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$R_2Ge{=}SnR'_2$ and $RR'Ge{=}SnRR'$ ($R = SiMe^tBu_2$, $R' = 2,4,6\text{-}{}^iPr_3C_6H_2$): The New Stable Germastannenes

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1,1-Bis(di-*tert*-butylmethylsilyl)-2,2-bis(2,4,6-triisopropylphenyl)-1-germa-2-stannaethene (**2**), containing a >Ge═Sn< double bond, was prepared as highly air- and moisture-sensitive deep violet crystals by the coupling reaction of bis(di-*tert*-butylmethylsilyl)dilithiogermane with dichlorobis(2,4,6-triisopropylphenyl)stannane in THF. The germastannene **2** easily undergoes thermal isomerization to form the corresponding symmetrically substituted isomer (*E*)-1,2-bis(di-*tert*-butylmethylsilyl)-1,2-bis(2,4,6-triisopropylphenyl)-1-germa-2-stannaethene (**3**) by the dyotropic 1,2-shifts of the silyl and aryl substituents.

Introduction

The chemistry of unsaturated compounds containing group 14 elements heavier than carbon is a recent subject of considerable interest.[1] Among the variety of stable multiply bonded derivatives of main-group elements, those of group 14 occupy a special, very important position, since they represent the direct heavier alkene analogues. The structural and chemical aspects of such dimetallaalkenes (dimetallenes) M═M′ (M, M′ = heavier group 14 elements) are of particular interest, because they are known to differ greatly from those of alkenes in organic chemistry, contributing a new insight to bonding theory for the elements heavier than carbon. Despite such evident interest, until now there has been very limited experimental success in the synthesis of such stable heteronuclear dimetallenes M═M′, in sharp contrast to homonuclear congeners M═M, whose chemistry has been greatly developed during the last two decades.[1] Thus, the first structurally authenticated heteronuclear double bond (stable silagermene >Si═Ge<) was reported by us in 2000.[2] Very recently we have succeeded in the synthesis and structural identification of another heteronuclear dimetallene—the first stable silastannene, >Si═Sn<.[3] As for germastannenes >Ge═Sn<, only one example has been previously reported by Escudié and co-workers, $(2,4,6\text{-}Me_3C_6H_2)_2Ge{=}Sn(2,4,6\text{-}{}^iPr_3C_6H_2)_2$, which was characterized by a low-temperature ^{119}Sn NMR spectrum and trapping reactions, but was not isolated due to its thermal instability, resulting in the transformation to a distannagermirane at room temperature.[4] Quite recently, during the preparation of our paper, the first example of germastannene, which is stable in the solid state and gradually decomposes in solution, $(2,4,6\text{-}{}^iPr_3C_6H_2)_2Ge{=}Sn(2,4,6\text{-}{}^iPr_3C_6H_2)_2$, was reported by Weidenbruch.[5]

We report here on the synthesis of another representative of stable germastannenes stable in both the solid state and solution, which was prepared by the coupling reaction of 1,1-dilithiogermane with a dichlorostannane derivative, utilizing an advantage of 1,1-dilithiogermanes as an extremely useful building block for the preparation of a variety of doubly bonded compounds of the type >Si═Ge< and >Ge═Ge<.[6]

Results and Discussion

Bis(di-*tert*-butylmethylsilyl)dilithiogermane (**1**), prepared by the reaction of 1,1-bis(di-*tert*-butylmethylsilyl)-2,3-bis(trimethylsilyl)-1-germacycloprop-2-ene with an excess amount of Li in dry THF/Et_2O,[6] cleanly reacted with dichlorobis(2,4,6-triisopropylphenyl)stannane[7] in THF at room temperature to form the corresponding coupling product 1,1-bis(di-*tert*-butylmethylsilyl)-2,2-bis(2,4,6-triisopropylphenyl)-1-germa-2-stannaethene (**2**), as a violet solid in 68% yield (Scheme 1).

