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DECHALCOGENATION OF PENTACHALCOGENADISTANNA-BICYCLO[3.1.1]HEPTANES

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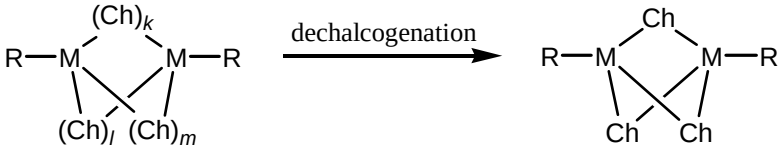
Abstract – Pentathia- and pentaselena-distannabicyclo[3.1.1]heptanes reacted with tributylphosphine to afford tetrathia- and tetraselena- distanna-bicyclo[2.1.1]hexanes, respectively. The novel heterocyclic framework of a tetrathiadistannabicyclo[2.1.1]hexane was demonstrated by X-ray structural analysis. Structures of a series of pentachalcogena and tetrachalcogena derivatives are discussed.

INTRODUCTION

The chemistry of cage-like compounds containing heavier Groups 14 and 16 elements has received considerable attention for over the past decade from the standpoints of their unique structure and reactivity.[1, 2] Among cage-like compounds, some cage compounds such as double decker- and adamantane-type compounds of heavier Groups 14 and 16 elements have been synthesized and characterized.[3-9] Trichalcogenadimetallabicyclo[1.1.1]pentanes, $H_2M_2Ch_3$ (M = Si, Ge, Sn; Ch = O, S, Se, Te), are also of considerable interest as another category of cage-like compounds because short non-bonded distances between the two bridgehead atoms are predicted by theoretical calculations.[10] Although no report on the synthesis of trioxadimetallabicyclo[1.1.1]pentanes, $R_2M_2O_3$ (M = Si, Ge, Sn), has so far appeared, trithia- and triselena-derivatives have been relatively well-investigated. Ando et al. reported the synthesis of trithia- and triselena-dimetallabicyclo[1.1.1]pentanes, $R_2M_2Ch_3$ (R = tris(trimethylsilyl)methyl; M = Si, Ge; Ch = S, Se) **1**, by the dechalcogenation of the corresponding polythia- and polyselena-dimetallabicyclo[k.l.m]alkanes **2** (Scheme 1).[11] With regard to tin analogues, however, neither trichalcogenadistannabicyclo[1.1.1]pentane derivative **1** (M = Sn) nor polychalcogenadistannabicyclo[k.l.m]alkanes **2** (M = Sn) was reported.[12] Very recently, we have reported the first synthesis of novel tin-containing cage-like polychalcogenides, polythia- and

polyselena-distannabicyclo[k.l.m]alkanes **2** by the chalcogenation of the corresponding trihydro- or trichloro-stannanes having a steric encumbered 2,6-bis(2,4,6-triisopropylphenyl)phenyl[13] (denoted as Ar hereafter) and their structural properties.[14] We report herein the synthesis of novel tetrachalcogenadistannabicyclo[2.1.1]hexanes by dechalcogenation of pentachalcogenadistannabicyclo[3.1.1]heptanes. Structures of the polychalcogenadistannabicyclo[k.l.m]alkanes are also discussed.



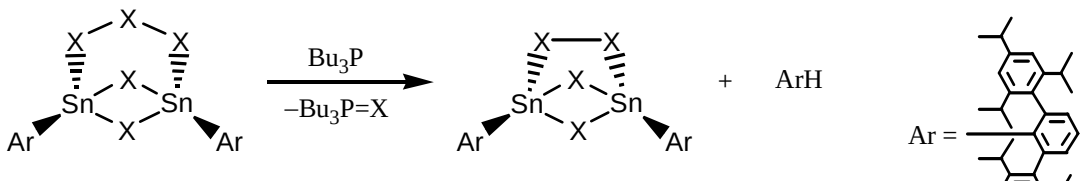
2 **1**

Scheme 1 Dechalcogenation of Polychalcogenadimetallabicyclo[k.l.m]alkanes.

