

Stepwise Oxidation of the Stannole Dianion

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This paper is dedicated to Professor Renji Okazaki on the occasion of his 70th birthday

Abstract: Tin oxidation of stannole dianion **1** with 1.3 equivalents of oxygen gave terstannole-1,3-dianion **3**. The non-aromatic nature of **3** was confirmed by X-ray crystallographic analysis. Treatment of **1** with 1,2-dibromoethane (3 equiv) gave poly(1,1-stan-

nole) **4**, the formation of which was proven by reduction of **4** with lithium to revert to the starting dianion **1**. Re-

Keywords: anions • oxidation • tin • UV/Vis spectroscopy

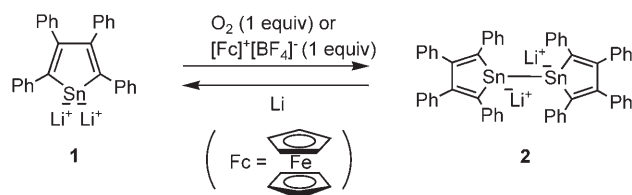
action of **1** with 1,2-dibromoethane (3 equiv) in the presence of phenyllithium gave phenyl-capped ter(1,1-stannole) **7**. The electronic absorption spectra of newly obtained stannoles were also measured.

Introduction

The group 14 metallole dianions have received considerable interest from both synthetic and theoretical points of view as heavier congeners of the cyclopentadienyl anion, and play an important role in organic and organometallic chemistry.^[1] The structure of silole and germole dianions has been discussed extensively, and their aromatic character is well established.^[2,3] The reactions of these dianions, however, have been mostly limited to those with simple electrophiles,^[2,4] which were often used as trapping reagents, except a few reports on unique reactions by West et al.^[5] as well as coupling reactions for the formation of oligo- or poly(1,1-metallole)s.^[6]

Very recently, we reported the synthesis of the first stannole dianion and showed that it was aromatic by NMR analysis, X-ray structural analysis, and theoretical calculations.^[7] We have also reported the oxidation of the stannole anion to lead to the formation of a tin–tin bond, which is a novel useful method for the synthesis of bi(1,1-stannole)s.^[7b,8] The results prompted us to investigate on the oxidation of stannole dianion **1** for the formation of oligo- or poly(1,1-stannole)s. The group 14 oligo- or polymetallanes exhibit unique optical and electronic properties resulting from σ -conjugation

along the metal backbone chain.^[9] On the other hand, the group 14 metalloles display low reduction potentials and a low-lying LUMO energy level (attributed to σ^* – π^* conjugation between the σ^* orbital of the group 14 metal moiety and the π^* orbital of the butadiene moiety) that lead to unusual electronic properties.^[10] As a result of these properties, oligo- and poly(1,1-metallole)s are being applied gradually as electron-transporting materials in organic LEDs^[6c] and as chemical sensors.^[6f,11] Although oxidation of 1,1-dianions of group 14 metalloles might be useful as a novel, straightforward method for the synthesis of oligo- and poly(1,1-metallole)s that have metal–metal bonds, no study of systematic, stepwise oxidation has ever been demonstrated. Very recently, we reported our preliminary results of the synthesis of bistannole-1,2-dianion **2** by reaction of stannole dianion **1** with an equivalent of oxygen and the reversible redox behavior between stannole dianion **1** and bistannole-1,2-dianion **2** (Scheme 1).^[12] We report herein the oxidation of stannole dianion **1** to a novel terstannole-1,3-dianion. Stepwise formation of oligo- and poly(1,1-stannole)s by oxidation of stannole dianion **1** is also described.

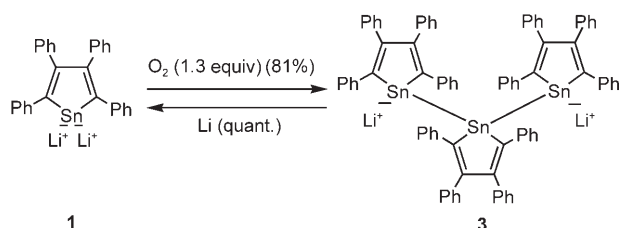


Scheme 1. Reversible redox behavior between 1,1-dianion **1** and 1,2-dianion **2**.