Germastannene **2** represents a rare example of isolated compound with a >Ge═Sn< double bond, and it was characterized by all spectroscopic data. Due to the hindered rotation around the Sn−C(Tip) bonds, the Me

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[1] For recent reviews on metallenes and dimetallenes of group 14 elements, see: (a) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J. *Coord. Chem. Rev.* **1994**, *130*, 427. (b) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828. (c) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (d) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (e) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 1, Chapter 5. (f) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373. (g) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (h) Escudié, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113. (i) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, Chapter 5. (j) Tokitoh, N.; Okazaki, R. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 2002; Vol. 2, Part 1, Chapter 13. (k) Lee, V. Ya.; Sekiguchi, A. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; Wiley: Chichester, U.K., 2002; Vol. 2, Part 1, Chapter 14. (l) Sekiguchi, A.; Lee, V. Ya. *Chem. Rev.*, in press.

[2] (a) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2000**, *122*, 12604. For other stable silagermenes, see: (b) Lee, V. Ya.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 9034. (c) Ichinohe, M.; Arai, Y.; Sekiguchi, A.; Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 4141. For a silagermene stable only at low temperature, see: (d) Baines, K. M.; Cooke, J. A. *Organometallics* **1991**, *10*, 3419.

[3] Sekiguchi, A.; Izumi, R.; Lee, V. Ya.; Ichinohe, M. *J. Am. Chem. Soc.* **2002**, *124*, 14822.

[4] Chaubon, M.-A.; Escudié, J.; Ranaivonjatovo, H.; Satgé, J. *J. Chem. Soc., Chem. Commun.* **1996**, 2621.

[5] Schäfer, A.; Saak, W.; Weidenbruch, M. *Organometallics* **2003**, *22*, 215.

[6] Sekiguchi, A.; Izumi, R.; Ihara, S.; Ichinohe, M.; Lee, V. Ya. *Angew. Chem., Int. Ed.* **2002**, *41*, 1598.

[7] Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390.

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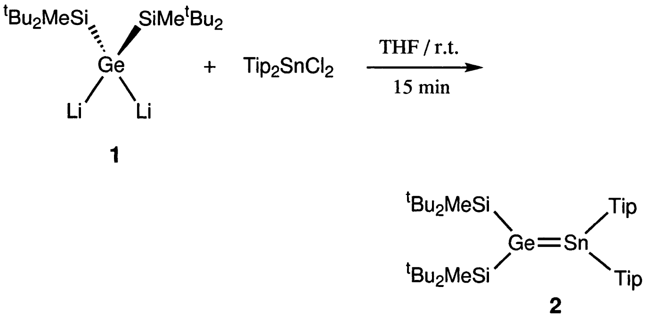
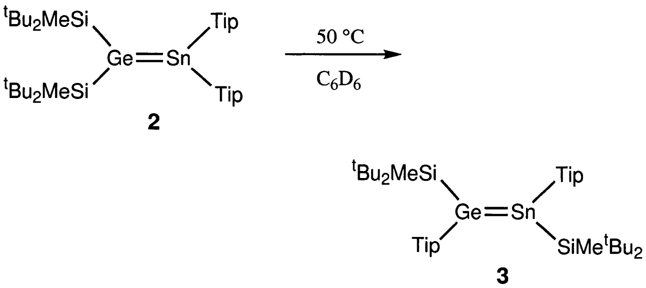
Scheme 1



Tip = 2,4,6-triisopropylphenyl

Scheme 2



groups of isopropyl substituents in ortho positions of each aromatic ring became nonequivalent, resulting in the appearance of three doublet signals of Me groups in the ratio 1:1:1. As expected, the sp^2 Sn atom in **2** is greatly deshielded, appearing at +525.1 ppm in the ^{119}Sn NMR spectrum.[8] In the UV−vis spectrum of **2** there are two distinct absorption bands, of which the longer wavelength band, 551 nm, was attributed to a $\pi-\pi^*$ transition.

