Formation of the Dianion and the Dimer of 9,10-Distannaanthracene

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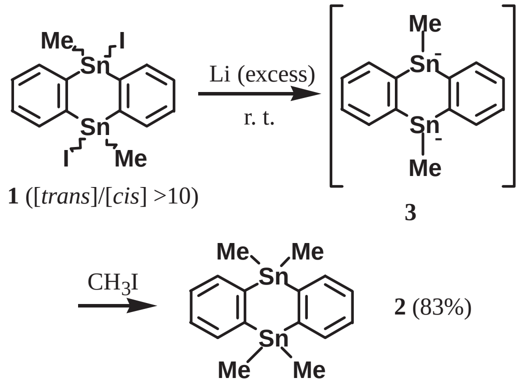
The reaction of 9,10-diiodo-9,10-dihydro-9,10-distannaanthracene with lithium naphthalenide (2.5 equiv.) or excess lithium gave the 9,10-distannaanthracene dimer or the 9,10-distannaanthracene dianion. The formation of the latter was evidenced by NMR spectral analysis and a trapping experiment.

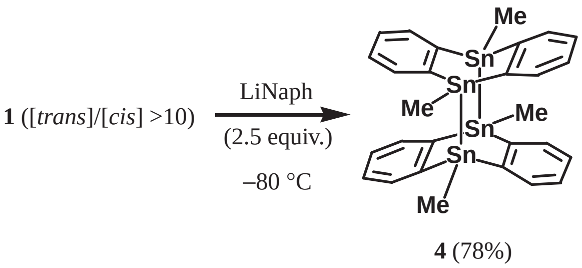
Since the first synthesis of 9,9,10,10-tetraphenyl-9,10-dihydro-9,10-disilaanthracene,[1] studies on the synthesis, structures, and reactions of 9,10-dihydro-9,10-disilaanthracene have been developed.[2] The corresponding germanium analogs, 9,10-dihydro-9,10-digermaanthracenes, were also synthesized and characterized.[3] One of the most interesting features of 9,10-dihydro-9,10-dimetallaanthracene derivatives is their utility as potential precursors for metal-containing reactive species. Also of interest is the conformation of their central six-membered ring. Very recently, fascinating silicon-containing reactive species such as a bis(silyl anion),[4] relatively stable silyl radicals,[5] and a 9-silaanthracene[6] have been reported to be derived from 9,10-dihydro-9,10-disilaanthracenes. As for tin analogs, we have recently reported the first synthesis and structures of 9,10-dihydro-9,10-distannaanthracenes.[7,8] In the course of our studies on the synthesis of reactive species having a 9,10-distannanthracene skeleton, we report herein the first synthesis of the 9,10-distannaanthracene dimer as well as the 9,10-distannaanthracene dianion by the reduction of 9,10-diiodo-9,10-dihydro-9,10-distannaanthracene.

Reaction of a trans/cis mixture ([trans]/[cis] > 10) of 9,10-diiodo-9,10-dihydro-9,10-distannaanthracene **1**[9,10] (18 mg, 0.026 mmol) with excess lithium (18 mg, 2.61 mmol) in THF (2 mL) at room temperature gave a deep red solution, suggesting the formation of an anionic species. After treatment of the reaction mixture with excess methyl iodide, 9,9,10,10-tetramethyl-9,10-dihydro-9,10-distannaanthracene (**2**) was obtained in 83% yield (Scheme 1). The formation of **2** could be reasonably explained in terms of the methylation of intermediary 9,10-distannaanthracene dianion **3**.

The reaction of **1** with lithium was monitored by NMR. Compound **1** (45 mg, 0.066 mmol) and excess lithium in THF were placed in an NMR tube with C_6D_6 for NMR lock. After ultrasonication, the color of the solution changed to deep red. The ^{119}Sn NMR signal attributable to 9,10-distannaanthracene dianion **3** (-254.9 ppm) with $^3J(^{119}\mathrm{Sn}–^{117}\mathrm{Sn})$ of 559 Hz appeared in upper field than that for **1** (-149.1 ppm in $CDCl_3$). A minor signal ($<1/10$) was observed at -220.0 ppm, possibly due to a conformational or stereoisomer of **3**, the structure of which is still unclear.[11] In ^{13}C NMR, the α-carbon of **3** in the six-membered ring resonated in the characteristic lowfield (171.71 ppm) as observed in arylstannyl anions.[12–14]



Scheme 1.



Scheme 2.

Next, we examined the controlled reduction of **1** using lithium naphthalenide (Scheme 2). After addition of lithium naphthalenide (0.66 M in THF; 0.2 mL, 0.13 mmol, 2.5 equiv.) to a THF (2 mL) solution of **1** (36 mg, 0.05 mmol) at $-80\,^\circ$C, the color of the solution turned to yellow. After the mixture was warmed to room temperature, the residue was chromatographed to give 9,10-distannaanthracene dimer **4**,[15] a tin analog of the anthracene dimer, in 78% yield. The ^{1}H, ^{13}C, and ^{119}Sn NMR signals for **4** have two sets of coupling satellites resulting from an Sn–Sn bond.

The structure of **4** was finally established by X-ray analysis (Figure 1).[16] Because of the symmetrical structures of **4** with respect to the Sn–Sn bond, half of each moiety was refined. The central six-membered ring has a boat conformation and hence the tricylic framework has a butterfly conformation with the dihedral angle C(1)–Sn(1)–Sn(2)–C(7) of 122°, which is the narrowest among those of 9,10-dihydro-9,10-distannaanthracene derivatives.[7] The length of the Sn–Sn bond (2.7836(5) Å) is in the normal range.[17]

The formation of **4** could be reasonably interpreted as the result of the reaction of dianion **3** with the starting **1** (Scheme 3). Alternatively, monoanion **5** may be coupled with each other to give **4**.