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Results and Discussion

Oxidation of stannole dianion to terstannole-1,3-dianion **3 and its structure:** The reaction of **1** with 1.3 equivalents of oxygen in THF yielded a different product. Upon oxidation of **1** with 1.3 equivalents of oxygen in THF at room temperature, the color of the reaction solution changed from bright red to dark violet and finally to bright red. The first terstannole-1,3-dianion **3** was isolated as a deep-red powder in 81% yield (Scheme 2). In the ^{119}Sn NMR spectrum, two sig-



Scheme 2. Synthesis of 1,3-dianion **3** from 1,1-dianion **1** and its reduction to 1,1-dianion **1**.

nals at $\delta = -61.7$ and -145.1 ppm were observed with an intensity ratio of 1:2, resulting from the single central and two terminal tin atoms, respectively. The signal attributed to the central tin atom was accompanied by a pair of satellite signals, $^1J(^{119}\text{Sn}-^{119}\text{Sn}, ^{117}\text{Sn})$, owing to the terminal Sn nuclei, whereas that of the terminal tin atom was accompanied by two sets of satellite signals, $^1J(^{119}\text{Sn}-^{119}\text{Sn}, ^{117}\text{Sn})$ and $^2J(^{119}\text{Sn}-^{117}\text{Sn})$, owing to the central and another terminal Sn nuclei. In the ^{13}C NMR spectrum, a characteristic lowfield signal assignable to the α -carbon atom in **3** was observed at $\delta = 178.89$ ppm with two tin-carbon coupling constants of $^1J(\text{C}-\text{Sn}) = 158$ Hz and $^2J(\text{C}-\text{Sn}) = 39$ Hz, as was observed in bistannole-1,2-dianion **2**. The ^7Li signals were observed at $\delta = -0.60$, and 1.67 ppm (broad), suggesting that the lithium cations were in an environment similar to that of common organolithium compounds in solution.^[13] Contrary to bistannole-1,2-dianion **2**, the oxidation of **1** with 1.3 equivalents of ferrocenium tetrafluoroborate in THF gave a complex mixture without the formation of terstannole-1,3-dianion **3**.

The bright-red crystals of terstannole-1,3-dianion **3** suitable for X-ray analysis were obtained by recrystallization from THF/hexane in the presence of 12-crown-4 at -33°C in a glovebox. As compound **3** has a plane of symmetry perpendicular to the center of the middle stannole ring, a half moiety of the molecule was refined. Compound **3** has 1:1 disordered two molecules, one of which is shown in Figure 1. The long Sn-Li distance (≈ 5.7 Å) indicates the absence of significant bonding interaction between the tin and the lithium atoms, as was observed in bistannole-1,2-dianion **2**. The C-C bond lengths within the middle stannole ring (the bond distances of C(5)-C(6) and C(6)-C(6)* are 1.356(4) and 1.498(7) Å, respectively) are similar to these of typical stannoles.^[14] Bond alternation in the C-C bonds in the five-membered terminal stannole rings is observed (the

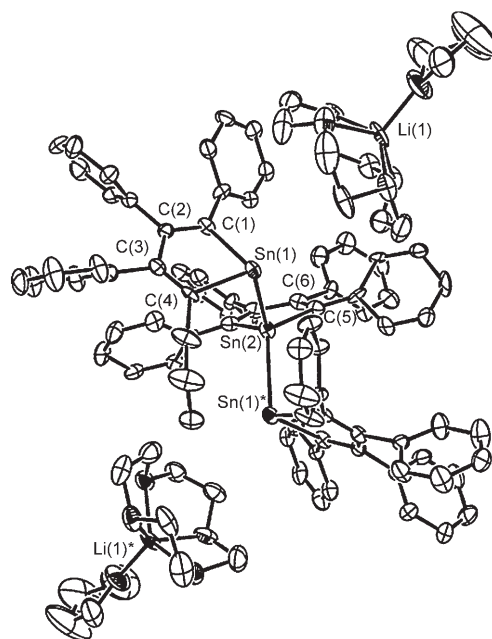
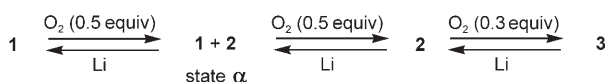