Most importantly, the unsymmetrically substituted germastannene **2**, being a room temperature stable compound, easily and quantitatively undergoes isomerization on gentle heating to form the corresponding symmetrically substituted isomer (*E*)-1,2-bis(di-*tert*-butylmethylsilyl)-1,2-bis(2,4,6-triisopropylphenyl)-1-germa-2-stannaethene (**3**) (Scheme 2).[9]

Such an isomerization may proceed in two different ways: the first one is a concerted pathway, which involves the simultaneous (*dyotropic*) 1,2-shifts of silyl and aryl groups from Ge to Sn and from Sn to Ge atoms, respectively, through the initial twisting of the Ge═Sn double bond followed by a hypothetical bicyclobutane-type transition state to form the thermodynamically stable *E* isomer **3** (pathway A in Scheme 3).[10] Alternatively, one can imagine another, stepwise, mechanism involving initial 1,2-silyl (or -aryl) group migration to form stannylgermylene (or germylstannylene) intermediates[11] followed by the second 1,2-migration of the aryl (or silyl) group to give the final *E* isomer **3** (pathway B in Scheme 3).

To distinguish between these two possibilities, we performed kinetic measurements of the isomerization of **2** to **3**. The activation parameters were determined by monitoring of the isomerization by ^{1}H NMR spectroscopy using Arrhenius and Eyring equations: E_a = 22 kcal mol^{-1}, $\Delta H^\ddagger$ = 22 kcal mol^{-1}, and $\Delta S^\ddagger = -12$ cal K^{-1} mol^{-1}. The relatively low value of $\Delta H^\ddagger$ and the negative value of $\Delta S^\ddagger$ are more consistent with the concerted rather than the stepwise mechanism, with the more ordered and rigid transition state lacking the high degree of freedom typical for linear intermediates in pathway B.[12] Moreover, such intermediate germylene (or stannylene) species in pathway B would lead to a nonstereospecific isomerization to give a mixture of *E* and *Z* isomers of **3**, which is not consistent with our experimental data (formation of only one *E* isomer of **3**). From all these kinetic data it seems more likely that the isomerization from **2** to **3** proceeds through the dyotropic migration of silyl and aryl groups (pathway A) rather than through the stepwise mechanism involving the intermediate formation of carbene-like species (pathway B). Indeed, we were not able to observe any trapping products when the isomerization was carried out in the presence of excess Et_3SiH, which is well-known to be an effective trapping reagent for both germylenes and stannylenes.

The isomerization product **3** was isolated in a pure form as red crystals and was also fully characterized by spectral data. The doubly bonded Sn atom in **3** resonates at a higher field (+373.4 ppm) than that in **2** (+525.1 ppm), due to the different environment around it: **3** has one electron-withdrawing aryl group and one electron-donating silyl substituent, whereas **2** has two aryl groups. In the UV spectrum of **3** there is a blue shift of the longest wavelength absorption band in comparison with that of **2** (465 vs 551 nm). The constitution of **3** was proved by X-ray diffraction analysis, which confirmed its symmetrical *E* isomer structure. Although the accurate determination of bond lengths and angles was impossible due to disorder in the positions of the doubly bonded Ge and Sn atoms, we were able to determine the geometry of the double-bond system. As one might expect, the Ge═Sn double bond has a trans-bent configuration with bending angles of ca. 28°.

The Ge═Sn double bond exhibits the high reactivity typical for other heavy alkenes. Thus, **2** easily reacts with propylene sulfide to form finally the four-membered 2,2-bis(di-*tert*-butylmethylsilyl)-4,4-bis(2,4,6-triisopropylphenyl)-1,3-dithia-2-germa-4-stannacyclobutane (**5**), isolated by GPC as colorless crystals in 37% yield (Scheme 4). The formation of **5** can be rationalized as a result of the initial [2 + 1] cycloaddition of sulfur across the Ge═Sn double bond in **2** to form the three-membered-ring compound **4**, followed by insertion of the second sulfur atom into the Ge−Sn single bond of **4** to yield the final product **5**.[13] The structure of **5** was determined by X-ray crystallography, which showed a

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[8] The typical ^{119}Sn NMR resonances of the doubly bonded Sn atoms lie in the region above +400 ppm.[1c]

