about 100 times those of rate constants (k') for decomposition of R_3SnLi in the absence of R_3SnSnR_3 . Reformation of R_3SnLi from the $(\overline{RLi})(\overline{R_2Sn})$ complex is highly significant.

Introduction

In the previous paper, we reported a rapid exchange of the R_3Sn group between R_3SnLi and R_3SnSnR_3 [1]. In the course of this study, we observed that exceedingly fast decomposition of R_3SnLi proceeded in the presence of R_3SnSnR_3 to give a large amount of R_4Sn together with R_3SnR_2SnLi , $(R_3Sn)_3SnLi$, alkylstannyl polymers, metallic tin and lithium in one day at room temperature. In contrast, R_3SnLi alone in tetrahydrofuran (THF) decomposes much more slowly [2].

Hitherto, we have found unusually quick decomposition of R_3SnLi in the

presence of R_3SnSnR_3 , as follows. When R_3SnLi is prepared by the reaction of a trialkyltin halide, R_3SnX ($R = Cl, Br$), or R_3SnSnR_3 with Li metal (eq. 1, 2) [3,4], the presence of an excess amount of Li metal is essential for pre-



paring R_3SnLi in an acceptable yield. Otherwise, shortage of Li metal causes the formation of a large amount of R_4Sn as a by-product. In addition, when R_3SnSnR_3 is prepared by the reaction of R_3SnX with Li metal (eq. 3), the presence of a small excess amount of Li metal leads to a low yield of



R_3SnSnR_3 , because of the formation of by-products. The high yield of R_4Sn as a by-product in the above preparative experiments can be interpreted by postulating the equilibrium shown in eq. 4, followed by reaction of the RLi formed with R_3SnSnR_3 to give R_4Sn and R_3SnLi (eq. 5).



Coates, Blake and Tate suggested a significant conversion of Bu_3SnLi into $BuLi$ and Bu_2Sn : in the reaction mixture of $BuLi$ and stannous chloride in ether [5]. In contrast, Tamborski, Ford, and Soloski reported that the formation of $BuLi$ and Bu_2Sn : could not be detected in THF solution of Bu_3SnLi prepared by the reaction of Bu_3SnCl or $Bu_3SnSnBu_3$ with Li metal (eq. 1, 2) [4]. Recently, Wursthorn, Kuivila, and Smith proposed the dissociation of Me_3SnNa into $MeNa$ and (Me_2Sn) [6].

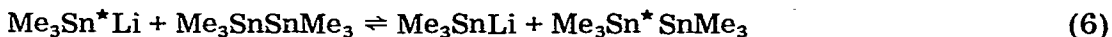
We have investigated the decomposition mechanism of R_3SnLi in the presence of R_3SnSnR_3 kinetically, and wish to suggest the transient existence of an alkyllithium-dialkylstannylylene complex formed by the partial dissociation of R_3SnLi .

Results and discussion

The decomposition process of Me_3SnLi in the presence or absence of $Me_3SnSnMe_3$ was followed by 1H and ^{119}Sn NMR spectra, and kinetically investigated by analyses of the decomposition mixtures.

In the presence of R_3SnSnR_3

A mixture of Me_3SnLi and $Me_3SnSnMe_3$ in THF at room temperature showed only a single peak due to the rapid exchange of Me_3Sn groups (eq. 6) in both 1H and ^{119}Sn NMR spectra [1].



The chemical shifts of these single peaks are dependent on the ratio (r) of Me_3SnLi to $Me_3SnSnMe_3$. The singlet in the 1H NMR spectrum gradually collapsed into three or four singlets during 20 h at room temperature (Fig. 1). However, the chemical shift of the original singlet remained unchanged within

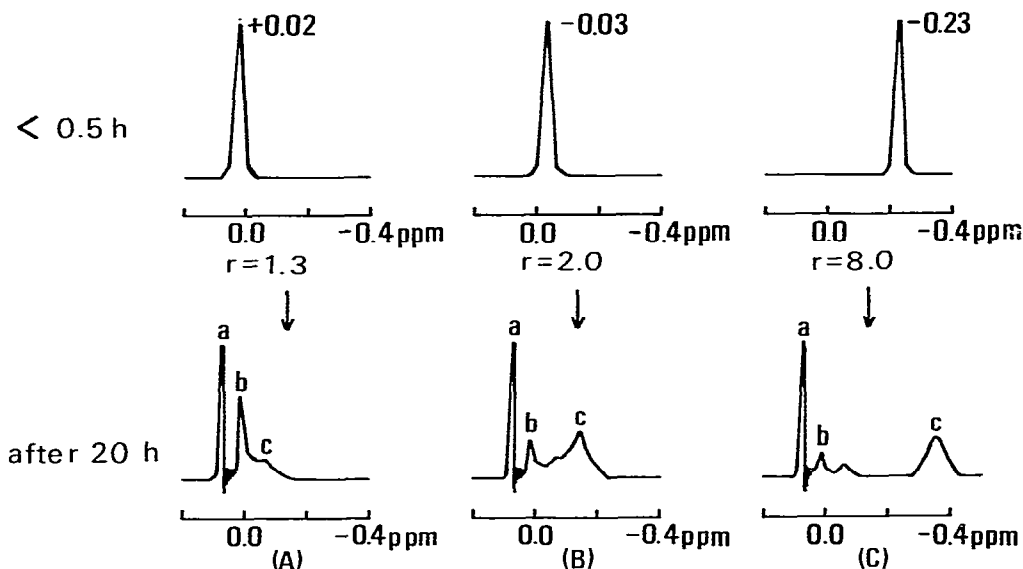


Fig. 1. ^1H NMR spectra of the system $\text{Me}_3\text{SnLi}-\text{Me}_3\text{SnSnMe}_3$; $r = [\text{Me}_3\text{SnLi}]/[\text{Me}_3\text{SnSnMe}_3]$.

