

Synthesis and Reactions of Stannole Anions

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The synthesis of stannole anions bearing various substituents on the tin atom is described. The reduction of hexaphenylstannole by the proper amount of lithium gave 1,2,3,4,5-pentaphenylstannole anion **1**. The reaction of **1** with 1,*n*-dihaloalkanes (*n* = 1, 3, 4, 5, 6) gave the corresponding 1,*n*-bis(1-stannacyclopentadien-1-yl)alkanes. In contrast, the re-

action of **1** with 1,2-dihaloalkanes gave the 1,1'-bistannole. The reactions of stannole dianion **3** with an equimolar amount of bulky alkyl, aryl, silyl, and stannyl halides gave the corresponding stannole anions.

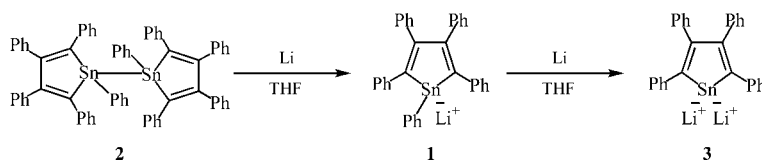
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Introduction

Metalolyl anions of heavier group 14 elements have received considerable attention in view of their potential aromatic character as heavier congeners of the cyclopentadienyl anion,^[1] since the first report on the generation of a silole anion in 1958.^[2] Over the past few decades, silole and germole anions have already been synthesized by deprotonation, dehalogenation, or transmetalation of the corresponding metaloles, and their structures have been discussed extensively by NMR, or X-ray structural analysis.^[3–6] Boudjouk reported the first NMR characterization of a silole anion.^[5] The negative charge was concluded to delocalize in the silole ring. In contrast to Boudjouk's silole anion, in some silole and germole anions, the negative charge localizes on the central atom, as evidenced by NMR^[4] and/or X-ray structural analyses.^[6] Although remarkable progress has been made on silicon and germanium analogues, no stannole anion had been reported before we undertook a study on such species a few years ago.^[7] First, we reported the synthesis of 1,2,3,4,5-pentaphenylstannole anion **1** by the reaction of 1,1'-bistannole

2 with lithium (Scheme 1).^[8] However, it was difficult to manipulate the stoichiometry or reaction conditions to produce stannole anion **1** without stannole dianion **3** from the 1,1'-bistannole **2** because no sufficient amount of **2** could be obtained in several steps from diphenylacetylene.^[7–9] To investigate the chemistry of stannole anions, alternative methods for the synthesis of stannole anions using an easily accessible starting material were required. Very recently, we reported an efficient synthesis of the first tin-containing carbocyclic aromatic stannole dianion **3** by the reaction of hexaphenylstannole (**4**) with excess lithium and discussed its aromaticity by the aid of NMR studies, X-ray analysis and theoretical calculations (Scheme 2).^[10,11] Furthermore, we reported the oxidation of the stannole dianion **3** to the 1,1'-bistannole dianion **5** as a novel method for the synthesis of a stannole anion.^[12]

Herein we describe novel methods for the preparation of stannole anions: (i) the reduction of hexaphenylstannole (**4**) with the proper amount of lithium, and (ii) the reaction of the stannole dianion **3** with various halogen reagents. NMR studies on stannole anions and their reactions are also reported.



Scheme 1.

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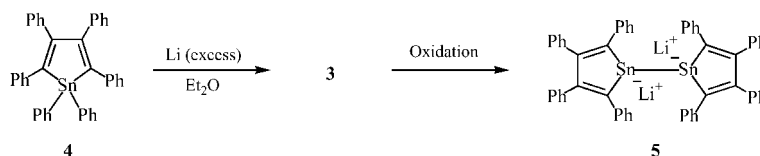
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Results and Discussion

Synthesis and Reactions of 1,2,3,4,5-Pentaphenylstannole Anion (**1**)