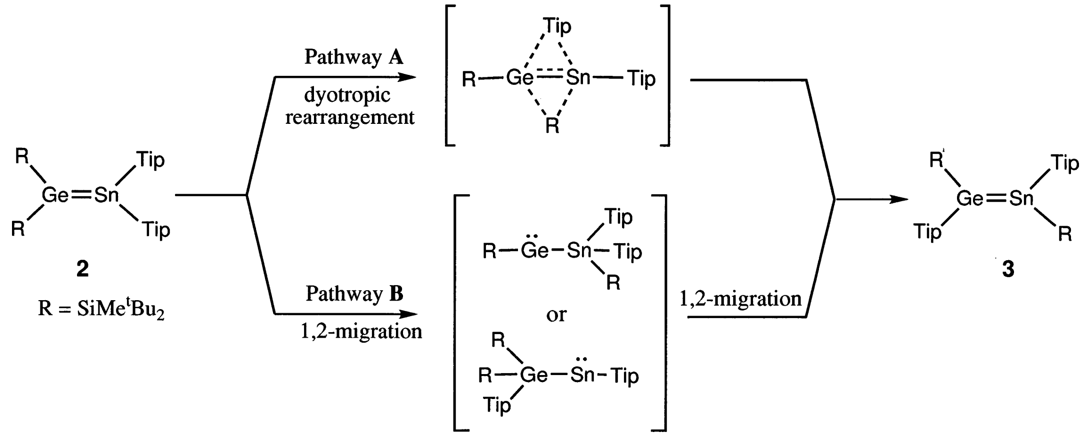
[9] This type of isomerization was reported for the first time by West in the case of 1,1-bis(2,6-dimethylphenyl)-2,2-bis(2,4,6-trimethylphenyl)disilene: Yokelson, H. B.; Maxka, J.; Siegel, D. A.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 4239.

[10] We did not observe the formation of the *Z* isomer of **3**, which is probably thermodynamically less favorable due to steric reasons.

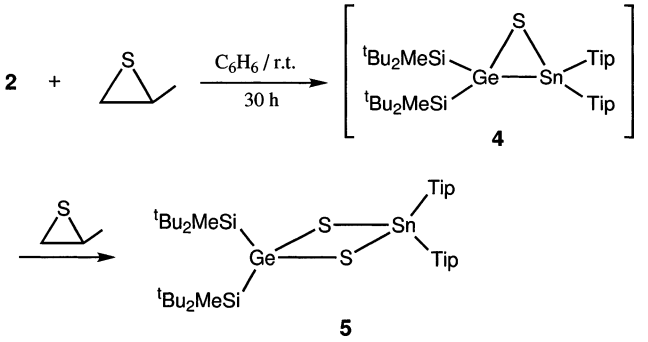
[11] Examples of stable aryl(germyl)-substituted germylene and stannylene were recently reported by Kira: Setaka, W.; Sakamoto, K.; Kira, M.; Power, P. P. *Organometallics* **2001**, *20*, 4460.

[12] For the isomerization of 1,1-bis(2,6-dimethylphenyl)-2,2-bis(2,4,6-trimethylphenyl)disilene to 1,2-bis(2,6-dimethylphenyl)-1,2-bis(2,4,6-trimethylphenyl)disilene, the following activation parameters were reported: $\Delta H^\ddagger$ = 15 kcal mol^{-1} and $\Delta S^\ddagger = -36$ cal K^{-1} mol^{-1}, which was explained by the concerted intramolecular migration of the two aryl groups across the silicon−silicon bond: Yokelson, H. B.; Siegel, D. A.; Millevolte, A. J.; Maxka, J.; West, R. *Organometallics* **1990**, *9*, 1005.

