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Diarylstannylene reactions with some aryl azides: formation of different ring systems☆

Ulrike Fooken, Wolfgang Saak, Manfred Weidenbruch *

Fachbereich Chemie der Universität Oldenburg, Carl-von-Ossietzky-Straße 9–11, D-26111 Oldenburg, Germany

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Abstract

The reactions of the diarylstannylene Ar_2Sn: (**1**), Ar = 2,4,6-$t$$Bu_3C_6H_2$ with the azides RN_3, R = 2,6-$i$$Pr_2C_6H_3$ (**3**) or 2,4,6-$Me_3C_6H_2$ (**4**), proceed via the stannanimines, which rearrange by intramolecular addition of a C–H bond of one of the *ortho*-*tert*-butyl groups across the Sn=N bond to furnish the stannaindan derivatives **7** and **8**. Treatment of **1** with excess 3,5-bis(trifluoromethyl)phenyl azide (**9**) affords the tetraazastannoline derivative **10** by a [3 + 2] cycloaddition reaction of **9** to the stannanimine intermediate The structures of **7** and **10** were determined by X-ray crystallography. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tin; Stannylene; Stannaindan; Tetraazastannoline

1. Introduction

Structurally characterized diarystannylenes without donor-stabilization are still very rare [2]. One such example is compound **1**, which is stable in the solid state but undergoes rearrangement to afford the alkylarylstannylene **2** in solution (Scheme 1, [3]). Accordingly, all reactions of **1** with the heavier chalcogens of transition metal substrates yielded products arising exclusively from the rearranged stannylene **2** [4–6].

An exception to this behaviour pattern is the reaction of **1** with carbon disulfide which proceeds without isomerization by insertion of one or two molecules of CS_2 in the Sn–C bonds to furnish tri- or tetracoordinated stannylenes [7]. We now report on reactions of **1** with some aryl azides—also proceeding without isomerization—to furnish initially stannanimines which then undergo further intra- or intermolecular reactions to provide various cyclic products.

2. Results and discussion

Some of the most interesting reactions of stannylenes are those with azides to form mainly the thermally labile stannanimines [8,9]. Recently Meller and coworkers isolated and completely characterized the first and as yet only stannanimine that is stable at − 30°C from the reaction of $[(Me_3Si)_2N]_2Sn$: with the azide RN_3 (R = 2,6-$i$$Pr_2C_6H_3$) [10]. Thus, it seemed worthwhile to make use of the steric overcrowding in the diarylstannylene **1** in an attempt to generate more stable stannanimines.

Reaction of the diarylstannylene **1** with the azide **3** does indeed furnish a colourless crystalline product in 44% yield with analytical data suggestive of a stannanimine. However, the spectral data are not compatible with such a structure; for example, the ^1H-NMR spectrum reveals signals for an NH group and an AB spin system for a ring CH_2 group thus indicating that a rearrangement of the primarily formed stannanimine **5** has occurred (Scheme 2).

An X-ray crystallographic analysis (Fig. 1, Table 1) shows that the stannaindan derivative **7** has been

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☆ See Ref. [1].

* Corresponding author. Tel.: + 49-441-7983655; fax: + 49-441-7983352.

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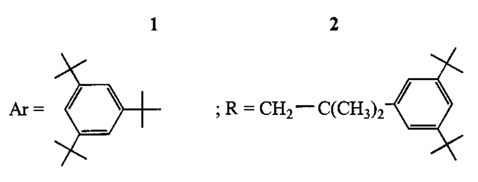
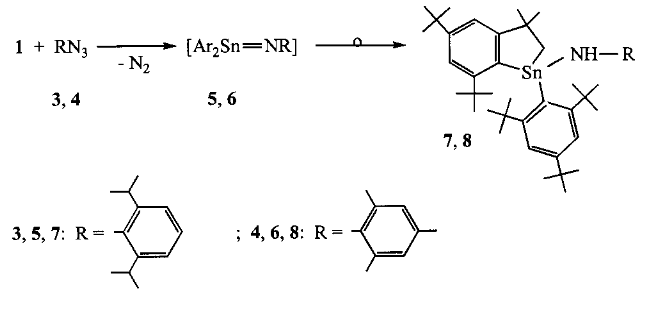
formed through intramolecular addition of a C–H bond of one of the *ortho*-*tert*-butyl groups to the Sn=N bond of **5**. Meller and co-workers [10] had observed a similar subsequent reaction on thermal treatment of their stannanimine, albeit with the difference that the C–H addition to the double bond proceeded from the *N*-substituent and not, as in our case, from the one of the *Sn*-aryl subsitutents.