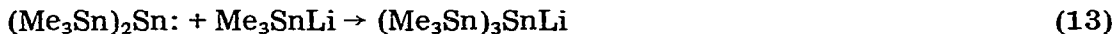
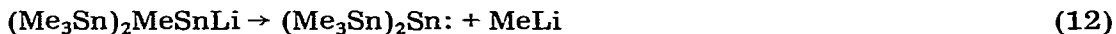
4 h. The two peaks *a* and *b* in Fig. 1 were assigned to Me_4Sn (at 0.07 ppm) and $(\text{Me}_3\text{Sn})_3\text{SnLi} \cdot 3\text{THF}$ (at 0.01 ppm [3]), respectively. In each mixture, another broad signal (*c*) appeared at -0.06 , -0.12 and -0.37 ppm for $r = 1.3$, 2.0 and 8.0, respectively, which could be assigned to a mixture of partially decomposed polymethylpolystannyl lithium compounds such as $\text{Me}_3\text{SnMe}_2\text{SnLi}$ and $(\text{Me}_3\text{Sn})_3\text{SnLi}$. These broad peaks (*c*) gradually moved to a lower field and finally changed into the peaks of Me_4Sn and $\text{Me}_3\text{SnSnMe}_3$ after one week. During this process deposition of metallic lithium and tin was observed.

The ^{119}Sn NMR spectrum of an equimolar mixture of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ showed a singlet at -127.0 ppm. Its magnitude decreased gradually and two new peaks at -114.4 and 0.0 ppm (Me_4Sn) appeared after 2.5 h. In the spectrum after 4 h there appeared another peak at -98.0 ppm, assignable to $(\text{Me}_3\text{Sn})_3\text{SnLi} \cdot 3\text{THF}$ [7] in addition to the three peaks. The chemical shift of the original singlet (at -127.0 ppm) remained unchanged for 4 h. The singlet at -114.4 ppm, assignable to $\text{Me}_3\text{SnMe}_2\text{SnLi}$ as described below, disappeared in 20 h. The spectrum after 20 h displayed two major peaks at 0.0 ppm (Me_4Sn) and -98.0 ppm ($(\text{Me}_3\text{Sn})_3\text{SnLi} \cdot 3\text{THF}$) and a minor broad one at -180.1 ppm.

The equimolar mixture of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ was kept at room temperature for 4 h and treated with Me_3SiCl to convert stannyl lithium components into the stannylsilanes. The ^{119}Sn NMR spectrum showed two new peaks at -110.0 and -196.5 ppm in addition to five peaks assignable to Me_4Sn (0.0), $\text{Me}_3\text{SnSiMe}_3$ (-125.6) [8], $\text{Me}_3\text{SnSnMe}_3$ (-108.7) [9], and $(\text{Me}_3\text{Sn})_3\text{SnSiMe}_3^*$ (-89.6 , -748.3 ppm). Comparing the latter NMR spectrum with the former one, the original singlet at -127.0 ppm in the former corresponds to the two peaks at -125.6 ppm ($\text{Me}_3\text{SnSiMe}_3$) and -108.7 ppm

($\text{Me}_3\text{SnSnMe}_3$) in the latter [1]. Therefore, the peak at -114.4 ppm in the former spectrum corresponds to the two peaks at -110.0 and -196.5 ppm in the latter, assignable to $\text{Me}_3\text{SnMe}_2\text{SnSiMe}_3^*$, and is correlated to the Me_3Sn of $\text{Me}_3\text{SnMe}_2\text{SnLi}^*$.

In the initial process of the decomposition during 4 h, Me_4Sn was a major product, while in the later stage (Me_3Sn) $_3\text{SnLi}$ was a major product in addition to Me_4Sn . The peak at -114.4 ppm assigned to $\text{Me}_3\text{SnMe}_2\text{SnLi}$ began to decrease after 2.5 h, while that of (Me_3Sn) $_3\text{SnLi}$ gradually appeared after 4 h. This suggests that (Me_3Sn) $_3\text{SnLi}$ was produced at the expense of $\text{Me}_3\text{SnMe}_2\text{SnLi}$. The formation of these products could be explained mainly by the following mechanism (eq. 7–13). In order to interpret this decomposition kinetically, we postulate the equilibrium between Me_3SnLi and solvent-separated MeLi and Me_2Sn : in eq. 7, although we will suggest later a partially aggregated complex $(\text{RLi})(\text{R}_2\text{Sn}\cdot)$ in our conclusion instead of the solvent-separated MeLi and Me_2Sn . In the presence of $\text{Me}_3\text{SnSnMe}_3$, the recombination of MeLi and Me_2Sn : could not occur, since MeLi formed was removed by $\text{Me}_3\text{SnSnMe}_3$ (eq. 8) very rapidly [10].



Aliquots of an equimolar mixture of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ kept at room temperature were treated with Me_3SiCl at suitable time intervals during 4.5 h, and the reaction mixtures were analyzed by ^{119}Sn NMR and GLC (Table 1). The amounts of $\text{Me}_3\text{SnSiMe}_3$ and $\text{Me}_3\text{SnSnMe}_3$ decreased with the passage of time, while those of Me_4Sn and $\text{Me}_3\text{SnMe}_2\text{SnSiMe}_3$ increased. The increased amount of Me_4Sn corresponded to the decreased amount of $\text{Me}_3\text{SnSnMe}_3$. (Me_3Sn) $_3\text{SnSiMe}_3$ was not detected within 3.5 h. These results indicate that the initial reaction during 3.5 h corresponds to eqs. 7–9. The logarithms of the molarities of $\text{Me}_3\text{SnSiMe}_3$ and $\text{Me}_3\text{SnSnMe}_3$ and those of the differences between the initial molarity of $\text{Me}_3\text{SnSnMe}_3$ and the molarity of Me_4Sn formed are plotted against time in Fig. 2. Notably the rates of disappearance of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ followed first-order kinetics during 3.5 h. In addition, it was confirmed that the rates of disappearance of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ were independent of the initial molar concentrations of Me_3SnLi

* See Experimental part for the assignment.

