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# Tetrakis(trimethylstannyl)cyclopentadiene. Improved synthesis, $^{1}$H-, $^{13}$C- and $^{119}$Sn-NMR data and crystal structure

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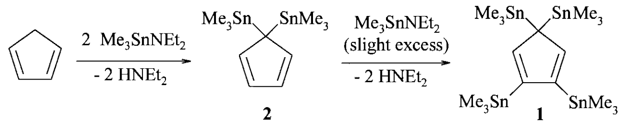
## Abstract

An improved synthesis of tetrakis(trimethylstannyl)cyclopentadiene (**1**) is reported. $^{1}$H-, $^{13}$C- and $^{119}$Sn-NMR data, including a low temperature $^{119}$Sn-NMR spectrum in toluene-$d_8$, are given. A crystal structure analysis of **1** is presented. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Cyclopentadiene; Tin; Crystal structure; NMR spectroscopy

## 1. Introduction

After Jones and Lappert [1] introduced aminostannanes like $Me_3SnNMe_2$ as stannylating agents, several multiply stannylated cyclopentadienes such as $C_5H_4(SnMe_3)_2$ ($CpSn_2$) (**2**), $C_5H_3(SnMe_3)_3$ and $C_5H_2(SnMe_3)_4$ ($CpSn_4$) (**1**) have become accessible [2]; their structures have been established by NMR spectroscopy [3], mass spectrometry [4] and in the case of $CpSn_2$ (**2**) also by X-ray structural analysis [5]. The title compound tetrakis(trimethylstannyl)cyclopentadiene ($CpSn_4$) (**1**) has been characterized only by $^{119}$Sn-NMR spectroscopy at 20°C [3a]; $^{1}$H-, $^{13}$C- or variable temperature-NMR data are as yet unpublished. We have improved the preparation of **1**, because we needed it as a starting material for the synthesis of 1,1′,2,2′,4,4′-hexakis(trimethylstannyl)ferrocene [6]. Here we wish to report the synthesis, NMR and mass spectrometry data as well as the molecular structure of $CpSn_4$ (**1**).



Scheme 1. Synthesis of **1**.

## 2. Results and discussion

$CpSn_4$ (**1**) was prepared in a one-pot reaction in yields of up to 90% by heating $CpSn_2$ (**2**) with three equivalents of $Me_3SnNEt_2$ at 80°C for 12 h (Scheme 1). To obtain good yields of **1**, the developing $HNEt_2$ was removed in vacuo at regular intervals. **1** is highly soluble in aliphatic and aromatic solvents; crystals suitable for X-ray analysis were afforded by recrystallization from hexane.

The mass spectrum of **1** exhibits the $M^+$ peak at $m/z = 718$ and the most intense peak of $M^+ - (CH_3)$ at $m/z = 703$. Peaks for further fragments are listed in Section 3.1.

The structure of **1** in solution was shown to be highly dynamic [7]. The room temperature $^{1}$H-, $^{13}$C- and $^{119}$Sn-NMR spectra in $C_6D_6$ show only one sharp resonance signal for the four trimethylstannyl groups. The $^{119}$Sn-NMR spectrum at $-80$°C in $CD_2Cl_2$ shows two broadened resonance signals, one for the allylic and one for the vinylic bonded stannyl groups [3a], whereas the corresponding $^{1}$H- and $^{13}$C-NMR spectra at $-80$°C in $CD_2Cl_2$ show only one broadened resonance signal for the four trimethylstannyl groups. If the solvent is changed to toluene-$d_8$ the $^{119}$Sn-NMR spectrum reveals at $-80$°C a further separation into four signals, as shown in Fig. 1. This phenomenon is not observed in the $^{1}$H- and $^{13}$C-NMR spectra. The $^{1}$H-NMR spectrum shows at $-80$°C in toluene-$d_8$ two broadened signals

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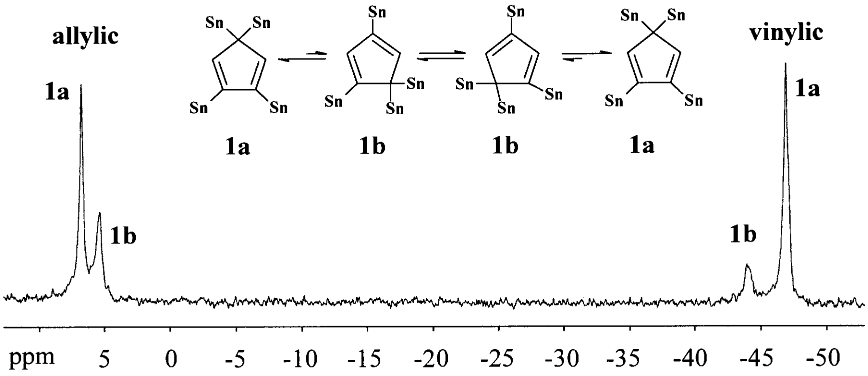

Fig. 1. $^{119}$Sn-NMR spectrum of **1** at −80°C in toluene-$d_8$; (**Sn**≡SnMe$_3$).

whereas the $^{13}$C-NMR spectrum reveals only one broadened signal for the trimethylstannyl groups.