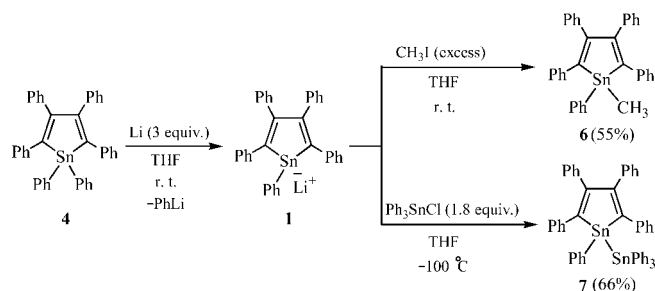
Synthesis of Stannole Anion **1** from Hexaphenylstannole **4**

Treatment of hexaphenylstannole (**4**) with 3 equiv. of lithium^[13] in THF at room temperature gave a dark-red solu-



Scheme 2.

tion, suggesting the formation of an anion species. After stirring the reaction mixture for 6 h, addition of excess methyl iodide to this reaction mixture gave 1-methyl-1,2,3,4,5-pentaphenylstannole (**6**)^[8] in 55% yield, indicating the effective formation of pentaphenylstannole anion **1** from **4** (Scheme 3). Treatment of **1** thus obtained with 1.8 equiv. of chlorotriphenylstannane at -100°C gave 1-triphenylstannyl-1,2,3,4,5-pentaphenylstannole (**7**) in 66% yield.



Scheme 3.

The reaction of **4** with 3 equiv. of lithium was monitored by NMR spectroscopy. In the ^{119}Sn NMR spectrum, only one signal was observed at $\delta = -28.6$ ppm in the same region as that in the previous synthesis from the 1,1'-bistannole **2**,^[8,9] suggesting the formation of **1**. In contrast to the reduction of 1,1'-bistannole **2** to form both stannole anion **1** and the stannole dianion **3**, the ^{13}C NMR spectrum revealed the clean formation of the stannole anion **1**. Although some unidentifiable signals were observed, the signals due to the stannole anion **1** could be completely assigned by the comparison of the chart of the mixture of the stannole anion **1** and the stannole dianion **3** obtained by the reduction of the 1,1'-bistannole **2**.^[14] A phenyl group of hexaphenylstannole (**4**) was eliminated probably as phenyllithium, as in the reduction of hexaphenylstannole (**4**) to form the stannole dianion **3**,^[10] although the signals due to phenyllithium were not observed in the reaction mixture. The signal assignable to the α -carbon atom in the five-membered ring was observed at $\delta = 176.5$ ppm, judging from the large tin–carbon coupling constant of about 171 Hz. The low-field resonance of the α -carbon atom could be explained by paramagnetic contribution of a tin–carbon bond as was observed in the stannole dianion **3**.^[10] In the ^7Li NMR spectrum, a single resonance was observed at $\delta = -0.64$ ppm. In contrast to the successful isolation of the

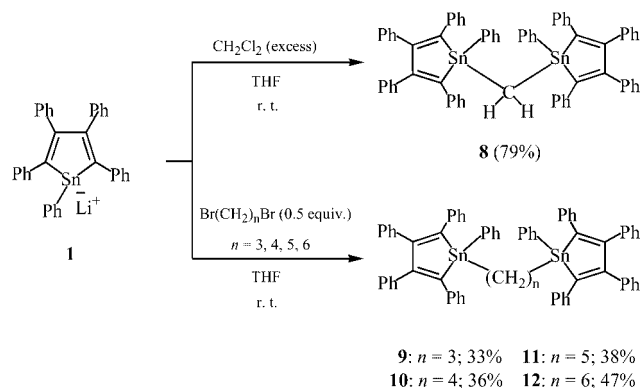
stannole dianion **3**, recrystallization of the reaction mixture to purify the stannole anion **1** was not successful. Thus, the degree of aromaticity of **1** using the ^7Li chemical shift could not be estimated because intermolecular exchange of lithium cations between **1** and phenyllithium could not be suppressed. Although the yield of **1** could not be estimated, the yields of the trapping products **6** and **7**, and the NMR spectra of **1**, especially the ^{119}Sn NMR spectrum, suggest that the generation efficiency should be very high.