Scheme 3



Scheme 4



planar four-membered ring consisting of Ge, Sn, and two S atoms in the sequence Ge−S−Sn−S (Figure 1).[14]

Experimental Section

General Procedures. All experiments were performed using high-vacuum-line techniques or under an argon atmosphere in an MBraun MB 150B-G glovebox. All solvents were predried over sodium benzophenone ketyl and finally dried and degassed over a potassium mirror under vacuum prior to use. NMR spectra were recorded on Bruker AC-300FT (^{1}H NMR at 300.1 MHz; ^{13}C NMR at 75.5 MHz; ^{29}Si NMR at 59.6 MHz; ^{119}Sn NMR at 149.3 MHz) and Bruker ARX-400FT (^{1}H NMR at 400.2 MHz; ^{13}C NMR at 100.6 MHz; ^{29}Si NMR at 79.5 MHz; ^{119}Sn NMR at 111.8 MHz) NMR spectrometers. Direct mass spectra (EI) were obtained on a JEOL JMS SX-102 instrument. UV spectra were recorded on a Shimadzu UV-3150 UV−vis spectrophotometer in hexane solution. GPC separation was carried out with an LC-08 liquid chromatograph (Japan Analytical Industry Co., Ltd.). Elemental analysis was performed at the Analytical Center of Tohoku University (Sendai, Japan).

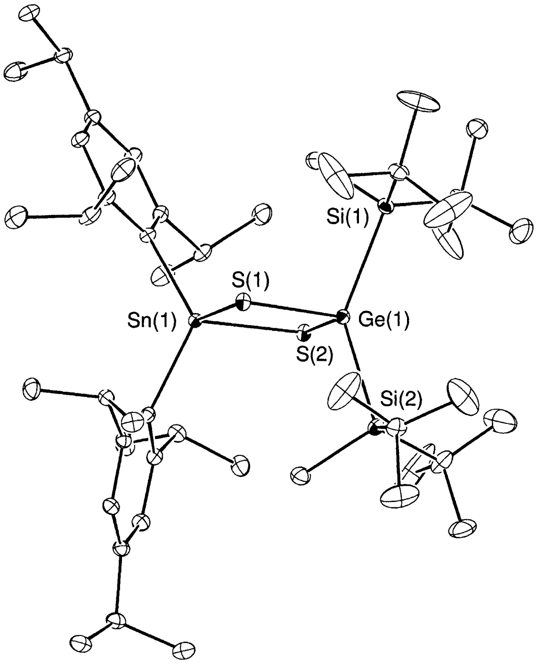


Figure 1. Molecular structure of **5** with thermal ellipsoids drawn at the 30% probability level (hydrogen atoms are omitted for clarity). Selected bond distances (Å): Sn(1)−S(1) = 2.4303(7), Sn(1)−S(2) = 2.4324(7), Ge(1)−S(1) = 2.2929(7), Ge(1)−S(2) = 2.2854(7). Selected bond angles (deg): S(1)−Sn(1)−S(2) = 88.38(2), S(2)−Ge(1)−S(1) = 95.52(2), Ge(1)−S(1)−Sn(1) = 87.97(2), Ge(1)−S(2)−Sn(1) = 88.09(2).

1,1-Bis(di-*tert*-butylmethylsilyl)-2,2-bis(2,4,6-triisopropylphenyl)-1-germa-2-stannaethene (2). Bis(di-*tert*-butylmethylsilyl)dilithiogermane (**1**) was prepared from 1,1-bis(di-*tert*-butylmethylsilyl)-2,3-bis(trimethylsilyl)-1-germacycloprop-2-ene (54 mg, 0.10 mmol) and lithium (15 mg, 2.20 mmol) in mixed solvent (diethyl ether and THF) at room temperature.[6] Compound **1** was reacted with dichlorobis(2,4,6-triisopropylphenyl)stannane (40 mg, 0.07 mmol) in dry THF (1.5 mL) for 15 min at room temperature to form a violet solution. After evaporation of the solvent, dry benzene (0.5 mL) was added to the residue. After filtration of inorganic salts, benzene was evaporated to give germastannene **2** as a violet solid in 68% yield. ^{1}H NMR (C_6D_6, δ): 0.33 (s, 6 H, CH_3), 1.03 (d, J = 6.6 Hz, 12 H, (CH_3)$_2$CH(Tip)), 1.15 (d, J = 6.6 Hz, 12 H, (CH_3)$_2$CH(Tip)), 1.25 (s, 36 H, C(CH_3)$_3$), 1.40 (d, J = 6.6 Hz, 12 H, (CH_3)$_2$CH(Tip)), 2.76 (sept, J = 6.6 Hz, 2 H, (CH$_3$)$_2$CH(Tip)), 3.74 (sept, J = 6.6 Hz, 4 H, (CH$_3$)$_2$CH(Tip)), 7.09 (s, 4 H, Ar H). ^{13}C NMR (C_6D_6, δ) −2.4 (CH$_3$), 22.5 (C(CH$_3$)$_3$), 24.1 ((CH$_3$)$_2$-

