

New synthesis of a stable dialkylstannylene and its reversible complexation with tetrahydrofuran

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Dedicated to Professor Oleg Matveevich Nefedov on the occasion of his 70th birthday

Abstract

A stable dialkylstannylene [2,2,5,5-tetrakis(trimethylsilyl)stannacyclopentane-1,1-diy] was synthesized by the reduction of the corresponding dichlorostannane with KC_8 in THF at low temperature. The stannylene showed reversible complexation with tetrahydrofuran (THF) with $\Delta H = -7.0 \text{ kcal mol}^{-1}$ and $\Delta S = -48 \text{ cal mol}^{-1} \text{ K}^{-1}$, suggesting that the complexation is energetically favored but disfavored by the steric hindrance. No such complexation with THF was observed for the corresponding germylene and silylene. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Although a number of monomeric stannylenes have been isolated and their structure, spectroscopic properties, and reactions have been investigated extensively, very few dialkylstannylenes are known to date [1]. Lappert et al. have reported the synthesis of bis[bis(trimethylsilyl)methyl]stannylene (**1**) [2], which is dimeric in the solid state but monomeric in dilute solution as well as in the gas phase (Chart 1). 2-Pyridyl-bis(trimethylsilyl)methyl-substituted stannylenes **2** were synthesized and characterized by X-ray crystallography by Lappert et al. [3], while the stannylenes showed the intramolecular contacts between the tin atom and neighboring nitrogen atoms in the solid state. In 1991, we reported the synthesis and structural characteristics of the first monomeric dialkylstannylene **3** with coordination number 2 in the solid state as well as in solution [4]. More recently, Eaborn et al. have isolated a cyclic stannylene **4** that is monomeric in the solid state [5a].

The Lewis acidity of stannylenes has been revealed in the complexation of stannylenes **1** and **4** with various nitrogen bases; the red stannylene **1** (λ_{max} 495 nm) formed colorless weak 1:1 adducts with pyridine, 4-picoline, and

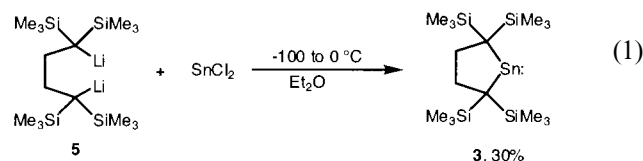
piperidine [6] and a complex of **4** with TMEDA was isolated [5b]. Neumann described the complexation of transient dialkyl- and diarylstannylenes with THF as evidenced by the rate retardation of the polymerization and NMR spectroscopy [1d].

We wish herein to report a new synthetic method for the stannylene **3** and its reversible complexation with tetrahydrofuran (THF) observed using UV spectroscopy.

2. Results and discussion

2.1. A novel method for the synthesis of dialkylstannylene **3**

Stannylene **3** was first synthesized by the reaction of 1,4-dilithio-1,1,4,4-tetrakis(trimethylsilyl)butane (**5**) with tin dichloride (Eq. (1)) [4]. The yield determined by $^1\text{H-NMR}$ was ca. 30% but the isolation yield was much lower due to contamination by unidentified by-products and the laborious procedure for purification.



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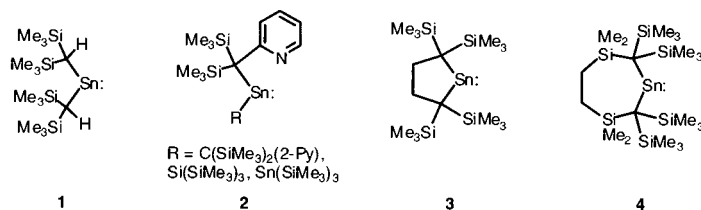
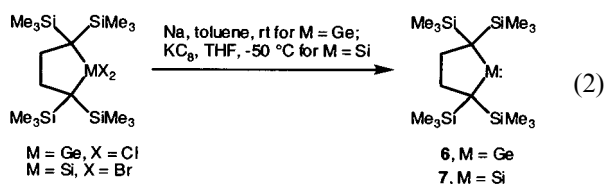
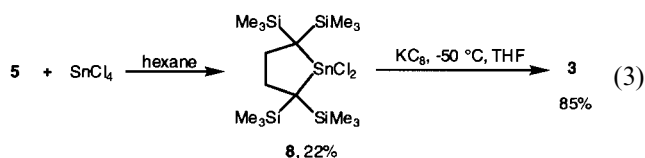


Chart 1.

Recently, we have synthesized dialkylgermylene (**6**) [7a] and dialkylsilylene (**7**) [7b] by reduction of the corresponding dichlorogermene and dibromosilane, respectively, as shown in Eq. (2). The success has prompted us to investigate a similar method for an improved synthesis of the stannylene **3**.