The reaction of **1** with mesityl azide (**4**) takes a similar course to afford the stannaindan **8** by way of the stannanimine **6**. The structure of **8** was confirmed by a complete NMR spectral analysis. An interesting result of both reactions is that the formation of **7** or **8** via the intermediates **5** or **6** takes place without the almost always observed aryl/alkyl isomerization of the stannylene **1**. It would seem that, like the C–S bonds in CS_2, the N–N bonds of the employed azides have a sufficient ability to adequately protect the electron sextet molecule from a rearrangement.



Scheme 1.



Scheme 2.

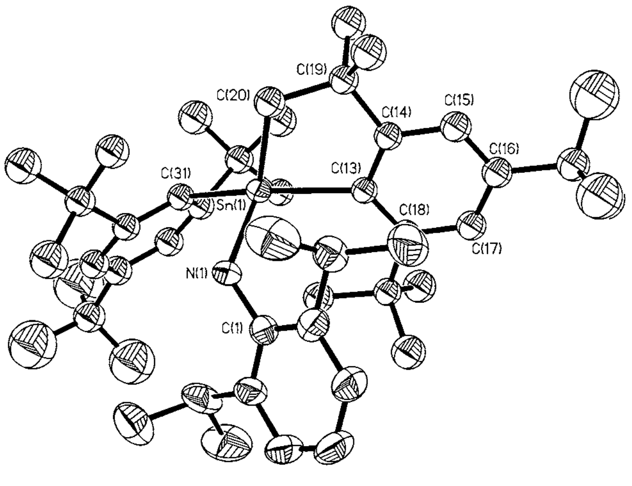


Fig. 1. Molecular structure of **7** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability.

The reaction of **1** with the aryl azide **9**, however, follows a different course. Although no unambiguously identified products have as yet been isolated from the equimolar reaction of the two components, use of an excess of **9** does lead to the formation of the tetraazastannoline **10** (Scheme 3, Fig. 2 and Table 2). Compound **10** is presumably the result of a [3 + 2] cycloaddition of **9** to the stannanimine intermediate. Similar tetrazastannolines have been reported previously but a search of the Cambridge Crystallographic Data File showed that no structure determination has yet been reported.

The X-ray crystallographic analysis of **10** revealed major similarities with the structures of the corresponding tetraazasilolines [11,12] and tetraazagermolines [13,14]. With an angular sum of 539.7° the SnN_4 ring is practically planar. In comparison with the analogous silicon and germanium compounds [11–14,17,18], the markedly longer Sn–N bond lengths in **10** result in a much smaller N–Sn–N bond angle of 72.9(1)°. To accommodate this very small angle in a five-membered ring the angles at N(1) and N(2) are appreciably widened. This very acute angle together with the lower Sn–C bond energy as compared to Si–C and Ge–C bonds are presumably responsible for the low thermal stability of **10**.

3. Experimental

3.1. General procedure

All reactions were carried out in oven-dried glassware under an atmosphere of dry argon.

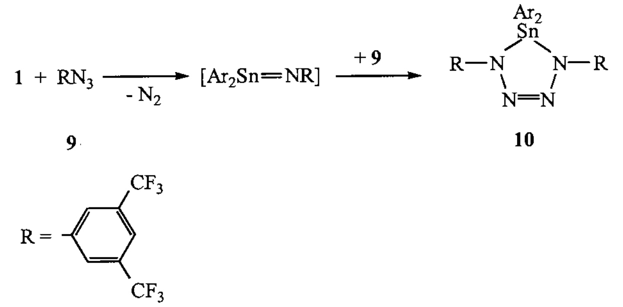
The ^{1}H-, ^{13}C-, and ^{119}Sn-NMR spectra were obtained on a Bruker AM 300 or Bruker AMX 500 spectrometer using C_6D_6 or toluene-d_8 as solvents. The assignments of the ^{1}H- and ^{13}C-signals were confirmed by DEPT, COSY, and COLOC spectra. Mass spectra were recorded on a Varian-MAT 212 instrument. UV/vis spectra were taken on a ConSpec spectrometer with fiber optics. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