TABLE 1

TREATMENT OF AN EQUIMOLAR MIXTURE OF Me_3SnLi AND $\text{Me}_3\text{SnSnMe}_3$ WITH Me_3SiCl .
MOLAR DISTRIBUTION OF THE REACTION PRODUCTS

Time (h)	$\text{Me}_3\text{SnSiMe}_3$	$\text{Me}_3\text{SnSnMe}_3$	Me_4Sn	$\text{Me}_3\text{SnMe}_2\text{SnSiMe}_3$	$(\text{Me}_3\text{Sn})_3\text{SnSiMe}_3$
0	2.80	2.81	—	—	—
0.5	2.69	2.54	0.25	0.07	—
1.0	2.45	2.41	0.31	0.08	—
1.5	2.38	2.36	0.54	0.10	—
2.0	2.19	2.25	0.62	0.17	—
2.5	2.12	2.17	0.93	0.22	—
3.5	1.62	1.78	1.05	0.14	—
4.5	1.26	1.62	1.7	0.14	0.10
22.0	0.54	0.82	1.7	0.0	0.16

and $\text{Me}_3\text{SnSnMe}_3$. If the disappearance of $\text{Me}_3\text{SnSnMe}_3$ and the formation of Me_4Sn is attributed to eq. 8, the rate constant for disappearance of $\text{Me}_3\text{SnSnMe}_3$ obtained from Fig. 2 could correspond to k_1 in eq. 7. Since the reaction of MeLi with $\text{Me}_3\text{SnSnMe}_3$ can be regarded as a very rapid reaction [10], the dissociation of Me_3SnLi into MeLi and Me_2Sn : could be the rate determining step, and is equal to the rate of disappearance of $\text{Me}_3\text{SnSnMe}_3$ (eq. 14). In addition, the rate of disappearance of Me_3SnLi is equal to that of $\text{Me}_3\text{SnSnMe}_3$. This is consistent with the persistence of the original chemical shift of the peak in ^1H and ^{119}Sn NMR spectra of the mixture of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ during 3.5 h; that is, the ratio of Me_3SnLi to $\text{Me}_3\text{SnSnMe}_3$

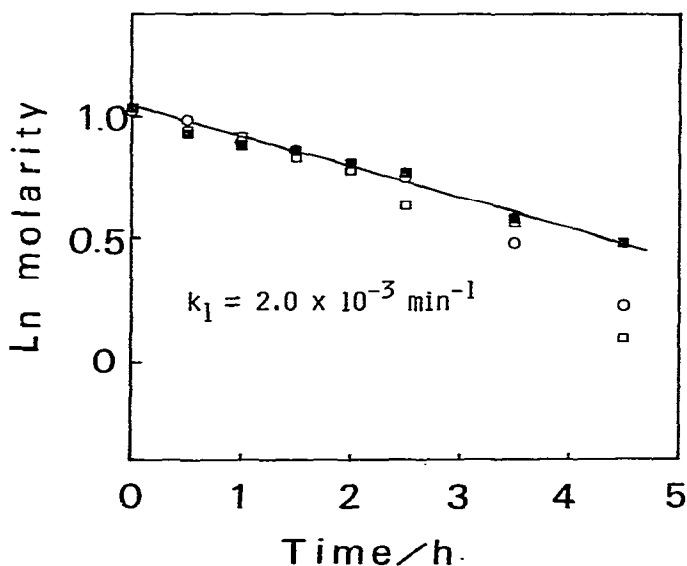


Fig. 2. Plots of the logarithm of molarity vs. time in an equimolar mixture of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$.
○ $\text{Me}_3\text{SnSiMe}_3$; ■ $\text{Me}_3\text{SnSnMe}_3$; □ $[\text{Me}_3\text{SnSnMe}_3]_0 - [\text{Me}_4\text{Sn}]$.

remains equal to the initial ratio. By using this relation, eq. 14 can be transformed into eq. 15. The rate of disappearance of Me_3SnLi also followed eq. 16, since the ratio of Me_3SnLi to $\text{Me}_3\text{SnSnMe}_3$ remained constant during the 3.5 h.

$$-\frac{d[\text{Me}_3\text{SnSnMe}_3]}{dt} = k_1[\text{Me}_3\text{SnLi}] \quad (14)$$

$$-\frac{d[\text{Me}_3\text{SnSnMe}_3]}{dt} = rk_1[\text{Me}_3\text{SnSnMe}_3] \quad (15)$$

$$r = [\text{Me}_3\text{SnLi}]/[\text{Me}_3\text{SnSnMe}_3]$$

$$-\frac{d[\text{Me}_3\text{SnLi}]}{dt} = rk_1[\text{Me}_3\text{SnLi}] \quad (16)$$

The reaction mixture of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ in 2:1 molar ratio was treated with Me_3SiCl and the rates of disappearance of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ were measured (Fig. 3). The first-order rate constants for the disappearance of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ were equal to each other, and twice as much as that in the equimolar mixture, as expected from eqs. 15 and 16.

The reaction mixture of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ in 1:2 molar ratio gave the similar kinetic result and the rate constant for disappearance of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ was $0.5k_1$ (Fig. 4).

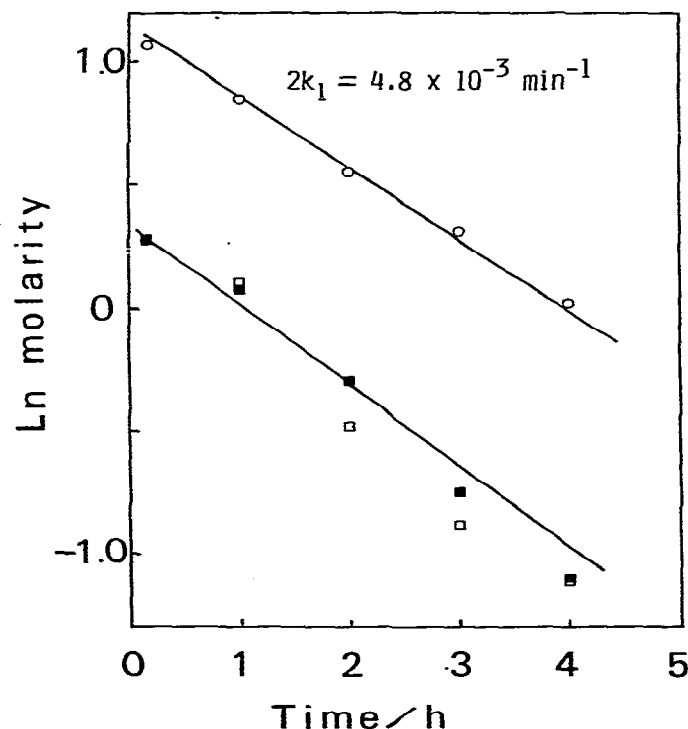


Fig. 3. Plots of the logarithm of molarity vs. time in the mixture of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ (2:1), \circ $\text{Me}_3\text{SnSiMe}_3$; \blacksquare $\text{Me}_3\text{SnSnMe}_3$; \square $[\text{Me}_3\text{SnSnMe}_3]_0 - [\text{Me}_4\text{Sn}]$.