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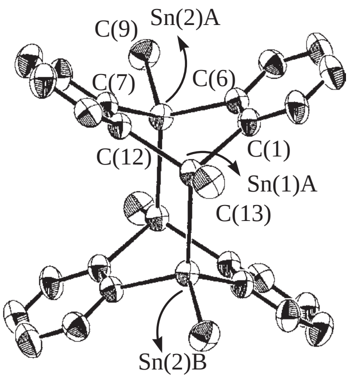
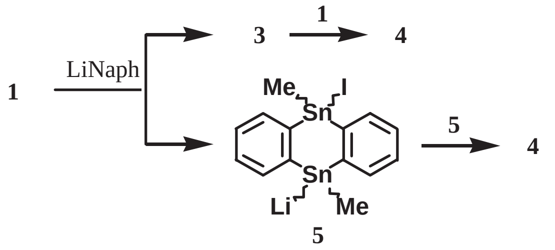


Figure 1. ORTEP drawing of **4** with thermal ellipsoids plots (40% probability for mono-hydrogen atoms). A chloroform molecule was omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)A–Sn(2)B, 2.7836(5), Sn(1)A–C(13), 2.148(6), Sn(1)A–C(1), 2.168(5), Sn(1)A–C(12), 2.155(5); C(1)–Sn(1)A–C(12), 99.9(2).



Scheme 3.

Society for the Promotion of Science, respectively. M. Saito acknowledges a research grant from Toray Science Foundation.

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9 **1**: ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 6H, ^{2}J(Sn–H) = 60 Hz), 7.39–7.42 (m, 4H), 7.65–7.78 (m, 4H). ^{13}C NMR ($CDCl_3$): δ −0.83 (q, ^{1}J(Sn–C) = 382 Hz, major), −0.27 (q, minor), 130.31 (d, J(Sn–C) = 56 Hz), 136.65 (d, J(Sn–C) = 51, 60 Hz), 149.56 (s, J(Sn–C) = 61, 526, 550 Hz). ^{119}Sn NMR: δ −149.1 (^{3}J(^{119}Sn–^{117}Sn) = 1129 Hz, major), −169.0 (minor). Anal. Calcd for $C_{14}H_{14}I_2Sn_2$: C, 24.97; H, 2.10%. Found: C, 24.98; H, 1.83%. The major signal is attributable to *trans*-**1**. The structure of *trans*-**1** was determined by X-ray analysis. The synthesis and structure of **1** will be described elsewhere.

10 The cis/trans ration was estimated by ^{13}C and ^{119}Sn NMR spectroscopy.

11 In the 9,10-dimethyl-9,10-disilaanthracene dianion, one lithium atom bridges with both silicon atoms and the other would interact with aromatic rings by weakly bonding.[4b]

12 **3**: ^{1}H NMR (THF–C_6D_6): δ 0.22 (s, 6H), 6.67–6.69 (m, 4H), 7.55–7.57 (m, 4H). ^{13}C NMR (THF–C_6D_6): δ −3.24 (q), 123.20 (d), 135.37 (d, J(Sn–C) = 32 Hz), 171.72 (s, J(Sn–C) = 79, 173 Hz). ^{119}Sn NMR (THF–C_6D_6): δ −254.9 (^{3}J(^{119}Sn–^{117}Sn) = 559 Hz); ^{7}Li NMR (THF–C_6D_6): δ 0.58.

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15 **4**: mp > 300 °C (recrystallized from hexane–dichloromethane). ^{1}H NMR ($CDCl_3$): δ 0.83 (s, J(Sn–H) = 14, 48 Hz, 12H), 7.02–7.07 (m, 8H), 7.32–7.46 (m, 8H). ^{13}C NMR ($CDCl_3$): δ −10.60 (q, J(Sn–C) = 63, 245, 257 Hz), 127.48 (d, J(Sn–C) = 12, 45 Hz), 134.99 (d, J(Sn–C) = 47, 53 Hz), 151.52 (s, J(Sn–C) = 56, 391, 410 Hz). ^{119}Sn NMR ($CDCl_3$): δ −189.3 (J(^{119}Sn–^{117}Sn) = 45, 730, 3624 Hz). Anal. Calcd for $C_{28}H_{28}Sn_4$: C, 40.07; H, 3.36%. Found: C, 39.99; H, 3.14%.

16 $C_{28}H_{28}Sn_4 \cdot 2(CHCl_3)$, $M_r = 1078.1$, $0.40 \times 0.30 \times 0.05\,mm^3$, monoclinic, $a = 13.4510(5)$, $b = 12.7790(5)$, $c = 11.2990(4)$ Å, $\beta = 108.127(2)°$, $V = 1845.8(1)$ Å^3, $D_{calcd} = 1.936$ Mg m^{-3}, μ(Mo Kα) = 3.128 mm^{-1}, $Z = 2$, space group $P2_1/c$. Data were collected by a Mac Science DIP3000 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SIR[18] and refined by full-matrix least-squares procedures (SHELXL-97)[19] on F^2 for all reflections (3434 reflections) for 194 variable parameters. R_1($_wR_2$) = 0.060 (0.163) for all data, GOF = 1.083. The chloroform molecule in the unit cell was disordered. The occupancies of the disordered chloroform molecules were fixed to be 0.50:0.50 and a hydrogen atom of chloroform was not refined. CCDC-267270 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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