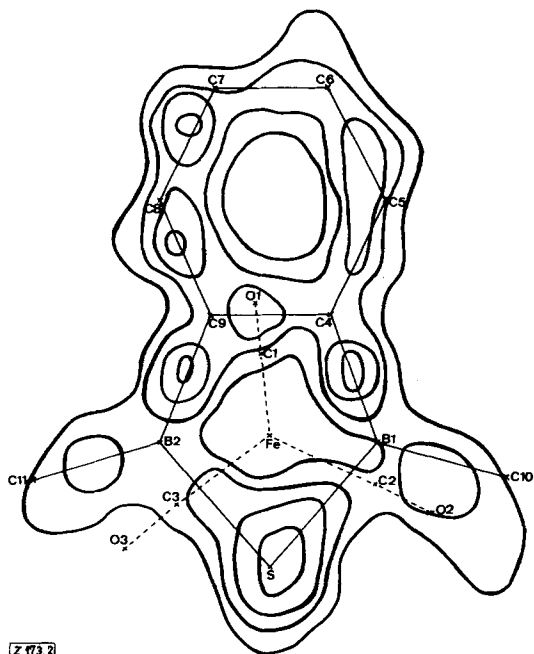


The structure of a *pentahapto*-thiadiborolenetricarbonyliron complex deduced from the spectroscopic data is confirmed by X-ray structure analysis of  $(2) \cdot \text{Fe}(\text{CO})_3$  (Fig. 1).

Crystal data:  $a=9.221(3)$ ,  $b=9.322(2)$ ,  $c=9.529(2)$  Å;  $\alpha=69.66(2)$ ,  $\beta=72.08(2)$ ,  $\gamma=60.71(3)^\circ$ ;  $Z=2$ ;  $d_{\text{calc}}=1.507 \text{ g cm}^{-3}$ ; space group  $P\bar{1}$ . Refined from 2848 measured structural amplitudes (763 unobserved; Nonius CAD 4 diffractometer) including hydrogen atoms to an  $R$  value of 0.0262 ( $R_w=0.0364$ )<sup>[6]</sup>.



[Z 173.2]

Fig. 2.  $\pi$ -Electron density in benzo-1,2,5-thiadiborolenetricarbonyliron. Contours in  $0.1 \text{ e } \text{Å}^{-3}$ .

The bond lengths in the ring system unequivocally establish the fixation of the  $\pi$ -electron system as cyclohexatriene with formation of a long  $\pi$  bond to the iron. Figure 2 shows a difference Fourier synthesis through the best plane ( $\pm 0.02$  Å) of the thiadiborolene ring; the Fourier coefficients were obtained on refinement of all atoms except hydrogen with 1468 reflections ( $\sin \theta/\lambda = 0.5$ ,  $R = 0.0305$ ,  $\lambda_{\text{Mo}} = 0.71069$  Å). The  $\pi$ -electron densities accord with the bond lengths found. The appearance of  $\pi$ -electron density in the B1—C4 and B2—C9 bonds warrants particular attention. The relatively long B—S bonds (1.874 Å) exceed those in trithiaborolanes<sup>[7]</sup> (1.803 Å) and thiaborins<sup>[8]</sup> (1.807 Å). Expectedly, a CO group on the iron is positioned *trans* to the sulfur.

#### Procedure:

Compound (2) is reacted with dodecacarbonyltriiron (molar ratio 1:1) in boiling toluene (1.5 h). After removal of solvent the dark red product is sublimed at  $50^\circ\text{C}/0.01$  torr and recrystallized from pentane at  $-10^\circ\text{C}$ . Yield 67%, m. p.  $82\text{--}84^\circ\text{C}$  (dec.).

Received: December 2, 1974;  
revised: December 20, 1974 [Z 173 IE]  
German version: Angew. Chem. 87, 286 (1975)

#### CAS Registry numbers:

(1), 54677-51-9; (2), 51926-30-8; (1)- $\text{Fe}(\text{CO})_3$ , 54688-79-8;  
(2)- $\text{Fe}(\text{CO})_3$ , 54688-80-1

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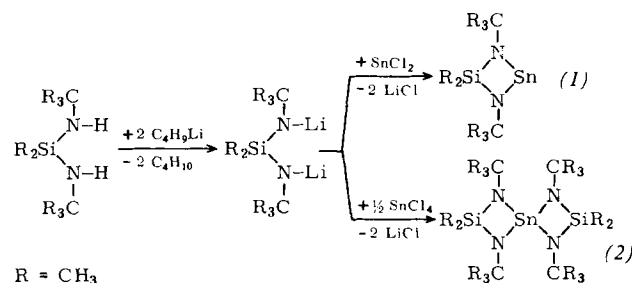
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## Cyclic Nitrogen Derivatives of Tetra- and Divalent Tin

By Michael Veith<sup>[\*]</sup>

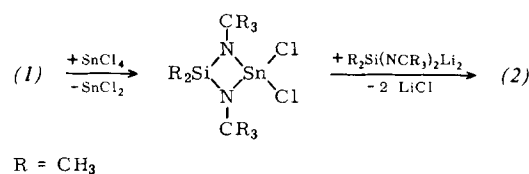
Whereas four-membered silicon-nitrogen rings (cyclodisilazanes) have been known for some time<sup>[1,2]</sup>, corresponding tin-nitrogen rings (cyclodistannazanes) were synthesized only recently<sup>[3]</sup>. The present communication reports the preparation and characterization of four-membered heterocycles containing tin atoms having a valency of 4 or 2, in addition to silicon and nitrogen atoms. In the latter case the product constitutes the first cyclic nitrogen derivative of a Group IV B element in the divalent state<sup>[7]</sup>.

