

Stepwise Carbon Disulfide Insertion into the Sn–C Bonds of a Diarylstannylene¹

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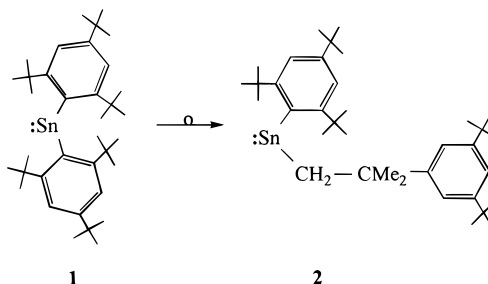
Summary: Bis(2,4,6-tri-*tert*-butylphenyl)stannylene reacted with carbon disulfide by stepwise insertion of CS₂ into the Sn–C bonds to furnish the aryltin(II) arene-dithiocarboxylate (**6**) and tin(II) bis(arene-dithiocarboxylate) (**7**). The structures of the three- and four-coordinated stannylenes **6** and **7** were determined by X-ray crystallography.

Introduction

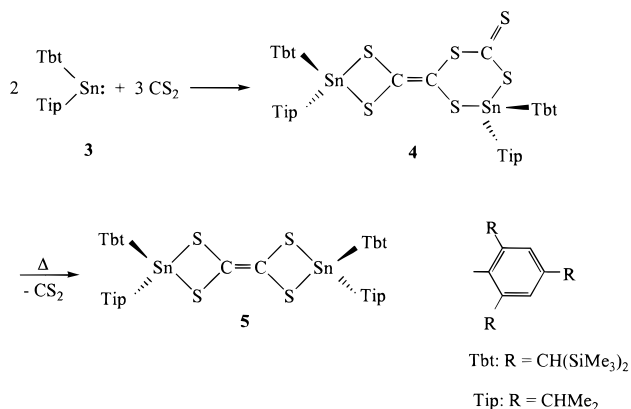
Structurally characterized diarylstannylenes have been known only for a few years. One of them is the compound [2,4,6-(CF₃)₃C₆H₂]₂Sn:, the stability of which is presumably attributable to the close contacts of the *ortho*-CF₃ fluorine atoms with the unsaturated tin atom.² The diarylstannylene **1** can exist without intramolecular stabilization since it is well protected from subsequent reactions by a large steric shielding.³ The stannylene [2,6-(2,4,6-Me₃C₆H₂)₂C₆H₃]₂Sn: is even more sterically overcrowded; this compound as well as the analogously substituted germylene and plumbylene were prepared and fully characterized recently.⁴ In contrast, the stannylene [2-*t*Bu-4,5,6-Me₃C₆H]₂Sn: is less well shielded; in the solid state it exists as a distannene with a very long Sn=Sn bond length of 2.910(1) Å.⁵

Although the stannylene **1** is stable in the solid state, it undergoes slow isomerization in solution to afford the alkylarylstannylene **2** (Scheme 1). Accordingly, all reactions of **1**, for example, with chalcogens or transition metal substrates exclusively furnish products containing the rearranged stannylene **2**.⁶ On the other hand a

Scheme 1



Scheme 2



(1) Compounds of Germanium, Tin, and Lead 27. Part 26: Stürmann, M.; Weidenbruch, M.; Klinkhammer, K. W.; Lissner, F.; Marsmann, H. *Organometallics*, in press.

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typical reaction of a diarylstannylene is observed when compound **3**, which is stable in solution, is treated with carbon disulfide. The unsymmetrically substituted olefin **4** is isolated, which, upon heating, is transformed with cleavage of CS₂ to the symmetrically substituted olefin **5**⁷ (Scheme 2).

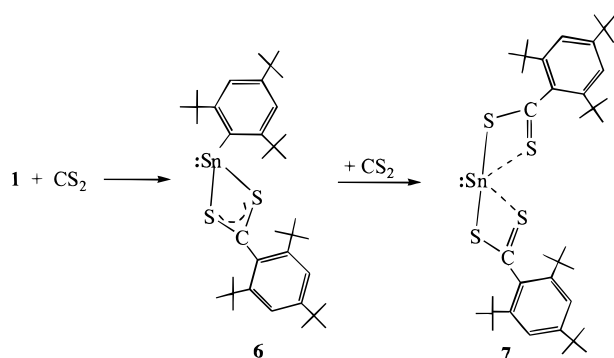
We now report on the reactions of **1** with CS₂, which proceed for the first time without isomerization and lead to completely different product palettes from those of the stannylene **3**.