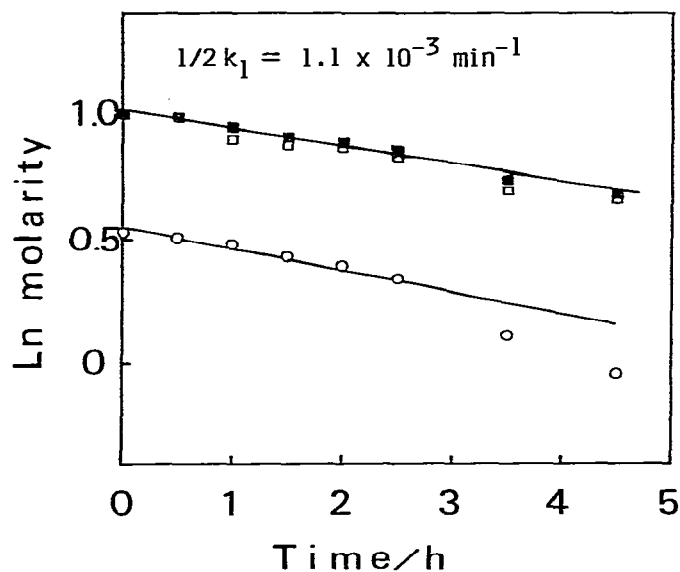


Fig. 4. Plots of the logarithm of molarity vs. time in the mixture of Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ (1 : 2), \circ $\text{Me}_3\text{SnSiMe}_3$; \blacksquare $\text{Me}_3\text{SnSnMe}_3$; \square $[\text{Me}_3\text{SnSnMe}_3]_0 - [\text{Me}_4\text{Sn}]$.

In the cases of $\text{Et}_3\text{SnLi}-\text{Et}_3\text{SnSnEt}_3$ and $\text{Bu}_3\text{SnLi}-\text{Bu}_3\text{SnSnBu}_3$ systems, similar treatments to the $\text{Me}_3\text{SnLi}-\text{Me}_3\text{SnSnMe}_3$ system were carried out. The rates of disappearance of R_3SnLi and R_3SnSnR_3 ($\text{R} = \text{Et}, \text{Bu}$) in both systems followed first-order kinetics. The rate constants for disappearance of R_3SnSnR_3 and R_3SnLi corresponded to the value of rk_1 ($r = [\text{R}_3\text{SnLi}]/[\text{R}_3\text{SnSnR}_3]$) in analogy with the $\text{Me}_3\text{SnLi}-\text{Me}_3\text{SnSnMe}_3$ system (Table 2).

These results for the $\text{R}_3\text{SnLi}-\text{R}_3\text{SnSnR}_3$ system ($\text{R} = \text{Me}, \text{Et}, \text{Bu}$) indicate that the dissociation of R_3SnLi into RLi and R_2Sn : could be operative and that the values of k_1 increase in the order of Et_3SnLi , Me_3SnLi , Bu_3SnLi at room temperature (Table 2).

In the absence of R_3SnSnR_3

R_3SnLi decomposes much more slowly in the absence of R_3SnSnR_3 than in the presence of R_3SnSnR_3 . In the absence of R_3SnSnR_3 , Gilman, Cartledge,

TABLE 2
RATE CONSTANT (k_1)^a AT 20°C

R	$k_1 \times 10^3$ (min^{-1})
Me	2.0
Et	1.3
Bu	2.8

^a The constants (k_1) determined here do not correspond to the complete dissociation of R_3SnLi into solvent separated RLi and R_2Sn : as shown in eq. 7, but to the partial dissociation of R_3SnLi to a solvent-caged $(\text{RLi})(\text{R}_2\text{Sn}:)$ shown in Scheme 1. A detailed discussion is given in the latter part of this paper.