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[13] The formation of four-membered 1,3-dioxa-2,4-disilacyclobutanes (or -digermacyclobutanes) in the reaction of disilenes (or digermenes) with oxygen is a well-documented motif,[1a,d] although in the case of sulfur only the primarily formed three-membered thiadisiliranes (or -digermiranes) were reported.[1c,d] Thus, compound **5** represents the first example of an adduct of heavy alkenes with 2 equiv of sulfur. The only examples related to **5** were reported in a different way by dimerization of silanethione (or germanethione and germaneselone): (a) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Goto, M. *J. Am. Chem. Soc.* **1998**, *120*, 11096. (b) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1999**, *121*, 8811.

[14] Single crystals of **5** suitable for X-ray analysis were grown from the saturated benzene solution. Crystal data for **5**·C_6H_6 at 120 K: molecular formula $C_{54}H_{94}GeS_2Si_2Sn$, MW = 1054.87, triclinic, space group $P\bar{1}$, a = 11.8000(4) Å, b = 14.3190(4) Å, c = 17.4830(6) Å, α = 84.664(2)°, β = 83.774(2)°, γ = 78.712(2)°, V = 2871.96(16) Å^3, Z = 2, D_{calcd} = 1.220 g cm^{-3}. The final R factor was 0.0425 (R_w = 0.1122 for all data) for 11 312 reflections with $I > 2\sigma(I)$. GOF = 1.028.

CH(Tip)), 25.8 ((CH$_3$)$_2$CH(Tip)), 30.7 (C(CH$_3$)$_3$), 34.6 ((CH$_3$)$_2$$C$H-(Tip)), 39.6 ((CH$_3$)$_2$$C$H(Tip)), 122.6 (Ar C), 149.9 (Ar C), 154.1 (Ar C), 156.4 (Ar C). ^{29}Si NMR (C_6D_6, δ): 35.4. ^{119}Sn NMR (C_6D_6, δ): 525.1. UV−vis (hexane; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 298 (11 300), 551 (5600).