Results and Discussion

Reaction of excess carbon disulfide with the dark red solution of **1** in toluene for 6 days at 60 °C furnished an orange-colored compound with the constitution of a 1:2

(7) Saito, M.; Tokitoh, N.; Okazaki, R. *Organometallics* **1995**, 14, 3620.

Scheme 3



adduct of **1** and CS_2 according to its analytical and spectral data. The shift of the ^{119}Sn NMR signal ($\delta = 56.3$ ppm) to higher field by more than 1000 ppm in comparison to the signal of **1** ($\delta = 1105$ ppm) as well as the unusual position of the CS_2 carbon atom signal at 259 ppm is indicative of a probable 2-fold insertion of CS_2 into the $\text{Sn}-\text{C}$ bonds of **1** to give the four-coordinated stannylene **7** in 40% yield (Scheme 3).

To gain a better insight into this unusual insertion sequence, the reaction was repeated under identical conditions except that the heating was stopped after 3 days. After workup a 2:1 mixture of light red- and orange-colored crystals was obtained in 51% yield which could not be separated by usual methods. After manual sorting of the two types of crystals it was found that the orange-colored solid was pure **7** (17% yield). Analytical and spectral data of the major product (34% yield) indicated that it was a 1:1 adduct of the stannylene **1** with CS_2 . The position of its ^{119}Sn NMR signal at 652 ppm, which lies between the signals of the two-coordinated stannylene **1** and the four-coordinated stannylene **7**, and the again unusual position of the signal for the CS_2 carbon atom at 253 ppm are indicative of the existence of the three-coordinated stannylene **6** resulting from a monoinsertion of CS_2 into one of the $\text{Sn}-\text{C}$ bonds.

X-ray crystallographic analyses of the compounds **6** and **7** not only supported the structures proposed on the basis of the analytical and spectral data but also revealed some interesting details. The stannylene **6** (Figure 1) crystallizes with two independent molecules in the unit cell; however, the differences in bond lengths and angles are not significant, so that only one molecule is discussed here.

Both the two $\text{Sn}-\text{S}$ and the two $\text{S}-\text{C}$ bonds have practically identical lengths and thus indicate electron delocalization within the SnS_2C four-membered ring. In comparison with the starting compound **1**, the still present tin-carbon bond is shortened by about 0.06 Å. On account of the steric effects of the free electron pair at tin, this electron pair and the three ligand atoms have a distorted trigonal pyramidal arrangement about the tin atom.

The situation in the four-coordinated stannylene **7** (Figure 2) is different in that the pairs of $\text{Sn}-\text{S}$ bonds differ in length by 0.21 Å. Thus, there are two strong and two weak $\text{Sn}-\text{S}$ bonds with the new chelating ligands within the SnS_4 skeletal unit. Despite these diverging bond lengths, the $\text{C}-\text{S}$ bond lengths are almost identical. The free electron pair at tin also has

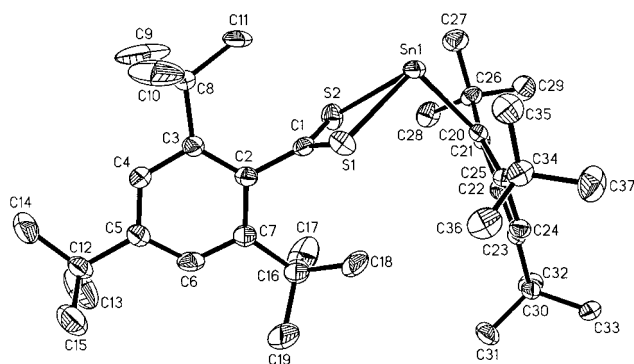


Figure 1. Structure of **6** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): $\text{Sn}-\text{S}(1)$ 2.663(1); $\text{Sn}-\text{S}(2)$ 2.654(1); $\text{Sn}-\text{C}(20)$ 2.224(3); $\text{S}(1)-\text{C}(1)$ 1.687(3); $\text{S}(2)-\text{C}(1)$ 1.679(4); $\text{C}(1)-\text{C}(2)$ 1.487(4); $\text{S}(1)-\text{Sn}-\text{S}(2)$ 66.24(3); $\text{S}(1)-\text{C}(1)-\text{S}(2)$ 119.4(2); $\text{S}(1)-\text{Sn}-\text{C}(20)$ 99.12(9); $\text{S}(2)-\text{Sn}-\text{C}(20)$ 91.67(8).