Obviously, the metallotropic rearrangements of **1** in toluene-$d_8$ can be frozen at low temperatures in such a way, that on the $^{119}$Sn-NMR time scale two isomers are observable, the 2,3,5,5-isomer (**1a**) (in accordance with the crystal structure) and to smaller extent presumably the 1,3,5,5-isomer (**1b**). $^{2}J$, $^{3}J$ or $^{4}J$ ($^{119}$Sn$^{117/119}$Sn) coupling constants were not observed, presumably due to the fast rearrangement processes even at low temperature.

An X-ray crystal structure analysis of **1** confirms the expected 2,3,5,5-isomer in the solid state. Fig. 2 shows the ORTEP plot of the molecular structure and the crystallographic numbering scheme of **1**. Selected bond lengths and angles are listed in Table 1.

The Cp ring is ideally planar with normal C–C (~1.46 Å) and C=C (~1.37 Å) bond lengths. The slight lengthening of the Sn(1)–C(1) and of the Sn(2)–C(1) bond (2.18 Å) and the widening of the Sn(1)–C(1)–Sn(2) angle (115.7°) might be due to mutual repulsion of the Me$_3$Sn(1) and of the Me$_3$Sn(2) group; almost the same bond lengths and angles have been found at the corresponding trimethylstannyl groups in CpSn$_2$ (**2**) [2]. The trimethylstannyl groups which are bonded in vinylic positions, Me$_3$Sn(3) and Me$_3$Sn(4) lie nearly ideally within the Cp plane (Cp–Sn(3): 1.2°; Cp–Sn(4): 0.7°). Repulsion of these groups might be responsible for the widened Sn(3)–C(3)–C(4) and the widened Sn(4)–C(4)–C(3) angles (~130°) compared to the Sn(3)–C(3)–C(2) and the Sn(4)–C(4)–C(1) angles (~122°). Other bond lengths and angles vary in the normal range (see Table 1).

## 3. Experimental

All manipulations were carried out under argon. Hexane was carefully dried and purified by distillation. Me$_3$SnNEt$_2$ [8] and CpSn$_2$ (**2**) [2] were prepared as described. — NMR measurements (NMR data see Table 1): Bruker Avance DRX 500 ($^{1}$H-NMR: 500.1 MHz; $^{13}$C{$^{1}$H}-NMR: 125.4 MHz; $^{119}$Sn{$^{1}$H}-NMR: 186.5 MHz). Chemical shifts are given relative to SiMe$_4$ and SnMe$_4$. $^{1}$H-NMR (C$_6$D$_5$H): δ 7.14. $^{13}$C-NMR (C$_6$D$_6$): δ 128.0. — Mass spectra: VG Autospec (EI, 70 eV, 200 μA emission).

### 3.1. Synthesis of tetrakis(trimethylstannyl)cyclopentadiene (1)

CpSn$_2$ (**2**) (6.25 g; 16.0 mmol) and Me$_3$SnNEt$_2$ (11.33 g; 48.0 mmol) were placed in a 50 ml Schlenk flask with

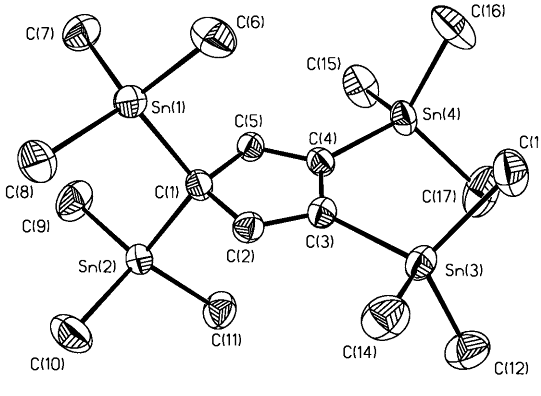

Fig. 2. ORTEP plot of the molecular structure of **1**.

Table 1
Selected bond lengths (Å) and angles (°) of **1**

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Sn(1)–C(1) | 2.174(4) | Sn(1)–C(1)–Sn(2) | 115.7(2) |
| Sn(2)–C(1) | 2.178(4) | Sn(3)–C(3)–C(2) | 123.1(3) |
| Sn(3)–C(3) | 2.124(4) | Sn(3)–C(3)–C(4) | 128.9(3) |
| Sn(4)–C(4) | 2.128(4) | Sn(4)–C(4)–C(5) | 122.2(3) |
| C(1)–C(2) | 1.468(6) | Sn(4)–C(4)–C(3) | 130.0(3) |
| C(1)–C(5) | 1.462(6) | Sn–C(1)–C | 108.8–109.7 |
| C(2)–C(3) | 1.366(6) | C–Sn–C | 103.1–114.1 |
| C(3)–C(4) | 1.459(6) | | |
| C(4)–C(5) | 1.370(6) | Cp–Sn(3) | 1.2 |
| Sn–C(Me) | 2.125–2.144 | Cp–Sn(4) | 0.7 |