3.2. 2,6-Diisopropylphenyl-[5,7-di-tert-butyl-3,3-dimethyl-1-(2,4,6-tri-tert-butylphenyl)-1-stannaindan-1-yl]amine (7)

At −30°C, the azide **3** (0.5 g, 2.5 mmol) was added to a solution of **1** (1.5 g, 2.5 mmol) in toluene (50 ml) with stirring. The mixture was allowed to warm to r.t. over a period of 2 h and concentrated to a volume of 20 ml. Cooling of the solution at 4°C afforded a yellow

Table 1
Selected bond lengths (pm) and angles (°) for **7**

Bond lengths (pm)			
Sn–C(31)	218.8(4)	Sn–C(13)	219.4(2)
Sn–C(20)	213.7(4)	Sn–N	208.4(3)
Bond angles (°)			
N–Sn–C(31)	95.5(1)	C(20)–Sn–C(31)	121.0(2)
N–Sn–C(13)	109.0(1)	C(13)–Sn–C(20)	85.8(1)
Sn–C(13)–C(14)	106.9(1)	C(13)–C(14)–C(19)	123.9(2)
C(14)–C(13)–C(20)	111.9(3)	C(19)–C(20)–Sn	109.3(3)



Scheme 3.

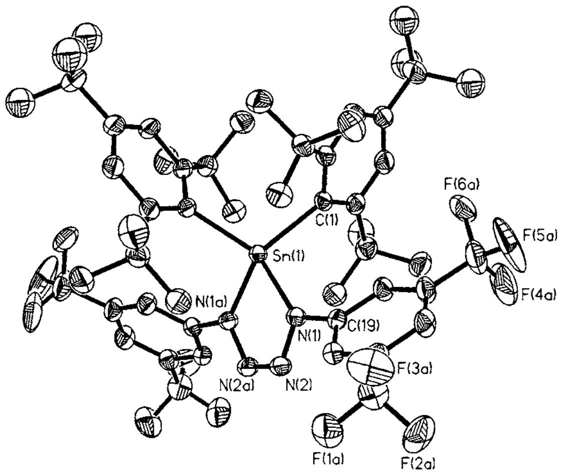


Fig. 2. Molecular structure of **10** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability.

Table 2
Selected bond lengths (pm) and angles (°) for **10**

Bond lengths (pm)			
Sn–C(1)	220.5(2)	Sn–N(1)	210.0(2)
N(1)–N(2)	138.0(3)	N(2)–N(2a)	126.2(4)
Bond angles (°)			
N(1)–Sn–N(1a)	72.9(1)	N(1)–N(2)–N(2a)	116.5(1)
Sn–N(1)–N(2)	116.95(14)	C(1)–Sn–C(1a)	108.2(1)