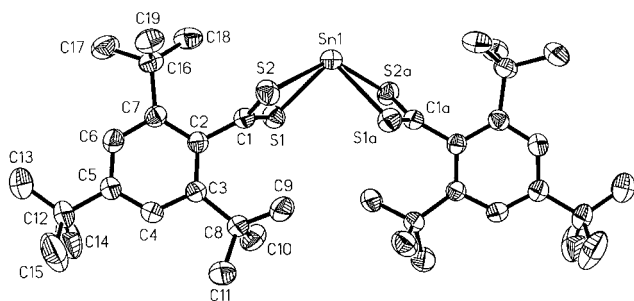


Figure 2. Structure of **7** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): $\text{Sn}-\text{S}(1)$ 2.567(1); $\text{Sn}-\text{S}(2)$ 2.771(1); $\text{S}(1)-\text{C}(1)$ 1.698(2); $\text{S}(2)-\text{C}(1)$ 1.675(3); $\text{C}(1)-\text{C}(2)$ 1.497(4); $\text{S}(1)-\text{Sn}-\text{S}(2)$ 66.4(1); $\text{S}(1)-\text{Sn}-\text{S}(1a)$ 96.0(1); $\text{S}(2)-\text{Sn}-\text{S}(2a)$ 138.6(1); $\text{S}(2)-\text{Sn}-\text{S}(1a)$ 85.8(1).

a steric effect in **7** and results in a quadratic pyramidal arrangement of the SnS_4 skeletal atoms. Although the compounds **6** and **7** and in particular their mode of formation are novel, the coordination polyhedron found in the stannylene **7** has previously been observed in tin(II) diethylthiocarbamate obtained very simply by reaction of the corresponding sodium salt with tin(II) chloride.^{8,9}

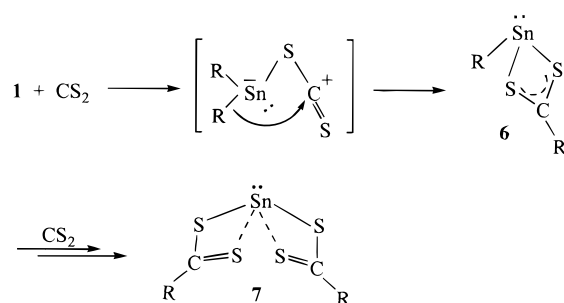
The following mechanism for the single and double insertion of CS_2 into the $\text{Sn}-\text{C}$ bonds of the diarylstannylene **1** appears to be feasible. It has been known for some time that CS_2 can form adducts with coordinatively unsaturated compounds and that the adducts undergo subsequent rearrangements.¹⁰ Very recently, Okazaki et al.¹¹ reported that CS_2 insertions into the $\text{Pb}-\text{S}$ bonds of lead(II) bis(arenethiolates) led to lead(II) bis(aryl trithiocarbonates). In analogy with this report,¹¹ we may assume that at first a side-on or end-on adduct of CS_2 to the stannylene **1** arises with subsequent migration of an aryl group to furnish the insertion product **6**. A repetition of this process should

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Scheme 4^a^a R = 2,4,6-*t*Bu₃C₆H₂

then be responsible for the formation of the double insertion product **7** (Scheme 4). A point in favor of this proposal is the weakness of the Sn–C bonds in **1**, which is otherwise reflected in the always occurring rearrangement to **2**. However, this process is hindered by the addition of CS_2 while concomitantly the labile Sn–C bond, unlike the stannylene **3**, makes the observed migration of the aryl group to the CS_2 carbon atom.

Experimental Section

General Procedure. All manipulations were carried out in oven-dried glassware under an atmosphere of dry argon. The ¹H, ¹³C, and ¹¹⁹Sn NMR spectra were obtained on a Bruker AM 300 spectrometer using C₆D₆ as solvent. UV/vis spectra were taken on a ConSpec spectrometer with fiber optics. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany. Stannylene **1** was prepared according to the literature procedure.^{3,12}