Figure 1. ORTEP drawing of **3** with thermal ellipsoid plots (40% probability for non-hydrogen atoms). All hydrogen atoms and another disordered molecule are omitted for clarity.

bond distances of C(1)-C(2), C(2)-C(3) and C(3)-C(4) are 1.36(4), 1.473(4) and 1.378(4) Å, respectively), indicating that the terminal stannole rings have considerable diene character and the negative charges of 1,3-dianion **3** would localize on both terminal tin atoms, as seen previously in other group 14 metallolene anions.^[12,15] Pyramidalization at the tin center is clearly evident from the angle between the C_4Sn plane and the Sn-Sn bond (106°). The angle between the terminal stannole ring and the middle stannole rings through the Sn-Sn bond (80°) indicates that the three stannole rings are arranged in an all-gauche conformation along with the Sn(1)-Sn(2)-Sn(1)* trisannane skeleton. A similar helical arrangement avoiding repulsion between the silole rings is found in ter(1,1-tetraphenylsilole).^[6c]

Upon treatment of 1,3-dianion **3** with lithium (10 equiv) in THF for 5 min, the color of the reaction mixture gradually changed from bright red to dark violet. Progress of the reaction was monitored by using NMR spectroscopy. Immediately after the reaction mixture became dark violet, the ^1H NMR revealed formation of **1** and **2**. After 1 h, the final color of the reaction mixture was bright red. NMR spectroscopy revealed quantitative formation of stannole dianion **1** from **3** (Scheme 2). The 1,3-dianion **3** was reduced to the 1,1-dianion **1** via the 1,2-dianion **2**.

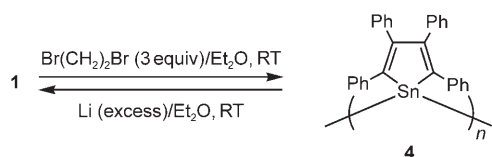
Mechanism for the oxidation of stannole dianion **1:** The mechanism for the redox reaction between stannole dianion **1**, bistannole-1,2-dianion **2** and terstannole-1,3-dianion **3** is shown in Scheme 3. The initial oxidation step, namely following the addition of 0.5 equivalents of oxygen to **1**, is the formation of a mixture of **1** and **2** (denoted as state α), as observed by ^1H NMR spectroscopy.^[12] In the next step, the



Scheme 3. Redox behavior between the three dianions, 1–3.

amount of oxygen affects the final product distribution, although the reason for this selectivity is not clear.^[16] Upon further treatment of **1** in the state α with 0.5 equivalents of oxygen, 1,1-dianion **1** is oxidized exclusively to form bistannole-1,2-dianion **2**. On the other hand, treatment of a mixture of **1** and **2** in the state α with 0.8 equivalents of oxygen relative to the starting amount of **1**, gives terstannole-1,3-dianion **3** in a very high yield. Reduction of **2** and **3** leads to the cleavage of an Sn–Sn bond to revert to the 1,1-dianion **1** as the sole product. Hence, the redox reactions between **1**, **2** and **3** can be controlled in a reversible fashion.

Synthesis of poly(1,1-stannole): Oxidation of the stannole dianion **1** leading to the formation of 1,2- and 1,3-dianions, **2** and **3** prompted us to prepare poly(1,1-stannole) from **1**. Reaction of **1** with excess oxygen, however, gave a complex mixture. Thus, 1,2-dibromoethane was chosen as an oxidant.^[17] Treatment of stannole dianion **1** with 1,2-dibromoethane (3 equiv) in ether at room temperature gave a yellow solution (Scheme 4). After removal of insoluble materials in