Preparation of 1,3-di-*tert*-butyl-2,2-dimethyl-1,3,2,4 $\lambda^2$ -diazasilastannetidine (1) and the spiro compound (2) is accomplished by reaction of dimethyl-*N,N'*-bis(*tert*-butyl)silazane<sup>[4]</sup> according to the following reaction scheme:



The structure of the resulting heterocycles follows from the <sup>1</sup>H-NMR spectra, which contain only two signals each in the intensity ratio 3:1 for (1) and (2), from the physical data, and from the molecular weights and molecular formulas determined by high-resolution mass spectrometry (Table 1).

Of the many possible reactions, that leading to (2) is cited as chemical proof for compound (1).



The reaction affords (2) almost quantitatively, and also offers the opportunity of preparing spiro compounds of type (2) having different kinds of ligands.

X-Ray structure analysis of compound (2)<sup>[5]</sup> confirms the spiro structure expected from chemical arguments. In the crystal the molecule has  $2(C_2)$  symmetry; in addition it also

[\*] Dr. M. Veith  
Institut für Anorganische Chemie der Universität  
75 Karlsruhe 1, Englerstrasse 11 (Germany)

Table 1. Physical data for compounds (1) and (2).

	(1)	(2)
Phase transitions	red liquid b.p. 55–57°C/0.1 torr m.p. 5°C	colorless crystals b.p. 110°C/0.01 torr m.p. 162°C
<sup>1</sup> H-NMR in benzene, TMS internal ref. (integrations in parentheses)	–22.0 Hz (1.0); –72.5 Hz (3.0)	–23.5 Hz (1.0); –80.0 Hz (3.0)
High resolution mass spectrometry (PKF as standard) MW (cryoscopic in benzene)	<sup>28</sup> Si <sub>2</sub> N <sub>2</sub> C <sub>9</sub> H <sub>21</sub> <sup>120</sup> Sn (M–CH <sub>3</sub> ) exp. 305.0482 calc. 305.0496 324	<sup>28</sup> Si <sub>2</sub> N <sub>4</sub> C <sub>20</sub> H <sub>48</sub> <sup>120</sup> Sn (M) exp. 520.2431 calc. 520.2439 515

possesses approximate 4 2 m (D<sub>2d</sub>) symmetry. The four-membered rings are oriented perpendicular to each other, the rings themselves being largely planar. The N–C bonds are inclined only slightly to the ring planes so that the nitrogen has a planar environment. A remarkable feature of the bond lengths and angles (a selection is given in Table 2) is the very small angle at the tin atom. The NSiN' and SiNSn angles are consequently larger than in the comparable structure of tetramethyl-N,N'-bis(trimethylsilyl)cyclodisilazane<sup>[6]</sup> (∠NSiN' = 88°, ∠SiNSi = 92°).

Table 2. Characteristic bond lengths and angles in the molecule (2) (the values given are the average values of chemically equivalent bond lengths, the deviations listed in parentheses are in units of the last decimal place).

Sn–N	2.033 (5) Å	∠ SiNSn	95.2°
Si–N	1.727 (7) Å	∠ NSiN	93.4°
C–N	1.469 (7) Å	∠ NSnN	76.3°

#### Procedure:

A solution of the dilithium salt of dimethyl-N,N'-bis(*tert*-butyl)silazane (0.05 mol) in hexane is added dropwise over 1 h to a suspension of SnCl<sub>2</sub> (0.05 mol) or a solution of SnCl<sub>4</sub> (0.025 mol), prepared with cooling, in diethyl ether (50 ml). The mixture warms up slightly and turns red (SnCl<sub>2</sub>) or yellowish (SnCl<sub>4</sub>). After 4 hours' stirring the LiCl is filtered off and the solvents removed under reduced pressure. In the case of compound (1) the residue is fractionally distilled, and for isolation of compound (2) the residue is taken up in ether and crystallized out at –20°C. Yields: (1) 12.0 g (74%), (2) 9.9 g (76%).