Reaction of Stannole Anion **1** with Dihaloalkanes

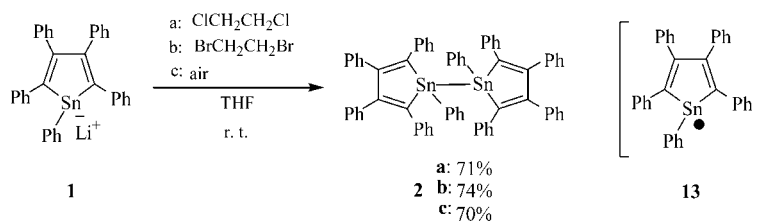
Connecting two stannole skeletons with a hydrocarbon chain is a subject of interest because two stannole rings could face each other to reveal unique electronic properties resulting from through-space π -facial interactions.^[15]

Reaction of **1** with excess dichloromethane gave bis(1,2,3,4,5-pentaphenyl-1-stannacyclopentadien-1-yl)methane (**8**) in 79% yield (Scheme 4). Compound **8** was proved to have a symmetrical structure having an Sn–C–Sn skeleton by $^2J(\text{Sn}–\text{Sn})$ of 284 Hz in the ^{119}Sn NMR spectrum. The bis(stannoies) **9–12**, whose two stannole rings are connected by a saturated hydrocarbon chain were also synthesized by the reaction of **1** with 0.5 equiv. of the corresponding 1, n -dibromoalkanes ($n = 3–6$) in moderate yields (Scheme 4). The structures of all the bis(stannoies) thus obtained were determined by NMR spectroscopy and elemental analysis. These results are similar to the formation of 1,3-bis(triphenylstannyl)propane from triphenylstannyl anion and 1,3-dibromopropane.^[16]

On the other hand, reactions of the stannole anion **1** with 1,2-dihaloethanes gave bi(1,2,3,4,5-pentaphenyl-1-stannacyclopentadien-1-yl) (**2**)^[8,9] in about 70% yields. Oxidation



Scheme 4.

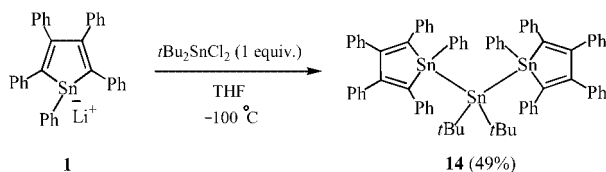


Scheme 5.

of the stannole anion **1** by air also gave **2** in high yield (Scheme 5). The formation of **2** can be reasonably interpreted in terms of the dimerization of stannole radical **13** resulting from oxidation of **1** by air or dihaloethanes. Evidently, dihaloethanes function as one-electron oxidants in these reactions.^[17]

Reaction of Stannole Anion **1** with Di-*tert*-butyldichlorostannane

Reaction of the stannole anion **1** with di-*tert*-butyldichlorostannane at -100°C gave di-*tert*-butylbis(1,2,3,4,5-pentaphenyl-1-stannacyclopentadien-1-yl)stannane (**14**) in 49% yield (Scheme 6). In the ^{119}Sn NMR spectrum, two signals are observed with an intensity ratio of 2:1, resulting from the two equivalent terminal and one central tin atoms, respectively.



Scheme 6.

Photophysical Properties of Bis(stannoies) **8–12** and **14**

We examined the photophysical properties of the newly obtained bis(stannoies) **8–12** and **14** whose two stannole rings are connected by a saturated hydrocarbon or a stannyl chain. UV/Vis absorption spectra for **4**,^[16] **8–12**, and **14** are listed in Table 1. The absorption maxima of **8–12** appear at almost the same wavelength as that of **4**, reflecting the same

chromophore. Namely, the absorption is derived from the $\pi-\pi^*$ transition of the stannole ring.^[18] The $\pi-\pi^*$ transitions of group 14 metaloles are observed in the same region at about 360 nm because the contribution of the diene moiety to both HOMO and LUMO is more predominant than that of the metal moiety.^[18] This spectral feature suggests no significant through-space interaction between the two stannole rings in solution. Compound **14** displays two shoulder absorption bands at about 310 and 370 nm. The latter band can be assigned to $\pi-\pi^*$ transition of the stannole ring. The shorter band can be assigned to the transition of $\sigma(\text{Sn}-\text{Sn})$ to π^* of the diene moiety because the corresponding band is absent in other bis(stannoies), **8–12** with no tin–tin bond.^[9]