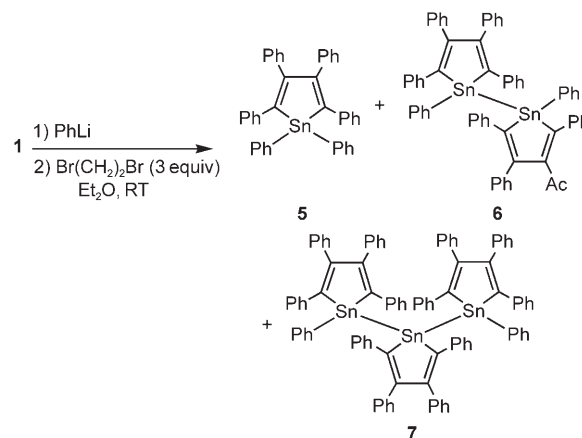


Scheme 4. Formation of poly(1,1-stannole) **4** by oxidation of 1,1-dianion **1**.

dichloromethane by filtration, the filtrate was concentrated to give a bright-yellow powder. The ¹H and ¹¹⁹Sn NMR spectra showed a simple pattern of signals and only one signal $\delta = -202.32$ ppm), respectively, to suggest that only a single product was formed. It was not possible to observe ¹³C NMR signals of the product because of its low solubility in inert solvents (e.g., [D₆]benzene and [D₈]toluene). Furthermore, the bright-yellow compound was sensitive to air or moisture and decomposed to a complex mixture in THF.

To gain insight into the structure of the product, reduction of the product by lithium was carried out (Scheme 4). After treatment of the bright-yellow compound with excess lithium in ether at room temperature, the reaction solution became dark red. The stannole dianion **1** was formed nearly quantitatively, as shown by NMR spectroscopy, indicating that the compound should have stannole skeletons. Thus, the bright-yellow compound can be assigned to the first poly(1,1-stannole) **4**, but compound **4** is highly unstable in solution and poorly characterized.

Synthesis of oligo(1,1-stannole)s: We examined the synthesis of oligo(1,1-stannole)s by oxidation of the stannole dianion **1** with 1,2-dibromoethane. After addition of phenyllithium to a solution of **1** in diethyl ether, treatment of the solution with 1,2-dibromoethane (3 equiv) gave some stannoles (Scheme 5). The product distribution (Table 1) depended on



Scheme 5. Synthesis of oligo(1,1-stannole)s, **6** and **7**.

Table 1. Yields [%] of **5**, **6** and **7** in the reactions of **1** with 1,2-dibromoethane (3 equiv and phenyllithium.

PhLi [equiv]	5	6	7
2	47	1	–
2/3	5	24	13
1/2	–	14	22

the ratio of phenyllithium to stannole dianion **1**. Reaction of **1** with 1,2-dibromoethane (3 equiv) in the presence of phenyllithium (2 equiv) gave hexaphenylstannole **5** and bi(1,1-stannole) **6**^[7a] in 47 and 1% yields, respectively. In the presence of 0.67 equivalents of phenyllithium, hexaphenylstannole **5**, bi(1,1-stannole) **6**^[7a] and novel ter(1,1-stannole) **7** were obtained in 5, 24, and 13% yields, respectively. Addition of 0.5 equivalents of phenyllithium provided bi(1,1-stannole) **6**^[7a] and ter(1,1-stannole) **7** in 14 and 22% yields, respectively without the formation of **5**. 1,2-Dibromoethane would function as a one-electron oxidant with the stannole dianion **1** and as a bromination reagent with phenyllithium.^[17] The resulting bi- or ter(1,1-stannole)-1,*n*-dianions would react with bromobenzene, generated in situ by reaction of phenyllithium with 1,2-dibromoethane to give the corresponding phenyl-capped bi- or ter(1,1-stannole)s. Although polymeric stannoles seemed to be formed, these compounds could not be isolated because of their instability.

The ter(1,1-stannole) **7** was characterized by means of ¹H, ¹³C, ¹¹⁹Sn NMR spectroscopy and elemental analysis. In the ¹¹⁹Sn NMR spectrum, two signals were observed at $\delta = -87.5$ and -205.5 ppm with an intensity ratio of 2:1, resulting from the two terminal and single central tin atoms, respectively. The signal assignable to the central tin atom was accompanied by a pair of satellite signals owing to the ter-

minal ^{119}Sn and ^{117}Sn nuclei, whereas the terminal tin atom signal was accompanied by two sets of satellite signals, a result of $^1J(^{119}\text{Sn}-^{119}\text{Sn}, ^{117}\text{Sn})$ and $^2J(^{119}\text{Sn}-^{117}\text{Sn})$.