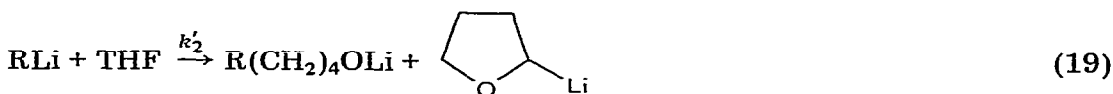
TABLE 3

RATE CONSTANT (k') FOR DISAPPEARANCE OF R_3SnLi IN THF SOLUTION IN THE ABSENCE OF R_3SnSnR_3 AT 20°C

R	$k' \times 10^5$ (min^{-1})
Me	2.6
Et	0.34
Bu	4.5 (9.8) ^a

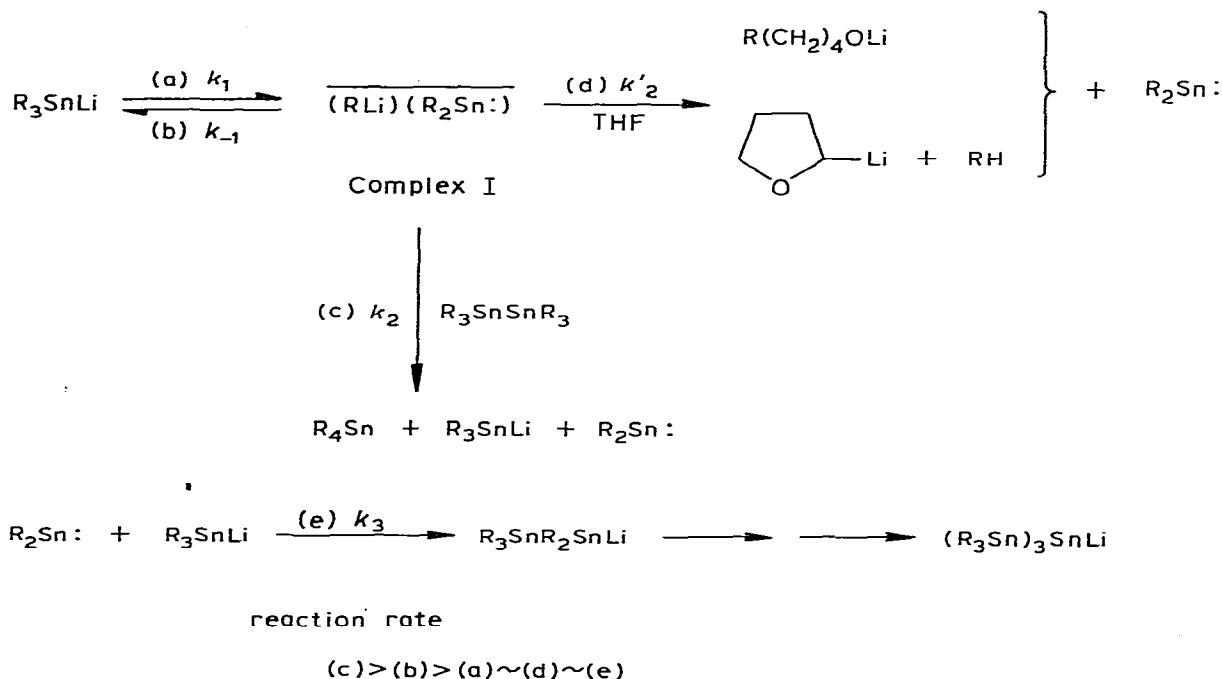
^a The datum reported by Gilman, Cartledge, and Sim was $5.9 \times 10^{-3} \text{ h}^{-1}$ [2]. $5.9 \times 10^{-3} \text{ h}^{-1} = 9.8 \times 10^{-5} \text{ min}^{-1}$.

and Sim reported that the decomposition of Bu_3SnLi in THF followed pseudo-first-order kinetics [2]. The rate constants of the decomposition of Me_3SnLi and Et_3SnLi have now been determined in the same manner as that of Bu_3SnLi . The observed rate constants (k') in Table 3 were much smaller than k_1 in Table 2. The decomposition reaction of R_3SnLi in THF has been reported as consisting of either the ring opening of THF with R_3SnLi [11] (eq. 17) or the reaction of THF with RLi [12,13] (eq. 19) formed by the dissociation of R_3SnLi (eq. 18). However, Weibel and Oliver [14] pointed out that the reaction shown in eq. 17 appeared to be an incorrect quotation of the work reported by Gilman [2], and there was no evidence for the formation of $R_3Sn(CH_2)_4OLi$. Therefore, eqs. 18 and 19 can be regarded as the main decomposition scheme in the absence of R_3SnSnR_3 . Using a steady state assumption, the rate of disappearance of R_3SnLi is expressed by eq. 20.



$$\begin{aligned} -\frac{d[R_3SnLi]}{dt} &= k'_1 [R_3SnLi] \\ &= \left(\frac{k_1 k'_2}{k_{-1} [R_2Sn:] + k'_2} \right) [R_3SnLi] \end{aligned} \quad (20)$$

If the reformation of R_3SnLi by recombination of RLi with $R_2Sn:$ in eq. 18 were much slower than the reaction of RLi with THF (eq. 19), $k_{-1} [R_2Sn:]$ should be negligibly small as compared with k'_2 in eq. 20, and the rate constant for disappearance of R_3SnLi (k') should be equal to k_1 . However, the observed rate constant (k') is much smaller than k_1 . This indicates that the reverse reaction in eq. 18 could be highly significant. Taking consideration of rather low reactivity of $R_2Sn:$ [15], it is unlikely that the recombination between the solvent-separated RLi and $R_2Sn:$ is very rapid. Instead of the solvent-separated RLi and $R_2Sn:$, we therefore propose the formation of an alkyl-lithium-dialkylstannylene complex (I) $[(RLi)(R_2Sn:)]$ in a solvent cage as shown in Scheme 1.



SCHEME 1

In the presence of R_3SnSnR_3 , (RLi) in the complex I is abstracted very rapidly by R_3SnSnR_3 (step c) and, accordingly, the reformation of R_3SnLi (step b) intrinsically cannot take place. Thus the counterpart $(\text{R}_2\text{Sn:})$ reacts with R_3SnLi to form $\text{R}_3\text{SnR}_2\text{SnLi}$ and finally $(\text{R}_3\text{Sn})_3\text{SnLi}$ (step e).

By contrast, in the absence of R_3SnSnR_3 , step b would become significant, since step b occurs much faster than step d. Assuming transient formation of complex I, the rate equation for disappearance of R_3SnLi in the absence of R_3SnSnR_3 becomes a simple first-order one (eq. 21).

$$\begin{aligned}
 -\frac{d[\text{R}_3\text{SnLi}]}{dt} &= k'[\text{R}_3\text{SnLi}] \\
 &= \frac{k_1 k'_2}{k_{-1} + k'_2} [\text{R}_3\text{SnLi}] \quad (21)
 \end{aligned}$$

The rate constant (k_{-1}) for the reformation of R_3SnLi from complex I is given by eq. 22.

$$k_{-1} = (k_1/k' - 1)k'_2 \quad (22)$$

In the case of Me_3SnLi , substituting the observed constants $k_1 = 2.0 \times 10^{-3} \text{ min}^{-1}$ and $k' = 2.6 \times 10^{-5} \text{ min}^{-1}$ in eq. 22, we obtain eq. 23.

$$k_{-1} = 7.6 \times 10^4 k'_2 \quad (23)$$

The rate of decomposition of (MeLi) in complex I may be slower than that of free MeLi in THF. The rate constant for the decomposition of free MeLi in

THF can be calculated as $4.1 \times 10^{-3} \text{ min}^{-1}$ (at 25°C) from the reported data [13a]. Therefore, the constant k'_2 is less than $4.1 \times 10^{-3} \text{ min}^{-1}$. Thus we can estimate the upper limit of k_{-1} .

$$k_{-1} \leq 3.1 \times 10^{-1} \text{ min}^{-1} \quad (24)$$

To summarize, the decomposition of R_3SnLi in both the presence and the absence of R_3SnSnR_3 apparently involves partial dissociation of R_3SnLi into a $(\text{RLi})(\text{R}_2\text{Sn}\cdot)$ complex (I) and rapid recombination.