solid. Recrystallization from a minimum amount of toluene furnished 0.90 g (44% yield) of rectangular colourless crystals of **7**, m.p. 196 °C. ^{1}H-NMR (500 MHz, 263 K, toluene-d_8): δ 0.43 (d, 3 H, $^3J = 6.3$ Hz), 0.87 (s, 9 H), 1.13 (m, 6 H), 1.23 (d, 3 H, $^3J = 6.3$ Hz), 1.26 (s, 18 H), 1.36 (s, 9 H), 1.53 (s, 3 H), 1.62 (s, 9 H), 1.80 (d, 1 H, $^2J = 13.2$ Hz), 1.81 (s, 3 H), 1.83 (d, 1 H), 2.24 (m, 1 H), 2.45 (m, 1 H), 2.86 (s, 1 H, NH), 6.73 (dd, 1 H), 6.80 (d, 1 H, $^3J = 7.3$ Hz), 6.97 (d, 1 H, $^3J = 7.3$ Hz), 7.33 (s, 1 H), 7.44 (s, 1 H), 7.59 (s, 1 H), 7.66 (s, 1 H) ppm. ^{13}C-NMR (298 K, toluene-d_8): δ 23.46 (C_p), 31.39 (C_p), 31.52 (C_p), 32.21 (C_p), 32.98 (CH_2), 33.74 (C_p), 34.35 (C_p), 34.58 (C_q), 34.83 (C_q), 35.78 (C_p), 36.57 (C_q), 37.48 (C_p), 39.66 (C_q), 40.38 (C_q), 41.39 (C_q), 119.34 (C_t), 121.59 (C_t), 121.82 (C_t), 123.18 (C_t), 123.31 (C_t), 123.94 (C_t), 135.82 (C_q), 137,81 (C_q), 145.90 (C_q), 150.32 (C_q), 151.33 (C_q), 154.21 (C_q), 158.16 (C_q), 158.23 (C_q), 158.81 (C_q) ppm. C_p, C_t, and C_q refer to primary, tertiary, and quaternary carbon atoms. ^{119}Sn-NMR (C_6D_6): δ 6.1 ppm. IR (KBr): ν 3358 (m, NH) cm^{-1}. MS (CI, isobutane): m/z 786 (MH$^+$, 2%). Anal. Found: C, 73.23; H, 9.77; N, 1.74. $C_{48}H_{75}NSn$ (784.82) Anal. Calc.: C, 73.46; H, 9.63; N, 1.78%.

*3.3. 2,4,6-Trimethylphenyl-[5,7-di-tert-butyl-3,3-dimethyl)-1-(2,4,6-tri-tert-butylphenyl)-1-stannaindan-1-yl]amine (**8**)*

At 0°C, azide **4** (0.34 g, 2.13 mmol) was added from a syringe to a solution of **1** (1.3 g, 2.13 mmol) in *n*-hexane (50 ml) over a period of 1 h with stirring. To complete the reaction, the solution was allowed to warm to r.t. and stirred for 12 h. During this time the colour of the solution changed from dark red to yellow. The solution was concentrated to a volume of 30 ml and cooled at 4°C. Recrystallization of the yellow solid from a minimum amount of toluene yielded 0.60 g (38%) of rectangular colourless plates of **8**, m.p. 179°C. ^{1}H-NMR (300 MHz, 298 K, C_6D_6): δ 0.92 (s, 9 H), 1.20 (s, 9 H), 1.23 (s, 9 H), 1.34 (s, 9 H), 1.62 (s, 9 H), 1.63 (s, 3 H), 1.75 (d, 1 H, $^2J = 13.3$ Hz), 1.76 (s, 3 H), 1.83 (s, 6 H), 1.89 (d, 1 H), 2.08 (s, 3 H), 2.70 (s, 1 H, NH), 6.55 (s, 2 H), 7.44 (d, 1 H, $^4J = 1.85$ Hz), 7.46 (d, 1 H, $^4J = 1.95$ Hz), 7.61 (d, 1 H, $^4J = 1.95$ Hz), 7.65 (d, 1 H, $^4J = 1.85$ Hz) ppm. ^{13}C-NMR (298 K, C_6D_6): δ 20.17 (C_p), 20.48 (C_p), 31.38 (CH_2), 31.42 (C_p), 32.08 (C_p), 33.75 (C_p), 34.04 (C_p), 34.57 (C_q), 34.84 (C_q), 36.59 (C_p), 36.78 (C_q), 36.83 (C_p), 39.28 (C_q), 40.12 (C_q), 41.46 (C_q), 121.37 (C_t), 122.23 (C_t), 123.34 (C_t), 123.92 (C_t), 126.33 (C_q), 126.37 (C_q), 128.29 (C_t), 129.49 (C_t), 135.47 (C_q), 137.14 (C_q), 146.64 (C_q), 150.25 (C_q), 151.97 (C_q), 154.51 (C_q), 158.12 (C_q), 158.56 (C_q), 159.11 (C_q) ppm. ^{119}Sn-NMR (C_6D_6, 298 K): δ 10.5 ppm. IR (KBr) ν: 3364 (m, NH) cm^{-1}. Anal. Found: C, 72.68; H, 9.40; N, 1.86. $C_{45}H_{68}NSn$ (741.73) Anal. Calc.: C, 72.87; H, 9.24; N, 1.89%.