UV/Vis spectra of stannoles, 4–7: UV/Vis absorption spectra of monostannole **5**,^[14] oligo- and poly(1,1-stannole)s in toluene are shown in Figures 2 and 3. The bi- and ter(1,1-stan-

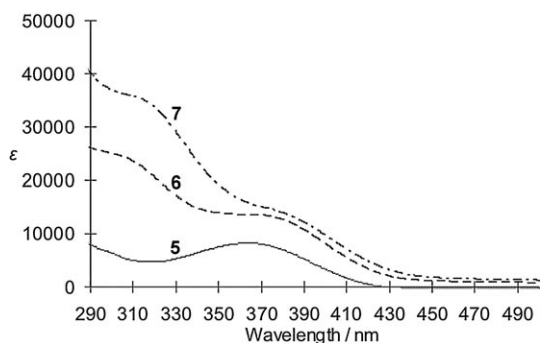


Figure 2. UV/Vis spectra of monostannole **5** (—), distannole **6** (----) and terstannole **7** (-.-.-).

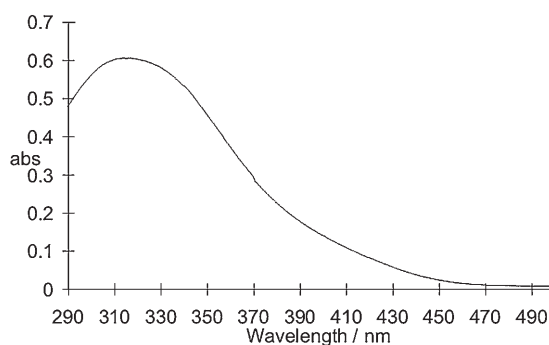


Figure 3. UV/Vis spectrum of poly(1,1-stannole) **4**.

nole)s, **6** and **7**, have two absorption maxima at around $\lambda = 310$ and 370 nm. The latter absorption can be assigned to $\pi-\pi^*$ transition of the stannole ring.^[18] The former absorption can be assigned to the transition from $\sigma(\text{Sn}-\text{Sn})$ to π^* of the diene moiety because the corresponding absorption is absent in monostannole **5** with no tin–tin bond.^[18] On the other hand, the UV/Vis absorption spectrum of poly(1,1-stannole) **4** displays a large absorption at about $\lambda = 310$ nm. This large and broad absorption can be assigned to the transition from $\sigma(\text{Sn}-\text{Sn})$ to π^* of the diene moiety, as was observed in **6** and **7**. The absorption maximum assigned to the $\sigma(\text{Sn}-\text{Sn})$ to π^* transition in **4** is also similar to that observed in poly(1,1-tetraphenylsilole)s^[6c,f] and poly(1,1-tetraphenylgermole).^[6f] Contrary to the di- and oligostannoles **6** and **7** and poly(1,1-tetraphenylmetallole)s,^[6c,f] the absorption assigned to the $\pi-\pi^*$ transition of the stannole ring in **4** is hidden by the broad band, indicating that the absorption of the $\sigma(\text{Sn}-\text{Sn})-\pi^*$ transition in **4** is remarkably stronger than

that of the $\pi-\pi^*$ transition of the stannole ring. Unfortunately, the molecular weight of **4** could not be determined because of instability to air and moisture, and the ϵ could not be estimated (Figure 3)

Conclusion

Oxidation of stannole dianion **1** with 1.3 equivalents of oxygen gave terstannole-1,3-dianion **3**. Controlling the amount of oxygen is essential for clean oxidation of the stannole dianion **1** to **2** and **3**. X-ray structural analysis showed that the terstannole-1,3-dianion has a non-aromatic nature, similar to the bistannole-1,2-dianion.^[12] Upon reduction, these anions revert to the stannole dianion. The redox reaction between the stannole dianion **1**, bistannole-1,2-dianion **2** and terstannole-1,3-dianion **3** can be controlled to be reversible. Furthermore, we succeeded in the synthesis of novel ter(1,1-stannole) **7** by reaction of stannole dianion **1** with 1,2-dibromoethane in the presence of phenyllithium. Controlled stepwise synthesis of oligo- and polymeric metalloles would allow control over their electronic properties.