Experimental

All reactions were carried out under a nitrogen atmosphere. ^1H NMR spectra were obtained on a Varian-EM390 (90 MHz) spectrometer. ^{119}Sn NMR spectra were measured in the pulse Fourier transform mode using a JEOL-FX90Q (33.41 MHz) spectrometer consisting of 8K data point with spectral width 10 kHz. ^1H chemical shifts were determined relative to that of β -methylene protons of THF (1.75 ppm) and are reported as ppm in the Me_4Si scale. ^{119}Sn chemical shifts were determined relative to external Me_4Sn . Gas-liquid chromatography (GLC) was run on a Silicone DC HV column.

R_3SnLi (R = Me [3,4], Bu [4]) was prepared by the reaction of R_3SnCl with Li metal. Et_3SnLi was formed by the reaction of Et_3SnBr with Li metal [16].

Decomposition of the $\text{Me}_3\text{SnLi}-\text{Me}_3\text{SnSnMe}_3$ system

(a) *Observations in ^1H NMR spectra.* Three samples containing Me_3SnLi and $\text{Me}_3\text{SnSnMe}_3$ in ratios of 1.3, 2.0 and 8.0 were prepared by adding a THF solution of the former compound to the latter. Each ^1H NMR spectrum of these three mixtures, measured after 0.1 h, displayed a broad singlet at 0.02, -0.03 and -0.23 ppm, respectively (Fig. 1). A broad singlet was observed at the same position in each mixture after 2 h. The singlet at 0.02 ppm for $\text{Me}_3\text{SnLi}/\text{Me}_3\text{SnSnMe}_3 = 1.3$, (A) in Fig. 1 collapsed into a broad single peak at 0.01 ppm and a peak of Me_4Sn at 0.07 ppm after 5 h at room temperature. The ^1H NMR spectrum of the mixture, kept at room temperature for 20 h, showed two singlets of Me_4Sn (at 0.07 ppm) and $(\text{Me}_3\text{Sn})_3\text{SnLi} \cdot 3\text{THF}$ (at 0.01 ppm, $J(^{119}\text{Sn}-\text{CH}_3) = 34.5 \text{ Hz}$) [3] and a very broad peak at -0.06 ppm. The singlet at -0.03 ppm (B in Fig. 1) collapsed into two signals at 0.07 and -0.05 ppm after 5 h, and then into three signals at 0.07, 0.01 and -0.12 ppm after 20 h. The single peak at -0.23 ppm (C in Fig. 1) collapsed into four signals at 0.07, 0.01, -0.07 and -0.34 ppm after 5 h. The spectrum after 20 h showed four signals at 0.07, 0.01, -0.07 and -0.37 ppm. The broad peaks observed at -0.06 , -0.12 and -0.37 ppm after 20 h (peak c in Fig. 1) moved to lower fields and were converted into the peaks of Me_4Sn (0.07 ppm) and $\text{Me}_3\text{SnSnMe}_3$ (0.22 ppm) in a week.

In every case metallic lithium and tin were deposited in the NMR tube. The lithium metal deposited on the inside of the NMR tube as a brown ring in the upper part of the solution. The decomposed mixture was poured off, and the brown ring was washed with dry THF and benzene. When a small amount of water was poured into the tube, the brown ring reacted violently with water with generation of a gas. Metallic tin was isolated by filtration from the hydrated reaction mixture.

(b) *Observations in ^{119}Sn NMR spectra.* To 266 mg (0.81 mmol) of $\text{Me}_3\text{SnSnMe}_3$ in an NMR tube was added 0.82 ml of a 1 M THF solution of Me_3SnLi and 122 mg (0.35 mmol) of Bu_4Sn (internal standard for integration). The ^{119}Sn NMR spectrum of the solution measured after 0.2 h showed a single peak at -127.0 ppm. The ^{119}Sn NMR spectrum after 2.5 h displayed three peaks at 0.0 ppm (Me_4Sn , 0.36 mmol), -114.4 ppm ($\text{Me}_3\text{SnMe}_2\text{SnLi}$, 0.11 mmol), and -127.0 ppm. The spectrum after 4 h exhibited four peaks at 0.0 ppm (Me_4Sn , 0.51 mmol), -114.4 ppm ($\text{Me}_3\text{SnMe}_2\text{SnLi}$, 0.11 mmol), -98.0 ppm ($(\text{Me}_3\text{Sn})_3\text{SnLi}$, 0.04 mmol) [7] and -127.0 ppm. The NMR spectrum after 20 h showed three singlets at 0.0 (0.55 mmol), -98.0 (0.26 mmol) and -180.1 ppm. The molar amounts of the products were calculated by the integral ratios of the products to Bu_4Sn .

Treatment of the $\text{Me}_3\text{SnLi}-\text{Me}_3\text{SnSnMe}_3$ system with Me_3SiCl

To 920.5 mg (2.81 mmol) of $\text{Me}_3\text{SnSnMe}_3$ and 644.0 mg (1.86 mmol) of Bu_4Sn (standard) was added 2.8 ml of a 1 M THF solution of Me_3SnLi , and the mixture was kept at room temperature. At the predetermined times 0.5 ml samples of the solution were added to 0.1 ml of Me_3SiCl at -10°C . The reaction mixtures were investigated by ^{119}Sn NMR spectroscopy and subjected to GLC analysis (Table 1). ^{119}Sn NMR: Me_4Sn (0.0 ppm), $\text{Me}_3\text{SnSiMe}_3$ (-125.6 ppm) [8], $\text{Me}_3\text{SnSnMe}_3$ (-108.7 ppm) [9], $\text{Me}_3\text{SnMe}_2\text{SnSiMe}_3$ (-110.0 ppm, Me_3Sn , and -196.5 ppm, Me_2Sn), $(\text{Me}_3\text{Sn})_3\text{SnSiMe}_3$ (-89.6 ppm, Me_3Sn , and -748.3 ppm, Sn).