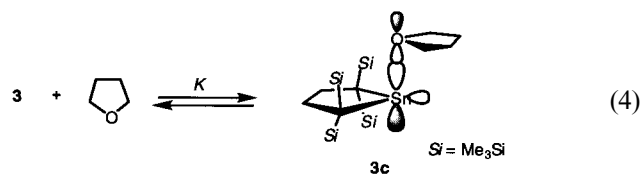
Actually, stannylene **3** was prepared in 85% yield by the reduction of the corresponding dichlorostannane **8**, which was obtained by the reaction of 1,4-dilithiobutane (**2**) [8] with tin tetrachloride in THF in 22%, with potassium graphite at $-50\text{ }^{\circ}\text{C}$ in THF (Eq. (3)). The isolation of pure **3** was achieved by evaporation of the solvent from the supernatant solution of the reaction mixture, while the overall yield of **3** is comparable with that for the reaction of Eq. (1).



2.2. Complexation of dialkylstannylene **3** with THF

As reported previously, the stannylene **3** shows absorption maxima at 484 nm (ϵ 400) and 370 nm (ϵ 90) in hexane [4]. No significant temperature dependence of the absorption spectrum of **3** was observed in methylcyclohexane between $-100\text{ }^{\circ}\text{C}$ and room temperature; the band width became slightly narrower at lower temperatures. On the other hand, the absorption spectrum of **3** in THF depended remarkably on temperature. At a temperature higher than $-60\text{ }^{\circ}\text{C}$, **3** showed similar spectra to those recorded in methylcyclohexane. However, at temperatures lower than $-60\text{ }^{\circ}\text{C}$, a new absorption band appeared at 341 nm and the absorbance increased with lowering temperatures (Fig. 1). The spectral change was reversible between room temperature and $-100\text{ }^{\circ}\text{C}$. The spectral change should not be

ascribed to the monomer–dimer equilibrium as observed in bis[bis(trimethylsilyl)methyl]stannylene (**1**) [2], because no such remarkable temperature dependence was observed in the spectra of **3** in methylcyclohexane. The new absorption band at 341 nm should be assigned to a complex between **3** and THF (**3c**). The blue shift of the absorption band of **3** from 484 to 341 nm by complexation is compatible with the tendency found in matrix-isolated silylenes and germylenes [9]; typically, the absorption band maxima for dimethylsilylene [9a] and diphenylgermylene [9b] observed at 450 and 466 nm in 3-methylpentane shifted to 294 and 325 nm, respectively, in their 2-methyltetrahydrofuran complexes at 77 K.



$$K = \frac{[3C]}{[3][\text{THF}]} \quad (5)$$

The equilibrium constant K was determined at various temperatures by assuming that the absorption coefficient of **3** at 484 nm in THF is identical with that in

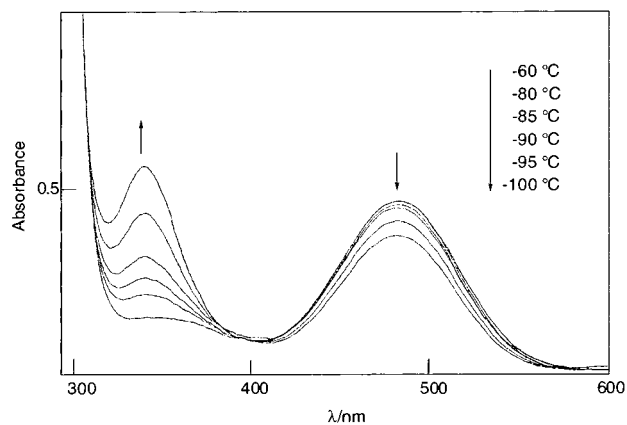


Fig. 1. Temperature-dependent UV–vis spectra of stannylene **3** in THF.

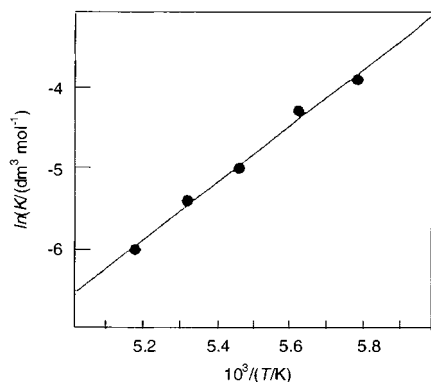


Fig. 2. A plot of logarithms of the formation constants (K) of the stannylene **3**–THF complex (**3c**) versus $1/T$.