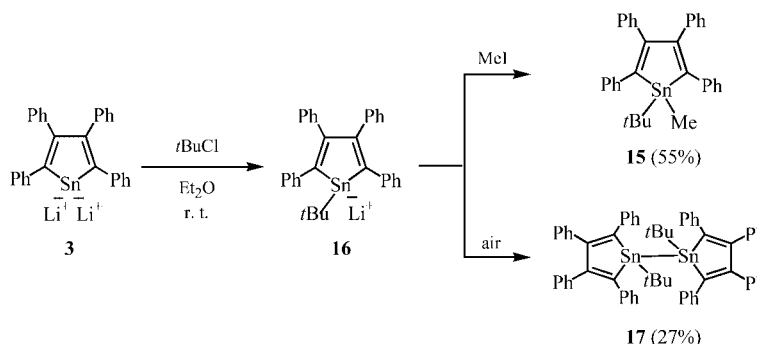
Table 1. UV/Vis absorptions of stannole **4** and bis(stannoies) **8–12**, **14** in CH_2Cl_2 .

Compound	$\lambda_{\text{max}}/\text{nm}$ (ϵ)
4	355 (12000)
8 ($n = 1$)	359 (20000)
9 ($n = 3$)	353 (10600)
10 ($n = 4$)	353 (8800)
11 ($n = 5$)	353 (16500)
12 ($n = 6$)	349 (4100)
14	315 (12000) 373 (6800)

Synthesis of Stannole Monoanions from Stannole Dianion **3**

Alkylation of Stannole Dianion **3**

Because the reaction of **3** with methyl iodide gave 1,1-dimethylstannole,^[8] *tert*-butyl chloride was chosen as a bulkier alkylating reagent than methyl iodide.^[19] When

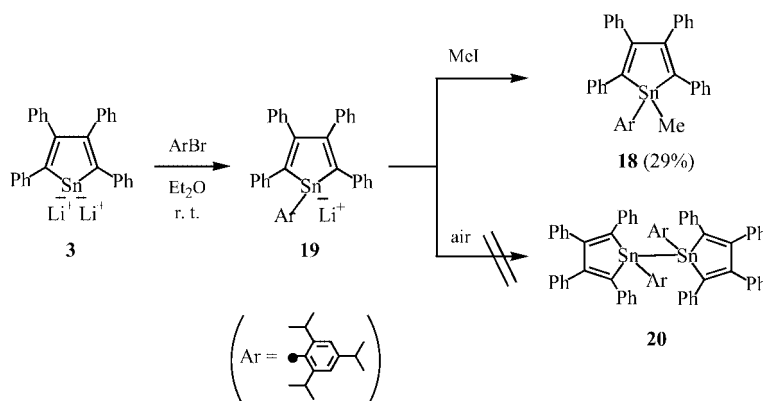


Scheme 7.

1 equiv. of *tert*-butyl chloride was added to a diethyl ether solution of the stannole dianion **3**, the color of the reaction mixture changed from deep red to bright red. By treatment of the reaction mixture with methyl iodide, the 1-*tert*-butyl-1-methylstannole **15**^[19] was obtained in 55% yield, suggesting the formation of the stannole anion **16** bearing a *tert*-butyl group on the tin atom (Scheme 7). The formation of **16** from **3** is reasonably explained by an electron-transfer mechanism, as observed in the reaction of the tributylstannyl anion with *tert*-butyl halides.^[20] The reaction of **3** with *tert*-butyl chloride followed by exposure of the reaction mixture to air gave the 1,1'-bistannole **17**^[8,9] in 27% yield. The formation of **17** is interpreted in terms of the dimerization of the 1-*tert*-butylstannole radical resulting from the oxidation of **16**, as was observed in the oxidation of pentaphenylstannole anion **1** (Scheme 5).