A mixture with the ratio $r = [\text{Me}_3\text{SnLi}]/[\text{Me}_3\text{SnSnMe}_3] = 2.0$ was prepared by the addition of 3.3 ml of a 1 M Me_3SnLi solution to 544.0 mg (1.66 mmol) of $\text{Me}_3\text{SnSnMe}_3$ and 332.3 mg (0.96 mmol) of Bu_4Sn . Another mixture with $r = 0.5$ was prepared similarly. At suitable intervals, 0.5 ml samples of these two mixtures were added to 0.1 ml of Me_3SiCl . The relation between the molarity and the time is shown in Figs. 3 and 4, respectively.

Assignment of the chemical shifts in ^{119}Sn NMR spectra of $\text{Me}_3\text{SnMe}_2\text{SnLi}$, $\text{Me}_3\text{SnMe}_2\text{SnSiMe}_3$ and $(\text{Me}_3\text{Sn})_3\text{SnSiMe}_3$

The chemical shifts of the unisolated compounds $\text{Me}_3\text{SnMe}_2\text{SnLi}$, $\text{Me}_3\text{SnMe}_2\text{SnSiMe}_3$, and $(\text{Me}_3\text{Sn})_3\text{SnSiMe}_3$ in the ^{119}Sn NMR spectra were determined as below.

	$\delta(\text{Me}_3\text{Sn})$	$\delta(\text{Me}_2\text{Sn})$	$\delta(\text{Sn})$	Ref.
$\text{Me}_3\text{SnSnMe}_3$	-108.7			9
$\text{Me}_3\text{SnMe}_2\text{SnSnMe}_3$	-99.5	-261.7		9
$\text{Me}_3\text{SnMe}_2\text{SnLi}$	(-114.4)	—		
$\text{Me}_3\text{SnMe}_2\text{SnSiMe}_3$	(-110.0)	(-196.5)		
$(\text{Me}_3\text{Sn})_3\text{SnSnMe}_3$	-80.3		-805.3	17
$(\text{Me}_3\text{Sn})_3\text{SnLi}$	-98.0		-1062.9	7
$(\text{Me}_3\text{Sn})_3\text{SnSiMe}_3$	(-89.6)		(-748.3)	

The data in parentheses are unreported, and are assigned in this paper.

$(\text{Me}_3\text{Sn})_3\text{SnSiMe}_3$ prepared by the reaction of an authentic sample of $(\text{Me}_3\text{Sn})_3\text{SnLi}$ [7] with Me_3SiCl displayed two peaks at -89.6 and -748.3 ppm. The

chemical shifts could reasonably be assigned to the Me_3Sn and Sn of $(\text{Me}_3\text{Sn})_3\text{SnSiMe}_3$, respectively, by comparison with the reported data of $(\text{Me}_3\text{Sn})_3\text{SnSnMe}_3$ [17] and $(\text{Me}_3\text{Sn})_3\text{SnLi}$ [7]. Since it is difficult to isolate $\text{Me}_3\text{SnMe}_2\text{SnLi}$ by the conventional method, the authentic sample of $\text{Me}_3\text{SnMe}_2\text{SnSiMe}_3$ could not be prepared by the reaction of $\text{Me}_3\text{SnMe}_2\text{SnLi}$ with Me_3SiCl . However, the peak at -114.4 ppm in the decomposition mixture disappeared on treatment with Me_3SiCl , and two peaks appeared at -110.0 , -196.5 ppm. The assignment of the peaks at -114.4 and -110.0 ppm to the Me_3Sn in $\text{Me}_3\text{SnMe}_2\text{SnLi}$ and $\text{Me}_3\text{SnMe}_2\text{SnSiMe}_3$, respectively, is reasonable when compared with the corresponding chemical shifts of $\text{Me}_3\text{SnSnMe}_3$ [9] and $\text{Me}_3\text{SnMe}_2\text{SnSnMe}_3$ [9]. The Me_2Sn of $\text{Me}_3\text{SnMe}_2\text{SnLi}$ could not be detected in the spectra of the decomposition mixture, since accumulation times longer than 30 min were not allowed in order to follow the decomposition process at intervals. However, the Me_2Sn of $\text{Me}_3\text{SnMe}_2\text{SnSiMe}_3$ was observed at -196.5 ppm. The assignment of the peak at -196.5 ppm to the Me_2Sn is reasonable when compared with that of $\text{Me}_3\text{SnMe}_2\text{SnSnMe}_3$ at -261.7 ppm [9]. In addition, the difference of the chemical shifts of 65.2 ppm due to replacement of SnMe_3 by SiMe_3 in $\text{Me}_3\text{SnMe}_2\text{Sn}-\text{R}$ corresponds to the similar lower field shift of 57.0 ppm in the pair of $(\text{Me}_3\text{Sn})_3\text{SnSnMe}_3$ (-805.3 ppm) and $(\text{Me}_3\text{Sn})_3\text{SnSiMe}_3$ (-748.3 ppm).