Table 2
Crystal data and data related to data collection and structure solution

| | **1** |
|---|---|
| Chemical formula | $C_{17}H_{38}Sn_4$ |
| Formula weight | 717.23 |
| Crystal size (mm) | $0.7 \times 0.6 \times 0.15$ |
| Color and habit | Colorless plates |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 10.309(2) |
| $b$ (Å) | 10.678(2) |
| $c$ (Å) | 13.251(2) |
| $\alpha$ (°) | 99.420(10) |
| $\beta$ (°) | 93.500(10) |
| $\gamma$ (°) | 114.240(10) |
| $V$ (Å$^3$) | 1298.7(4) |
| $Z$ | 2 |
| $D_{calc}$ (Mg m$^{-3}$) | 1.834 |
| $\mu$ (mm$^{-1}$) | 3.797 |
| $F(000)$ | 680 |
| Index range | $0 \leq h \leq 14$, $-15 \leq k \leq 13$, $-18 \leq l \leq 18$ |
| $2\theta$ Range (°) | 3–60 |
| Absorption correction | $\psi$-scans |
| Max/min transmission | 0.860, 0.297 |
| Reflections collected | 7923 |
| Reflections unique ($R_{int}$) | 7535 (0.0337) |
| Parameters | 202 |
| Goodness-of-fit on $F^2$ | 1.101 |
| Final $R$ [$I > 2\sigma(I)$] | 0.0476 [6630] |
| Final $wR_2$ [$I > 2\sigma(I)$] | 0.1310 [6630] |
| Largest difference peak and hole (e Å$^{-3}$) | 1.5 and 1.38 Sn(1) |

condenser and heated to 80°C for 12 h. $HNEt_2$ was removed in vacuo in regular intervals. Removal of excess $Me_3SnNEt_2$ and following fractional distillation gave **1** as a colorless solid (yield: 10.00 g; 87%; b.p. 120–125°C/0.1–0.05 Torr). Recrystallization from hexane afforded single crystals suitable for X-ray analysis. $^1$H-NMR ($C_6D_6$, 20°C): $\delta$ 7.06 (s, 2H, ring), 0.19 (s, 36H, $^2J(^1H^{119}Sn) = 52.7$ Hz, $CH_3$). $^1$H-NMR ($C_6D_5CD_3$, $-80$°C): $\delta$ 0.42, 0.09 (both: s, br, 18H, $CH_3$). $\delta^{13}C$ ($C_6D_6$, 20°C): 146.1 (ring), $-8.1$ ($^1J(^{13}C^{119}Sn) = 343$ Hz, $CH_3$). $\delta^{119}Sn$ ($C_6D_6$, 20°C): $-22.3$. $\delta^{119}Sn$ ($CD_2Cl_2$, $-80$°C): 7.6 (allyl), $-45.9$ (vinyl). $\delta^{119}Sn$ ($C_6D_5CD_3$, $-80$°C): 6.8 (**1a** allyl), 5.4 (**1b** allyl), $-43.9$ (**1b** vinyl), $-46.8$ (**1a** vinyl). IR (KBr, cm$^{-1}$): 3026, 2979, 2911, 2357, 1420, 1397, 1262, 1182, 1133, 985, 854, 836, 764, 741, 669, 524, 506. EI MS ($m/z$ %): 718 (4) [$M^+$], 703 (100) [$M^+ - CH_3$], 673 (31) [$M^+ - 3CH_3$], 643 (14) [$M^+ - 5CH_3$], 613 (7) [$M^+ - 7CH_3$], 553 (3) [$M^+ - Sn - 3CH_3$], 523 (37) [$M^+ - Sn - 5CH_3$], 493 (23) [$M^+ - Sn - 7CH_3$], 463 (18) [$M^+ - Sn - 9CH_3$], 433 (6) [$M^+ - Sn - 11CH_3$], 165 (84) [$SnMe_3$]. Anal. Found: C, 28.30; H, 4.81. Calc. for $C_{17}H_{38}Sn_4$ (717.32 g mol$^{-1}$): C, 28.47; H, 5.34%.

### 3.2. *X-ray crystallographic study of* ***1***

A single crystal was coated with a layer of hydrocarbon oil, attached to a glass fiber and cooled to 173 K. A P2(1) Siemens diffractometer (graphite monochromator, Mo–K$_\alpha$ radiation, $\lambda = 0.71073$ Å) was used for data collection. Data related to crystal, data collection and structure solution are listed in Table 2. Programs from SHELXTL PLUS (SHELX-93) were used for structure solution and refinement. The structure was solved by direct methods and refined by using full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were fixed at the calculated positions.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 140560. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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