hexane (ϵ_3 400) and independent of temperature (Fig. 1). The concentration of THF was estimated as $1000d/M$, where the temperature dependence of d (density of THF) was taken into account; $M=72.10$ (molecular weight of THF). The absorption coefficient at 341 nm of **3c** (ϵ_{3c}) was determined as 1600 using the absorbances at two different temperatures. As shown in Fig. 2, a plot of the logarithms of the equilibrium constants versus $1/T$ gave a straight line as expected, from which were calculated the enthalpy and entropy for the formation of the stannylene–THF complex **3c**: $\Delta H = -7.0$ kcal mol $^{-1}$ and $\Delta S = -48$ cal mol $^{-1}$ K $^{-1}$. The results constitute the first evaluation of the energetics of the reversible complexation between a Group 14 divalent species and a Lewis base. The large negative entropy would be ascribed to the severe steric hindrance between the two components in the complex; for the complexation, THF should approach from the most crowded side of the stannylene as shown in Eq. (4). No such complexation with THF was observed for the germylene **6** and silylene **7**; their absorption spectra in THF were identical with those in 3-methylpentane even at -100 °C. The complexation of **6** and **7** with THF may be prohibited by severer steric hindrance since Ge–C (2.02 Å) [7a] and Si–C (1.91 Å) [7b] bonds are significantly shorter than the Sn–C bond (2.22 Å) [4].

3. Experimental

3.1. General methods

$^1\text{H-NMR}$ (300 MHz), $^{13}\text{C-NMR}$ (75.4 MHz), and $^{29}\text{Si-NMR}$ (59.6 MHz) spectra were measured on a Bruker AC300P NMR spectrometer. EI mass spectra were recorded on JEOL JMS-D300 and JMS 600W mass spectrometers. Absorption spectra were obtained on a Shimadzu UV-2000 spectrometer and a Milton Roy SP-3000 spectrometer.

All the tin compounds were prepared using vacuum-line techniques and treated in a glove-box (VAC).

3.2. 1,1-Dichloro-2,2,5,5-tetrakis(trimethylsilyl)-1-stannacyclopentane (**8**)

A mixture of lithium wire (150 mg, 22.0 mmol) and 1,1-bis(trimethylsilyl)ethylene (2.21 g, 12.7 mmol) was degassed three times using freeze–pump–thaw cycles. Dry THF (10 ml) was introduced into the mixture by distillation in vacuo. Stirring the mixture for 3 h at room temperature afforded a THF solution of 1,4-dilithiobutane (**5**). The solution was added to an *n*-hexane (30 ml) solution of tin tetrachloride (2.34 g, 8.5 mmol) at 0 °C under argon atmosphere. The solution turned red–brown for a short time and then colorless. The solvent was evaporated and then benzene (30 ml) was added. The resulting solution was filtered and the solvent was evaporated. Recrystallization from hexane afforded dichlorostannane **8** in 22% yield as colorless needles. **9**: m.p. 187–188 °C (dec., sealed tube). $^1\text{H-NMR}$ (C_6D_6 , δ) 0.24 (s, 36 H), 1.91 (s, 4 H, $^3J(^1\text{H}-^{119}\text{Sn}) = 144.5$ Hz). $^{13}\text{C-NMR}$ (C_6D_6 , δ) 3.45 [CH_3 , $^3J(^{13}\text{C}-^{119}\text{Sn}) = 18.1$ Hz, $^1J(^{13}\text{C}-^{29}\text{Si}) = 51.4$ Hz], 25.0 [$\text{C}(\text{SiMe}_3)_2$, $^1J(^{13}\text{C}-^{119}\text{Sn}) = 157.7$ Hz, $^1J(^{13}\text{C}-^{29}\text{Si}) = 38.4$ Hz], 31.8 [CH_2 , $^2J(^{13}\text{C}-^{119}\text{Sn}) = 79.7$ Hz]. $^{29}\text{Si-NMR}$ (C_6D_6 , δ) 4.93. $^{119}\text{Sn-NMR}$ (C_6D_6 , δ) 182.0. MS (EI, 13 eV) m/z (%) 519 [$\text{M}^+ - 15$, 28], 499 [11], 157 [100], 73 [81].

3.3. 2,2,5,5-Tetrakis(trimethylsilyl)-1-stannacyclopentane-1,1-diyl (**3**)

Into a mixture of dichlorostannane **8** (0.96 g, 1.80 mmol) and KC_8 (0.55 g, 4.07 mmol) in a Schlenk tube with a magnetic stirrer, THF (40 ml) was transferred in vacuo. The resulting solution was stirred for 8 h at -50 °C. The solvent was removed by distillation and hexane (40 ml) was introduced to the mixture. The resulting supernatant solution was separated from the precipitates by using a cannula. Evaporation of the solvent gave almost pure **3** in 85%. The structure was confirmed by comparing the various spectroscopic data with those of the authentic **3** prepared by the use of the reaction in Eq. (1) [4].

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