2,4,6-Tri-*tert*-butylphenylltin(II) 2,4,6-Tri-*tert*-butylbenzenedithiocarboxylate (6). To the dark red solution of **1** (4.0 g, 6.6 mmol) in 60 mL of toluene was added carbon disulfide (4.0 mL, 67 mmol, large excess), and the mixture was heated at 60 °C for 3 days with stirring. After this time all volatile compounds were distilled off. The residue was redissolved in 60 mL of toluene and insoluble material filtered off. Concentration of the solution to a volume of 40 mL and cooling at 4 °C provided 2.4 g (51% yield) of a crude product which consisted of a 2:1 mixture of pure crystals of **6** and **7**. Manual selection furnished 1.6 g (34%) of light red crystals of **6**, mp 225 °C: ¹H NMR δ 1.23 (s, 9 H), 1.35 (s, 9 H), 1.47 (s, 18 H), 1.50 (s, 18 H), 7.45 (s, 2 H), 7.52 (s, 2 H); ¹³C NMR δ 31.33 (C_p), 31.60 (C_p), 33.40 (C_p), 33.93 (C_p), 34.62 (C_q), 35.00 (C_q), 39.04 (C_q), 41.03 (C_q), 123.25 (CH), 123.59 (CH), 145.29 (C_q), 146.57 (C_q), 148.77 (C_q), 149.61 (C_q), 151.88 (C_q), 159.12 (C_q), 253.28 (CS₂) (C_p and C_q refer to primary and quaternary carbon atoms); ¹¹⁹Sn NMR δ 652.0; UV/vis λ_{max} (ϵ) 466 (1530 nm). Anal. Calcd for C₃₇H₅₈S₂Sn: C, 64.81; H, 8.52; S, 9.35. Found: C, 64.65; H, 8.59; S, 9.40. Fraction 2 (0.8 g, 17%) was identified as the 2-fold insertion product **7** (see below).

Tin(II) Bis(2,4,6-tri-*tert*-butylbenzenedithiocarboxylate) (7). A dark red solution of **1** (4.0 g, 6.6 mmol) and carbon

Table 1. Crystallographic Data for **6** and **7**

	6	7
empirical formula	C ₃₇ H ₅₈ S ₂ Sn	C ₃₈ H ₅₈ S ₄ Sn
fw	685.64	761.85
<i>a</i> (Å)	14.327(2)	34.624(3)
<i>b</i> (Å)	15.644(2)	9.922(1)
<i>c</i> (Å)	18.568(2)	11.700(1)
α (deg)	112.112(14)	90
β (deg)	104.402(15)	101.408(6)
γ (deg)	95.141(15)	90
<i>V</i> (Å ³)	3655.7(8)	3940.1(5)
<i>Z</i>	4	4
<i>D</i> (calcd) (g cm ⁻³)	1.246	1.248
cryst size (mm)	0.52 × 0.27 × 0.26	0.3 × 0.2 × 0.2
cryst syst	triclinic	monoclinic
space group	<i>P</i> 1	<i>C</i> 2/ <i>c</i>
data collection mode		ω -scan
2 θ_{max} (deg)	52	55
no. of rflns measd	31 389	4869
no. of unique rflns	13 175	4527
lin abs coeff (mm ⁻¹)	0.835	0.88
data-to-parameter ratio	18.27	19.27
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0363	0.038
<i>wR</i> 2 (all data)	0.0905	0.039 (<i>R_w</i>)
residual electron density	961, -1065	430, -620
(e nm ⁻³)		

disulfide (4.0 mL, 67 mmol) in 60 mL of toluene was heated at 60 °C for 6 days with stirring. After this time all volatile compounds were distilled off. The residue was redissolved in 60 mL of toluene and insoluble material filtered off. Concentration of the solution to a volume of 40 mL and cooling at 4 °C afforded 2.0 g (40% yield) of orange crystals of **7**, mp 248 °C: ¹H NMR δ 1.28 (s, 18 H), 1.70 (s, 36 H), 7.61 (s, 4 H); ¹³C NMR δ 31.35 (C_p), 34.25 (C_p), 35.04 (C_q), 39.27 (C_q), 123.86 (CH), 145.05 (C_q), 147.24 (C_q), 149.77 (C_q), 259.23 (CS₂); ¹¹⁹Sn NMR δ 56.3; UV/vis λ_{max} (ϵ) 364 (9700), 464 (1080) nm. Anal. Calcd for C₃₈H₅₈S₄Sn: C, 59.91; H, 7.67; S, 16.83. Found: C, 60.06; H, 7.84; S, 16.69.

Crystallographic Analyses. Crystal and numerical data of the structure determinations are given in Table 1. Single crystals were grown from saturated solutions in toluene at 4 °C. Data were collected on a STOE IPDS diffractometer at 213 K (**6**) or a Siemens P4 diffractometer (**7**) at 296 K using graphite-monochromated Mo K α radiation (0.710 73 Å). The structures were solved by direct phase determination against *F*² (**6**) or *F* (**7**) with the SHELX 93¹³ or SHELXTL program systems and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically.

Acknowledgment. Financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Tables of crystal data, atomic coordinates for H atoms, bond lengths, bond angles, and anisotropic displacement coefficients for **6** and **7** (12 pages). Ordering information is given on any current masthead page.

OM980552E

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