Experimental Section

All reactions were carried out under argon atmosphere. THF, diethyl ether and $[\text{D}_6]$ benzene used in the synthesis or NMR analyses were distilled from sodium benzophenone ketyl under an argon atmosphere followed by from potassium mirror using trap-to-trap technique. Oxygen used was dried over activated molecular sieves. ^1H (400 MHz), ^{13}C (101 MHz), ^{119}Sn (149 MHz), and ^7Li NMR (156 MHz) spectra were recorded on a Bruker DPX-400 or a DRX-400 spectrometer. The $^nJ(\text{C}-\text{Sn})$ couplings were observed in the ^{13}C NMR spectra as satellite signals. Preparative gel permeation chromatography (GPC) was carried out by means of a LC-918 (Japan Analytical Ind.) with JAIGEL-1H and -2H columns. The melting point was determined by means of a Mitamura Riken Kogyo MEL-TEMP apparatus and is uncorrected. Elemental analysis was carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University.

Reaction of stannole dianion 1 with oxygen (1.3 equiv): Oxygen (1.8 mL, 0.073 mmol, 1 atm, 298.15 K) was added to a solution of stannole dianion **1** (28.6 mg, 0.057 mol) in THF (0.6 mL) and $[\text{D}_6]$ benzene (0.2 mL). The resulting bright-red solution was degassed by freeze-pump-thaw cycles and sealed. In a glovebox, after removal of insoluble materials by filtration, the filtrate was concentrated. The residue was washed with hexane to give 1,1''-dilithio-2,2',2'',3,3',3'',4,4',4'',5,5',5''-tetradecaphenyl-1,1',1''-terstannole (**3**) (22.2 mg, 0.015 mmol, 81 %).

Stannole 3: ^1H NMR (THF- $[\text{D}_6]$ benzene): $\delta = 6.45\text{--}6.54$ (m, 6H), 6.54–6.65 (m, 6H), 6.65–6.79 (m, 24H), 6.79–6.88 (m, 6H), 6.88–6.99 (m, 12H), 7.05 ppm (d, $J(\text{H,H}) = 8$ Hz, 6H); ^{13}C NMR (THF- $[\text{D}_6]$ benzene): $\delta = 121.69$ (d), 121.95 (d), 123.54 (d), 123.54 (d), 126.31 (d), 126.48 (d), 126.80 (d), 129.98 (d), 130.89 (d), 132.43 (d), 132.79 (d), 144.77 (s, $J(\text{C,Sn}) = 22$ Hz), 146.13 (s), 147.77 (s, $J(\text{C,Sn}) = 25$ Hz), 149.06 (s, $J(\text{C,Sn}) = 216$ Hz), 149.15 (s, $J(\text{C,Sn}) = 215$ Hz), 150.38 (s, $J(\text{C,Sn}) = 32$ Hz), 166.77 (s, $J(\text{C,Sn}) = 20$ Hz), 178.89 ppm (s, $J(\text{C,Sn}) = 39$, 191 Hz); ^{119}Sn NMR (THF- $[\text{D}_6]$ benzene): $\delta = -61.67$ ($^1J(^{119}\text{Sn}, ^{119}\text{Sn}) = 5909$ Hz, $^1J(^{119}\text{Sn}, ^{117}\text{Sn}) = 4732$ Hz), -145.12 ppm ($^1J(^{119}\text{Sn}, ^{119}\text{Sn}) = 5909$ Hz, $^1J(^{119}\text{Sn}, ^{117}\text{Sn}) = 4732$ Hz, $^2J(^{119}\text{Sn}, ^{117}\text{Sn}) = 405$ Hz); ^7Li NMR (THF- $[\text{D}_6]$ benzene): $\delta = -0.60$, 1.67 ppm (br). The elemental analysis of **3** could not be carried out because of its extremely high reactivity toward water and oxygen.