*3.4. 5,5-Bis(2,4,6-tri-tert-butylphenyl)-1,4-bis[3,5-bis-(trifluoromethyl)phenyl]-4,5-dihydro-1H-[1,2,3,4,5]tetrazastannole (**10**)*

At −40°C, azide **9** (1.06 g, 4.2 mmol) was added dropwise to a solution of **1** (1.27 g, 2.1 mmol) in toluene (40 ml). The mixture was allowed to warm to 0°C over a period of 2.5 h. During this time the colour of the solution changed from reddish–brown to yellowish–brown. Concentration of the solution to a volume of 30 ml and cooling at 4°C afforded 1.2 g (52%) of pale yellow rhombic crystals of **10**, m.p. 135°C (dec.). ^{1}H-NMR (500 MHz, 273 K, toluene-d$_8$): δ 0.76 (s, 18 H), 1.16 (s, 18 H), 1.34 (s, 18 H), 7.36 (s, 2 H), 7.53 (s, 2 H), 7.55 (s, 2 H), 8.14 (s, 4 H) ppm. ^{13}C-NMR (298 K): δ 30.90 (C$_p$), 32.68 (C$_p$), 33.12 (C$_p$), 34.66 (C$_q$), 37.94 (C$_q$), 39.20 (C$_q$), 117.98 (C$_t$), 123.83 (C$_q$, $^{1}J_{C,F} = 272.8$ Hz), 125.92 (C$_t$), 126.51 (C$_t$), 129.28 (C$_t$), 132.31 (C$_q$, $^{2}J_{C,F} = 32.9$ Hz), 140.67 (C$_q$), 150.79 (C$_q$), 152.10 (C$_q$), 154.76 (C$_q$), 156.01 (C$_q$) ppm. ^{119}Sn-NMR: δ −275.0 ppm. UV/vis: $\lambda_{max}(\varepsilon)$: 296 (22440) nm. Anal. Found: C, 57.32; H, 5.82; N, 5.11. $C_{52}H_{64}F_{12}N_4Sn$ (1091.77) Anal. Calc.: C, 57.21, H, 5.91; N, 5.13%.

*3.5. X-ray structure analyses of **7** and **10***

Crystal and numerical data of the structure determinations are given in Table 3. Data collection was performed at 293(2) K on a Siemens STOE AED 2 (**7**) or at 213(2) K on a STOE IPDS (**10**) diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation.

The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL 93 program system [15]. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically [16]. The fluorine atoms of the CF$_3$ groups are disordered and were refined on three positions with the occupancy factor of 1/3 each.

Table 3
Crystallographic data for **7** and **10**

	7	**10**
Empirical formula	$C_{47}H_{75}NSn$	$C_{56}H_{64}F_{12}N_4Sn$
Molar mass	784.85	1091.82
Unit cell dimensions		
a (pm)	1308.1(1)	2129.65(10)
b (pm)	1673.2(2)	1000.24(4)
c (pm)	2130.2(2)	2617.06(8)
β (°)	90.26(2)	107.144(4)
V (×10^6) (pm^3)	4644.0(8)	5327.1(4)
Z	4	4
D_{calc} (g cm^{-3})	1.118	1.361
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Crystal dimensions (mm^3)	0.61 × 0.42 × 0.32	0.70 × 0.68 × 0.50
Data collection mode	ω-scan	–
$2\theta_{max}$ (°)	50	52
No. of reflections	8199	19458
No. of unique reflections	8199	4916
No. of observed reflections ($I = 2\sigma(I)$)	6604	4493
Linear abs. coefficient (mm^{-1})	0.577	0.524
No. of parameters	433	417
R_1 (wR_2) ($I = 2\sigma(I)$)	0.0449 (0.1045)	0.0303 (0.0769)
R_1 (wR_2) (all data)	0.0653 (0.1296)	0.0351 (0.0811)
GOF on F^2	1.167	1.086

Acknowledgements

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[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-106609 (**7**) and CCDC-106610 (**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambrige CB2 1EZ, UK [Fax: +44-01223-336-093; e-mail: deposite@ccdc.cam.ac.uk].

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