RESULTS AND DISCUSSION

(a) Dechalcogenation of Pentachalcogenadistannabicyclo[3.1.1]heptanes by Tributylphosphine. After treatment of pentathiadistannabicyclo[3.1.1]heptane **3**[14] with excess tributylphosphine as a dechalcogenation reagent,[15] the color of the solution turned from pale yellow to deep yellow and finally to pale yellow. The ^{119}Sn NMR spectrum of the crude product revealed signals at –132.5, –66.8, –3.7 and 35.6 ppm, suggesting the reaction was complicated. When pentathiadistannabicyclo[3.1.1]heptane **3** was treated with an equivalent of tributylphosphine, the ^{119}Sn NMR spectrum of the crude product in C_6D_6 showed signals at 29.8 and 35.9 ppm with an intensity ratio of about 1 : 3, the former of which was assigned to the starting compound **3**. Consequently, reaction of pentathiadistannabicyclo[3.1.1]heptane **3** with 2 equivalents of tributylphosphine proceeded cleanly to afford novel tetrathiadistannabicyclo[2.1.1]hexane **4** in 96% yield, the structure of which was finally confirmed by X-ray structural analysis (Scheme 2).

In contrast, reaction of pentaselenadistannabicyclo[3.1.1]heptane **5** with 2 equivalents of tributylphosphine gave the corresponding tetraselena derivative **6**[14] (58%) together with ArH (19%), although the reason for the formation of ArH through the deselenation of **5** is still unclear.



3: X = S
5: X = Se

4: X = S (96%)
6: X = Se (58%)

– (19%)

Scheme 2 Dechalcogenation of Pentachalcogena Derivatives, **3** and **5**.

(b) X-ray Structural Analysis of Tetrathiadistannabicyclo[2.1.1]hexane 4. Single crystals of tetrathiadistannabicyclo[2.1.1]hexane **4,** suitable for X-ray structural analysis, were obtained by recrystallization from dichloromethane-ethanol. The *ORTEP* drawing and selected bond lengths and angles of **4** are shown in Figure 1. The 1,3,2,4-dithiadistannetane ring of **4** is found to be folded with the dihedral angle between the Sn1–S1–Sn2 and Sn1–S2–Sn2 planes of 133°, smaller than that (148°) found in pentathia derivative **3**,[14] reflecting a disulfide chain shorter than a trisulfide chain in **3**. The lengths of the Sn–S bonds (2.4103(14), 2.4200(15), 2.4304(13), and 2.4312(14) Å) in the four-membered ring of **4** are in the range of those reported for 1,3,2,4-dithiadistannetane rings (2.38-2.51 Å).[16] Each of the two five-membered rings has an envelope conformation and the two tin atoms and the disulfide chain are located almost on the same plane. The non-bonding distances between the two bridgehead tin atoms of **4** of 3.0646(5) Å are longer than the normal tin–tin single bond (2.81 Å),[2] suggesting no significant bonding interaction.