Crystal data of 3: Crystals suitable for X-ray diffraction were obtained by recrystallization in a solution of **3** in THF/hexane in the presence of [12]crown-4 at -33°C in a glovebox. The crystal was mounted in a glass capillary. The intensity data were collected at -175°C on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated $\text{Mo}_{\text{K}\alpha}$ radiation ($\lambda=0.71073\text{ \AA}$) and graphite monochromator. Formula $\text{C}_{108}\text{H}_{108}\text{Li}_2\text{O}_{10}\text{Sn}_3$, $F_w=1935.96$, crystal dimension $0.40\times 0.30\times 0.20\text{ mm}$, monoclinic, space group $C2/c$, $Z=4$, $a=21.778(2)$, $b=16.032(2)$, $c=27.081(3)\text{ \AA}$, $\beta=101.143(4)^{\circ}$, $V=9276.9(18)\text{ \AA}^3$, $D_{\text{calcd}}=1.386\text{ g cm}^{-3}$, $R_1=0.0438$ ($[I>2\sigma(I)]$), 6785 reflections, $wR_2=0.0996$ (for all reflections) for 8163 reflections and 1043 parameters, GOF=1.071. CCDC 645806 (**3**), contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reaction of stannole dianion 1 with ferrocenium tetrafluoroborate (1.3 equiv): Ferrocenium tetrafluoroborate (37 mg, 0.136 mmol) was added to a solution of stannole dianion **1** (51 mg, 0.104 mmol) in THF (2 mL) in a glovebox at room temperature. After filtration of materials insoluble in THF, a complex mixture (84.5 mg) was obtained.

Reaction of 1,3-dianion 3 with lithium: A mixture of 1,3-dianion **3** (19.7 mg, 0.014 mmol) and lithium (1.0 mg, 0.144 mmol) was placed in THF (0.5 mL). The resulting suspension was stirred 1 h in a glovebox. $[\text{D}_6]\text{benzene}$ (0.2 mL) was added to the resultant deep-red solution, and then the solution was degassed by freeze-pump-thaw cycles and sealed. The stannole dianion **1** was formed nearly quantitatively, as evidenced by NMR spectra.

Reaction of stannole dianion 1 with oxygen (excess): Oxygen (excess) was bubbled through a solution of stannole dianion **1** (80 mg, 0.16 mmol) in THF (1 mL) at room temperature. After removal of materials insoluble in dichloromethane, a complex mixture (75 mg) was obtained.

Synthesis of poly(1,1-stannole) 4. 1,2-Dibromoethane (0.07 mL, 0.86 mmol) was added to a solution of stannole dianion **1** (196 mg, 0.40 mmol) in diethyl ether (5 mL). The inorganic precipitate was removed by filtration. After the filtrate was concentrated, poly(1,1-stannole) **4** (102 mg) was obtained as bright-yellow powder. Compound **4** was sensitive to air and moisture. Thus, **4** was stored in a glovebox. The ^{13}C NMR signals of **4** were not observed because of the low solubility of **4** in $[\text{D}_6]\text{benzene}$. ^1H NMR ($[\text{D}_6]\text{benzene}$): $\delta=6.64\text{--}6.76$ (m), 6.77–6.82 ppm (m); ^{119}Sn NMR ($[\text{D}_6]\text{benzene}$): $\delta=-202.32$ ppm.

Reaction of poly(1,1-stannole) 4 with excess lithium: In a glovebox, a suspension of **4** (33 mg) and lithium (10 mg, 1.44 mmol) in diethyl ether (2 mL) was stirred overnight. The ^1H , ^{13}C , ^{119}Sn , and ^7Li NMR spectra of the reaction mixture revealed quantitative formation of stannole dianion **1**.

Reaction of stannole dianion 1 with 1,2-dibromoethane (3 equiv) in the presence of phenyllithium (2 equiv): 1,2-Dibromoethane (0.04 mL, 0.46 mmol) was added to a solution of stannole dianion **1** (73 mg, 0.15 mmol) and phenyllithium (0.98 M in cyclohexane and diethyl ether; 0.3 mL, 0.29 mmol) in diethyl ether (3 mL) at room temperature. After the mixture was stirred for 3 h the volatile substances were evaporated. The residue was subjected to GPC (CHCl_3) to afford hexaphenylstannole **5** (43 mg, 0.068 mmol, 47%) and bi(1,1-stannole) **6**^[7a] (0.8 mg, 0.0007 mmol, 1%).