Received: December 23, 1974 [Z 174 IE]  
German version: *Angew. Chem.* 87, 287 (1975)

#### CAS Registry numbers:

(1), 54724-62-8; (2), 54677-67-7; (CH<sub>3</sub>)<sub>3</sub>CNLiSi(CH<sub>3</sub>)<sub>2</sub>NLiC(CH<sub>3</sub>)<sub>3</sub>, 54677-64-4; SnCl<sub>2</sub>, 7772-99-8; SnCl<sub>4</sub>, 7646-78-8

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## A New Route to 4*H*-Benzo[*def*]carbazole<sup>[1]</sup>

By Richard Kreher and Wilfried Köhler<sup>[\*]</sup>

4*H*-Benzo[*def*]carbazole (2), as a tetracyclic hetarene with an integrated isoindole system, exhibits remarkable thermal

[\*] Prof. Dr. R. Kreher and Dipl.-Ing. W. Köhler  
Institut für Organische Chemie der Technischen Hochschule  
61 Darmstadt, Petersenstrasse 15 (Germany)

stability<sup>[3]</sup>. A versatile synthetic method has been developed<sup>[4]</sup> in order to facilitate a systematic study of the chemical properties and structure of the homologous [*def*]-annelated carbazoles.

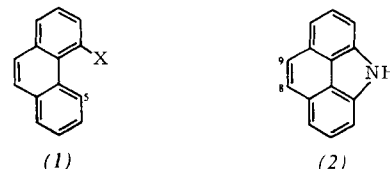


Table 1. Prepared compounds (1a)–(1d) and (2).

(1a), X = CN: m.p. 106–108°C (methanol); yield 70%; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): τ = 0.1–0.5 (m, H<sup>5</sup>), 1.9–2.8 (m, 8 arom. H); cf. [6]

(1b), X = CONH<sub>2</sub>: m.p. 266–267°C (ethanol); yield 95%; <sup>1</sup>H-NMR (hexadeuteriodimethyl sulfoxide): τ = 1.0–1.3 (m, H<sup>5</sup>), 1.7–2.7 (aromat. H and NH<sub>2</sub>)

(1c), X = NH<sub>2</sub>: m.p. 64–65°C (petroleum ether); yield 70%; <sup>1</sup>H-NMR (CS<sub>2</sub>): τ = 0.8–1.2 (m, H<sup>5</sup>), 2.0–3.0 (m, 7 arom. H), 3.2–3.6 (m, 1 arom. H), 6.02 (s, NH<sub>2</sub>); cf. [7]

(1d), X = N<sub>3</sub>: m.p. 95–96°C (*n*-hexane); yield 66%; <sup>1</sup>H-NMR (CS<sub>2</sub>): τ = 0.5–0.9 (m, H<sup>5</sup>), 2.4–3.3 (m, 8 arom. H); MS (70 eV/20°C): M<sup>+</sup> 219 (18%), [M–N<sub>2</sub>]<sup>+</sup> 191 (100%), [M–N<sub>2</sub>H]<sup>+</sup> 190 (48%)

(2): m.p. 174–175°C (sublimation) ([3]: 173–174°C); yield 63%; <sup>1</sup>H-NMR (hexadeuteriodimethyl sulfoxide): τ = –1.38 (s, NH), 1.9 (s, H<sup>8</sup>, H<sup>9</sup>), 2.1–2.5 (m, 6 arom. H); UV (*n*-hexane): λ<sub>max</sub> = 234 nm (log ε = 4.80), 270 (4.35), 327 (4.11); MS (70 eV/50°C): [M+H]<sup>+</sup> 192 (16%), M<sup>+</sup> 191 (100%), [M–H]<sup>+</sup> 190 (30%), [M–HCN]<sup>+</sup> 164 (7%)

The essential step consists in the synthesis of the carbazole ring by cyclization<sup>[5]</sup> of 4-azidophenanthrene (1d), which is obtained from 4-phenanthrenecarbonitrile (1a) (Table 1). This is readily and conveniently accessible from 1-naphthylacetonitrile and 1,3-bis(dimethylamino)trimethinium perchlorate by condensation and electrocyclic rearrangement<sup>[6]</sup>. Under optimized reaction conditions (25 h/80°C and 110 h/220–225°C) yields of up to 70% are achieved on a preparative scale. The partial hydrolysis of the carbonitrile (1a) to the 4-phenanthrenecarboxamide (1b) with conc. KOH solution and glycol monomethyl ether (2.5 h/120°C) is almost quantitative.

Hofmann degradation to 4-aminophenanthrene (1c) cannot be achieved under the usual conditions. This was successfully carried out by reaction with excess hypochlorite solution and dioxane; optimal yields are obtained only with gradual temperature adjustment (5 h/45°C and 2.5 h/80°C).

The primary amine (1c)<sup>[7]</sup> is diazotized with sodium nitrite and dilute hydrochloric acid (2 h/0°C) in a dioxane suspension, and after addition of urea is subsequently converted by reaction with excess sodium azide solution into (1d), which can be isolated by adsorptive filtration.

Of the known ring closing reactions<sup>[5, 8]</sup>, thermolysis of the azide (1d) in diphenyl ether (20 min/240°C) proved to be the best. While the thermally induced N<sub>2</sub>-elimination under