Treatment of $(\text{Me}_3\text{Sn})_3\text{SnLi} \cdot 3\text{THF}$ with Me_3SiCl

$(\text{Me}_3\text{Sn})_3\text{SnLi} \cdot 3\text{THF}$ was prepared by evaporation of THF from a Me_3SnLi solution in THF [3]. The ^{119}Sn NMR spectrum showed two peaks at -98.0 and -1062.9 ppm ($^1J(^{119}\text{Sn}-^{119}\text{Sn}) = 5493$ Hz, $^2J(^{119}\text{Sn}-^{119}\text{Sn}) = 952$ Hz) [7]. To the solution was added Me_3SiCl at -10°C and the ^{119}Sn NMR spectrum of the mixture was measured. The spectrum displayed several peaks assignable to $(\text{Me}_3\text{Sn})_3\text{SnSiMe}_3$ (at -89.6 ppm, Me_3Sn , and -748.3 ppm, Sn), $(\text{Me}_3\text{Sn})_4\text{Sn}$ (at -80.3 ppm, Me_3Sn , and -805.1 ppm, Sn) [17], $\text{Me}_3\text{SnSnMe}_3$ (at -108.7 ppm) [9], $\text{Me}_3\text{SnSiMe}_3$ (at -125.1 ppm) [8] and unidentified peak at -99.4 ppm. The integral ratio of ^{119}Sn in the above products was 1 : 1 : 0.2 : 0.2 : 0.3, respectively. The yield of $(\text{Me}_3\text{Sn})_3\text{SnSiMe}_3$ was low, as reported previously [3].

Treatment of the $\text{Et}_3\text{SnLi}-\text{Et}_3\text{SnSnEt}_3$ system with Me_3SiCl

To each of the two mixtures, one containing 271.0 mg (0.65 mmol) of $\text{Et}_3\text{SnSnEt}_3$ and 76.0 mg (0.22 mmol) of Bu_4Sn (standard), and the other 121.4 mg (0.30 mmol) of $\text{Et}_3\text{SnSnEt}_3$ and 48.6 mg (0.14 mmol) of Bu_4Sn , was added a 0.6 ml portion of a 1 M Et_3SnLi solution, ($[\text{Et}_3\text{SnLi}]/[\text{Et}_3\text{SnSnEt}_3] = 1.0$ and 2.0 respectively). Aliquots of the each mixture were treated with Me_3SiCl at -10°C after 0.1, 1.5, 2.75 and 4.0 h, and analyzed by GLC. The rate constant (k_1) was determined to be $1.3 \times 10^{-3} \text{ min}^{-1}$ (Table 2).

Treatment of the $\text{Bu}_3\text{SnLi}-\text{Bu}_3\text{SnSnBu}_3$ system with Me_3SiCl

A mixture with the ratio $r = [\text{Bu}_3\text{SnLi}]/[\text{Bu}_3\text{SnSnBu}_3] = 1.0$ was prepared by the addition of 0.8 ml of a 1 M Bu_3SnLi solution to 475.6 mg (0.82 mmol) of $\text{Bu}_3\text{SnSnBu}_3$ and 28.4 mg (0.12 mmol) of Et_4Sn (standard). Another mixture with $r = 1/3$ was prepared similarly. Aliquots of the each mixture were treated with Me_3SiCl after 0.1, 0.75, 1.5, 2.5, 3.5, and 4.5 h, and analyzed by GLC. The constant (k_1) was determined to be $2.8 \times 10^{-3} \text{ min}^{-1}$ (Table 2).

Acknowledgment

We are grateful for support of this work by a Grant-in-Aid for Scientific Research by the Ministry of Education (Grant No. 56430008).

References

- 1 K. Kobayashi (née Kuno), M. Kawanisi, S. Kozima, T. Hitomi, H. Iwamura, and T. Sugawara, *J. Organometal. Chem.*, **217** (1981) 315.
- 2 H. Gilman, F.K. Cartledge, and S.-Y. Sim, *J. Organometal. Chem.*, **4** (1965) 332.
- 3 W.L. Wells and T.L. Brown, *J. Organometal. Chem.*, **11** (1968) 271.
- 4 C. Tamborski, F.E. Ford, and E.J. Soloski, *J. Org. Chem.*, **28** (1963) 237.
- 5 G.E. Coates, D. Blake, and J.M. Tate, *J. Chem. Soc.*, (1961) 618.
- 6 K.W. Wursthorn, H.G. Kuivila, and G.F. Smith, *J. Amer. Chem. Soc.*, **100** (1978) 2779.
- 7 J.D. Kennedy and W. McFarlane, *J. Chem. Soc. Dalton*, (1976) 1219.
- 8 J.D. Kennedy, W. McFarlane, G.S. Pyne, and B. Wrackmeyer, *J. Chem. Soc. Dalton*, (1975) 386.
- 9 T.N. Mitchell and G. Walter, *J. Chem. Soc. Perkin II*, (1977) 1842.
- 10 W.C. Still, *J. Amer. Chem. Soc.*, **99** (1977) 4836.
- 11 R.C. Poller, *The Chemistry of Organotin Compounds*, Logos Press, London, 1970, p. 155.
- 12 A. Rembaum, S.-P. Siano, and N. Indictor, *J. Polymer Sci.*, **56** (1962) S17.
- 13 a) H. Gilman and B.J. Gaj, *J. Org. Chem.*, **22** (1957) 1165; b) H. Gilman and G.L. Schwebke, *J. Organometal. Chem.*, **4** (1965) 483.
- 14 A.T. Weibel and J.P. Oliver, *J. Organometal. Chem.*, **82** (1974) 281.
- 15 a) S. Kozima, K. Kobayashi, and M. Kawanisi, *Bull. Chem. Soc. Jpn.*, **49** (1976) 2837; b) K. Kobayashi, K. Kunō, M. Kawanisi, and S. Kozima, *Bull. Chem. Soc. Jpn.*, **50** (1977) 1353; c) K. Kunō, K. Kobayashi, M. Kawanisi, S. Kozima, and T. Hitomi, *J. Organometal. Chem.*, **137** (1977) 349; d) U. Schröder and W.P. Neumann, *Angew. Chem.*, **87** (1975) 247; e) W.P. Neumann and A. Schwarz, *Angew. Chem.*, **87** (1975) 844.
- 16 a) V.S. Zavgorodnii, B.I. Ionin, and A.A. Petrov, *Zh. Obshch. Khim.*, **37** (1967) 949; *Chem. Abstr.*, **68** (1968) 39754; b) S.-Y. Sim., Ph. D. Thesis, Iowa State Univ., (1966); *Chem. Abstr.*, **66** (1967) 85836.
- 17 T.N. Mitchell, personal communication; G.A. Webb (Ed.), *Annual Reports on NMR spectroscopy*, **8** (1978) 361.