Reaction of stannole dianion 1 with 1,2-dibromoethane (3 equiv) in the presence of phenyllithium (2/3 equiv): 1,2-Dibromoethane (0.05 mL, 0.58 mmol) was added to a solution of stannole dianion **1** (97 mg, 0.20 mmol) and phenyllithium (0.98 M in cyclohexane and diethyl ether; 0.13 mL, 0.13 mmol) in diethyl ether (3 mL), at room temperature. After the mixture was stirred for 3 h the volatile substances were evaporated. The residue was subjected to GPC (CHCl_3) to afford hexaphenylstannole **5** (5 mg, 0.01 mmol, 5%), bi(1,1-stannole) **6** (23 mg, 0.024 mmol, 24%) and 1,1'',2,2'',2'',3,3',3'',4,4',4'',5,5',5''-tetradecaphenyl-1,1',1''-terstannole (**7**) (12.4 mg, 0.015 mmol, 13%). **7**: m.p. 125°C (decomp). ^1H NMR ($[\text{D}]\text{chloroform}$): $\delta=6.50\text{--}6.55$ (m, 4H), 6.60–6.70 (m, 6H), 6.70–6.77 (m, 10H), 6.77–6.85 (m, 10H), 6.85–6.94 (m, 12H), 6.94–7.03 (m, 18H), 7.03–7.11 (m, 6H), 7.11–7.20 ppm (m, 4H); ^{13}C NMR ($[\text{D}]\text{chloroform}$): $\delta=125.18$ (d), 125.33 (d), 125.68 (d), 125.92 (d), 126.99 (d), 127.41 (d),

127.78 (d), 128.03 (d), 128.26 (d), 128.34 (d), 128.36 (d), 128.62 (d), 128.86 (d), 128.94 (d), 129.40 (d), 129.63 (d), 129.84 (d), 130.00 (d), 130.47 (d), 130.69 (d), 132.93 (s), 135.30 (s), 136.46 (s), 137.20 (d, $J(\text{C},\text{Sn})=9$, 47 Hz), 138.58 (s), 140.32 (s, $J(\text{C},\text{Sn})=97$, 102 Hz), 140.66 (s, $J(\text{C},\text{Sn})=60$, 64 Hz), 141.99 (s, $J(\text{C},\text{Sn})=46$ Hz), 143.27 (s, $J(\text{C},\text{Sn})=48$ Hz), 146.11 (s, $J(\text{C},\text{Sn})=21$, 34 Hz), 148.33 (s, $J(\text{C},\text{Sn})=17$ Hz), 153.70 (s, $J(\text{C},\text{Sn})=19$ Hz), 153.92 ppm (s, $J(\text{C},\text{Sn})=80$, 83 Hz); ^{119}Sn NMR ($[\text{D}]\text{chloroform}$): $\delta=-87.52$ ($^1J(^{119}\text{Sn},^{119}\text{Sn})=1576$ Hz, $^1J(^{119}\text{Sn},^{117}\text{Sn})=1446$ Hz, $^2J(^{119}\text{Sn},^{117}\text{Sn})=499$ Hz), -205.51 ppm ($^1J(^{119}\text{Sn},^{119}\text{Sn})=1576$ Hz, $^1J(^{119}\text{Sn},^{117}\text{Sn})=1446$ Hz); elemental analysis calcd (%) for $\text{C}_{96}\text{H}_{96}\text{Sn}_3$: C 72.99, H 4.47; found: C 72.42, H 4.42.

Reaction of stannole dianion 1 with 1,2-dibromoethane in the presence of phenyllithium (1/2 equiv): 1,2-Dibromoethane (0.03 mL, 0.37 mmol) was added to a solution of stannole dianion **1** (67 mg, 0.14 mmol) and phenyllithium (0.98 M in cyclohexane and diethyl ether; 0.07 mL, 0.069 mmol) in diethyl ether (3 mL), at room temperature. After the mixture was stirred for 3 h the volatile substances were evaporated. The residue was subjected to GPC (CHCl_3) to afford bi(1,1-stannole) **6** (11 mg, 0.01 mmol, 14%) and ter(1,1-stannole) **7** (16 mg, 0.01 mmol, 22%).

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