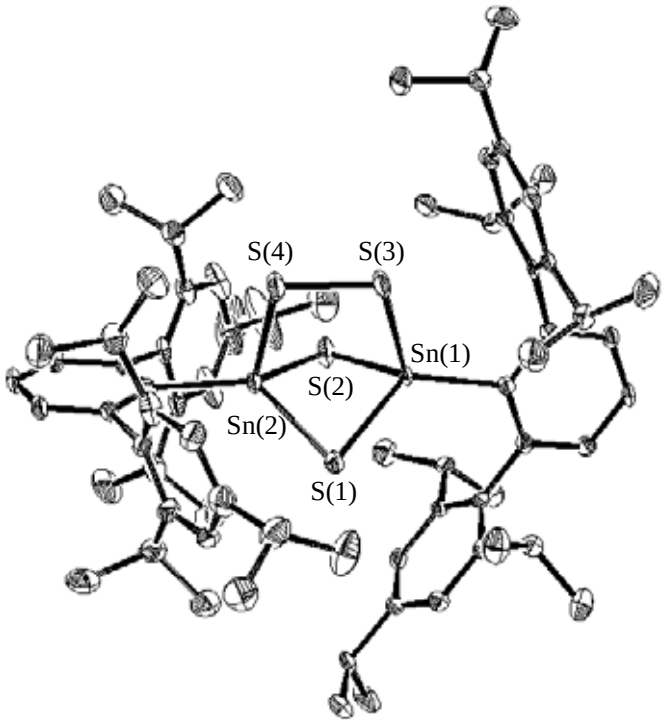


Figure 1 *ORTEP* drawing of **4** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–S(1), 2.4304(13); Sn(1) –S(2), 2.4200(15); Sn(1) –S(3), 2.4333(15); Sn(2) –S(1), 2.4103(14); Sn(2) –S(2), 2.4312(14); Sn(2) –S(4), 2.4193(15); S(3) –S(4), 2.0790(19); S(1) –Sn(1) –S(2), 90.55(5); S(1) –Sn(1) –S(3), 99.59(5); S(1) –Sn(2) –S(2), 90.77(5); S(1) –Sn(2) –S(4), 101.27(6).

(c) Comparison of Structures of Polychalcogenadistannabicyclo[k.l.m]alkanes, 3-6. As a series of penta- and tetra-chalcogena derivatives were successfully synthesized and characterized, comparison of structures of **3**-**6** is discussed. All the 1,3,2,4-dichalcogenadistannetane rings of **3**-**6** are found to be folded with the dihedral angle of 148, 133, 149, 155°, respectively, among which that of **4** is the smallest

because of a shorter Sn–S bond length and smaller numbers of chalcogen atoms, leading to a strained cage structure. The non-bonding distance between the two bridgehead tin atoms of **4** being 3.0646(5) Å is shorter than that of **6** being 3.1453(4) Å, probably due to a tin–sulfur bond shorter than a tin–selenium bond, leading to a small cage-like structure. A similar trend is found in **3** and **5**, that is, the non-bonding distance between the two bridgehead tin atoms of **3** (3.1736(8) Å) is shorter than that of **5** (3.3082(6) Å). Likewise, the non-bonding distance of between the two bridgehead tin atoms **4** is shorter than that of **3** because pentathia derivative **3** has a large cage-like structure.

EXPERIMENTAL

General Procedures: THF and diethyl ether were distilled over sodium/benzophenone. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), and ^{119}Sn NMR (149 MHz) spectra were recorded in $CDCl_3$ and C_6D_6 on a Bruker DRX-400 and a Bruker DPX-400 spectrometer. The ^{n}J(Sn-^{13}C) couplings were observed in the ^{13}C NMR spectra as satellite signals. Preparative gel permeation chromatography (GPC) was carried out on an LC-918 (Japan Analytical Ind. Co., Ltd.) with JAIGEL-1H and -2H columns with $CHCl_3$ as the eluant. Data for the X-ray crystallographic analyses were collected on a Bruker SMART APEX diffractometer with MoKα radiation (λ = 0.71073 Å) and the structures were solved by direct methods. All melting points were determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratry of Molecular Analysis and Life Science Center, Saitama University.

Reaction of Pentathiadistannabicyclo[3.1.1]heptane 3 with Tributylphosphine (excess). Tributylphosphine (0.05 mL, 0.20 mmol) was added to a benzene (1 mL) solution of pentathiadistannabicyclo[3.1.1]heptane **3** (47.5 mg, 0.030 mmol) at rt. After the resulting solution was stirred overnight, volatile substances were removed and the residue was purified by GPC to afford a complex mixture (34.5 mg).