(*E*)-1,2-Bis(di-*tert*-butylmethylsilyl)-1,2-bis(2,4,6-triisopropylphenyl)-1-germa-2-stannaethene (3). Heating of germastannene **2** (77 mg, 0.078 mmol) in deuteriobenzene (0.5 mL) at 50 °C for 40 h resulted in the formation of isomeric compound **3**, which was quantitatively isolated as red crystals. Mp: 179−180 °C. ^{1}H NMR (C_6D_6, δ): 0.04 (s, 3 H, CH_3), 0.24 (s, 3 H, CH_3), 1.00 (s, 18 H, C(CH_3)$_3$), 1.11 (s, 18 H, C(CH_3)$_3$), 1.24 (d, J = 6.9 Hz, 6 H, (CH_3)$_2$CH(Tip)), 1.25 (d, J = 6.9 Hz, 6 H, (CH_3)$_2$CH(Tip)), 1.40 (d, J = 6.9 Hz, 12 H, (CH_3)$_2$CH-(Tip)), 1.535 (d, J = 6.6 Hz, 6 H, (CH_3)$_2$CH(Tip)), 1.542 (d, J = 6.9 Hz, 6 H, (CH_3)$_2$CH(Tip)), 2.81 (sept., J = 6.9 Hz, 2 H, (CH$_3$)$_2$CH(Tip)), 3.55 (sept, J = 6.6 Hz, 2 H, (CH$_3$)$_2$CH(Tip)), 3.82 (sept, J = 6.6 Hz, 2 H, (CH$_3$)$_2$CH(Tip)), 7.10 (s, 2 H, Ar H), 7.17 (s, 2 H, Ar H). ^{13}C NMR (C_6D_6, δ): −4.8 (CH$_3$), −3.1 (CH$_3$), 22.5 (C(CH$_3$)$_3$), 23.5 (C(CH$_3$)$_3$), 24.3 ((CH$_3$)$_2$CH(Tip)), 24.7 ((CH$_3$)$_2$CH(Tip)), 25.2 ((CH$_3$)$_2$CH(Tip)), 25.5 ((CH$_3$)$_2$CH-(Tip)), 26.2 ((CH$_3$)$_2$CH(Tip)), 30.2 (C(CH$_3$)$_3$), 31.5 ((CH$_3$)$_2$$C$H-(Tip)), 34.5 ((CH$_3$)$_2$$C$H(Tip)), 34.7 ((CH$_3$)$_2$$C$H(Tip)), 36.9 ((CH$_3$)$_2$-$C$H(Tip)), 40.7 ((CH$_3$)$_2$$C$H(Tip)), 121.7 (Ar C), 121.8 (Ar C), 143.5 (Ar C), 144.9 (Ar C), 148.6 (Ar C), 149.4 (Ar C), 153.3 (Ar C), 154.9 (Ar C). ^{29}Si NMR (C_6D_6, δ): 34.8, 46.4. ^{119}Sn NMR (C_6D_6, δ): 373.4. UV−vis (hexane; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 241 (24 100), 261 (19 500), 310 sh (2900), 465 (6200). Anal. Calcd for $C_{48}H_{88}GeSi_2Sn$: C, 63.17; H, 9.72. Found: C, 63.04; H, 9.58.

2,2-Bis(di-*tert*-butylmethylsilyl)-4,4-bis(2,4,6-triisopropylphenyl)-1,3-dithia-2-germa-4-stannacyclobutane (5). An excess amount of dry propylene sulfide (1 mL) was added to a solution of germastannene **2** (77 mg, 0.078 mmol) in benzene (1 mL). After it was stirred at room temperature for 30 h, the reaction mixture was evaporated and the residue was purified by GPC to give product **5** (28 mg, 37%) as colorless crystals. Mp: 63−65 °C. ^{1}H NMR (C_6D_6, δ): 0.45 (s, 6 H, CH_3), 1.22 (s, 36 H, C(CH_3)$_3$), 1.24 (d, J = 6.9 Hz, 12 H, (CH_3)$_2$CH-(Tip)), 1.48 (d, J = 6.9 Hz, 24 H, (CH_3)$_2$CH(Tip)), 2.81 (sept, J = 6.9 Hz, 2 H, (CH$_3$)$_2$CH(Tip)), 3.57 (sept, J = 6.6 Hz, 4 H (CH$_3$)$_2$CH(Tip)), 7.18 (s, 4 H, Ar H). ^{13}C NMR (C_6D_6, δ): −5.5 (CH$_3$), 23.6 (C(CH$_3$)$_3$), 24.1 ((CH$_3$)$_2$CH(Tip)), 26.5 ((CH$_3$)$_2$CH-(Tip)), 30.3 (C(CH$_3$)$_3$), 34.5 ((CH$_3$)$_2$$C$H(Tip)), 37.9 ((CH$_3$)$_2$$C$H-(Tip)), 123.1 (Ar C), 142.6 (Ar C), 150.9 (Ar C), 155.9 (Ar C). ^{29}Si NMR (C_6D_6, δ): 19.6. ^{119}Sn NMR (C_6D_6, δ): −48.5. Anal. Calcd for $C_{48}H_{88}GeS_2Si_2Sn$: C, 59.02; H, 9.08. Found: C, 59.19; H, 9.33.

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Supporting Information Available: Tables giving details of the X-ray structure determination, fractional atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles and figures giving thermal ellipsoid plots for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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