Reaction of Pentathiadistannabicyclo[3.1.1]heptane 3 with Tributylphosphine (1 eq). To pentathiadistannabicyclo[3.1.1]heptane **3** (50.4 mg, 0.037 mmol) was added a benzene solution of tributylphosphine (0.012 M; 0.70 mL, 0.035 mmol) at rt, and then the resulting solution was stirred overnight. After removal of volatile substances, the residue was purified by GPC to afford a mixture (42.1 mg) containing the starting **3** (21%) and tetrathiadistannabicyclo[2.1.1]hexane **4** (64%), the yields of which were estimated by the ^{1}H NMR spectrum.

Reaction of Pentathiadistannabicyclo[3.1.1]heptane 3 with Tributylphosphine (2 eq). To pentathiadistannabicyclo[3.1.1]heptane **3** (69.4 mg, 0.051 mmol) was added a benzene solution of tributylphosphine (0.065 M; 1.5 mL, 0.098 mmol) at rt, and then the resulting solution was stirred overnight. After removal of volatile substances, the residue was purified by GPC to afford

1,3-bis[2,6-bis(2,4,6-triisopropylphenyl)phenyl]-2,4,5,6-tetrathia-1,3-distannabicyclo[2.1.1]hexane (**4**) (65.7 mg, 96%). **4**: mp 227-229 °C (recrystallized from CH_2Cl_2 - EtOH). ^{1}H NMR ($CDCl_3$): δ 0.97 (d, *J* = 7 Hz, 24H), 1.16 (d, *J* = 7 Hz, 24H), 1.25 (d, *J* = 7 Hz, 24H), 2.49 (sept, *J* = 7 Hz, 8H), 2.85 (sept, *J* = 7 Hz, 4H), 6.92 (s, 8H), 7.22 (d, *J* = 8 Hz, 4H), 7.43 (t, *J* = 8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 23.11 (q), 23.92 (q), 25.80 (q), 30.74 (d), 34.22 (d, *J*(C-Sn) = 29 Hz), 121.30 (d), 129.43 (d), 130.16 (d, *J*(C-Sn) = 72 Hz), 135.73 (s, *J*(C-Sn) = 58 Hz), 143.88 (s), 146.57 (s), 147.57 (s), 149.14 (s); ^{119}Sn NMR ($CDCl_3$): δ 34.53 (*J*(Sn-Sn) = 710 Hz); ^{119}Sn NMR (C_6D_6): δ 35.62 (*J*(Sn-Sn) = 703 Hz). Anal. Calcd for $C_{72}H_{98}S_4Sn_2$: C, 65.06; H, 7.43. Found: C, 64.53; H, 7.46.

Reaction of Pentaselenadistannabicyclo[3.1.1]heptane 5 with Tributylphosphine (2 eq). To pentaselenadistannabicyclo[3.1.1]heptane **5** (47.5 mg, 0.030 mmol) was added a benzene solution of tributylphosphine (0.066 M; 0.90 mL, 0.059 mmol) at rt, and then the resulting solution was stirred overnight. After removal of volatile substances, the residue was purified by GPC to afford 1,3-bis[2,6-bis(2,4,6-triisopropylphenyl)phenyl]-2,4,5,6-tetraselena-1,3-distannabicyclo[2.1.1]hexane (**6**)[14] (26.1 mg, 58%) and 1,3-bis(2,4,6-triisopropylphenyl)benzene (ArH) (2.8 mg, 19%).

Crystallographic data for 4. 0.25 X 0.20 X 0.10 mm, triclinic, *a* = 13.4445(9), *b* = 13.9320(9), *c* = 18.9624(13) Å, α = 83.850(2), *β* = 79.500(2), *γ* = 80.002(2)°, *V* = 3428.8(4) Å^3, *T* = 103 K, ρ_{calc} = 1.288 g cm^{-3}, *Z* = 2, space group *P*-1, R_1 = 0.055 ($I > 2\sigma(I)$, 9817 reflections), wR_2 = 0.141 (for all reflections) for 12323 reflections and 728 parameters. GOF = 1.037. CCDC-679360 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: (internet.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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