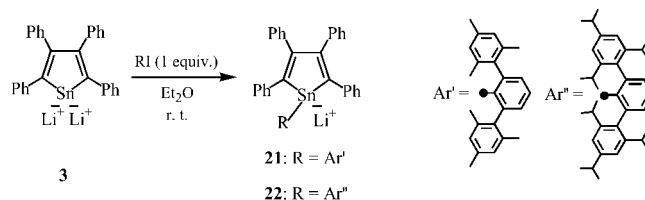
Arylation of Stannole Dianion **3**

Next we examined the synthesis of 1-arylstannole anions by the reaction of the stannole dianion **3** with aryl halides. Reactions with small aryl halides, however, became complicated because of the formation of mono- and disubstituted products. Thus, bromo-2,4,6-triisopropylbenzene was chosen as a bulky aryl halide. On treatment of the stannole dianion **3** with 1 equiv. of 1-bromo-2,4,6-triisopropylbenzene in diethyl ether at room temperature, the color of the reaction mixture remained deep red, indicating the existence of an anion species. After addition of methyl iodide to the reaction solution, the color of the reaction mixture changed to green. After usual workup, the 1-methyl-1-(2,4,6-triisopropylphenyl)stannole **18** was obtained in 29% yield, indicating the formation of the intermediary stannole anion **19** bearing a 2,4,6-triisopropylphenyl group on the tin atom (Scheme 8). Treatment of **3** with 1-bromo-2,4,6-triisopropylbenzene followed by exposure of the reaction mixture to air gave a complex mixture without the formation of the expected 1,1'-bistannole **20**. The dimerization of the intermediary stannole radical generated by oxidation of **19** is suppressed due to the steric congestion around the tin atom, preventing the formation of **20**.



Scheme 8.

We examined the synthesis of the stannole anions **21** and **22** having an *m*-terphenyl group, Ar' = C₆H₃-2,6-Mes₂ (Mes = C₆H₃-2,4,6-Me₃) and Ar'' = C₆H₃-2,6-Tip₂ (Tip = C₆H₃-2,4,6-*i*Pr₃), respectively, as a more bulky group than a Tip group on the tin atom (Scheme 9). The NMR spectra of these reaction mixtures suggest the formation of **21** or **22** (*vide infra*), although trapping of **21** and **22** with appropriate reagents was not successful.

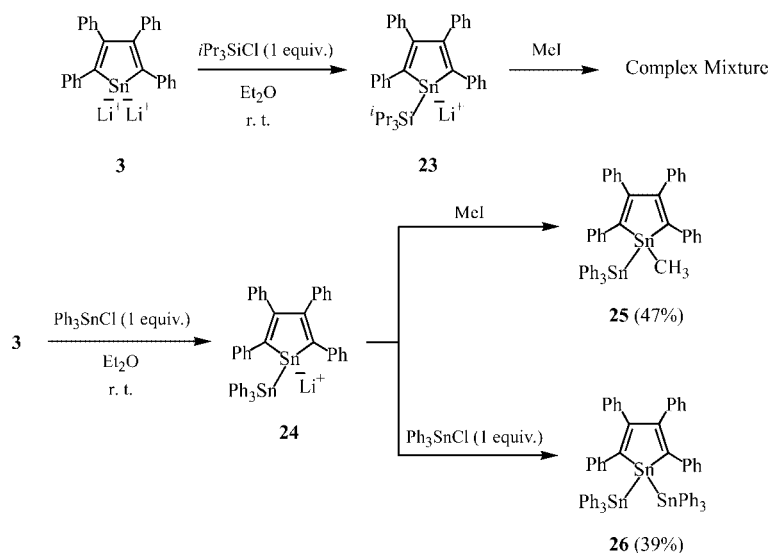


Scheme 9.

The formation of **19** from **3** can be also explained by an electron-transfer mechanism, as observed in the reaction of **3** with *tert*-butyl chloride (Scheme 7) because electrophilic substitution reactions rarely occur in simple aryl halides.

Silylation or Stannylation of Stannole Dianion **3**

On treatment of the stannole dianion **3** with 1 equiv. of chlorotriisopropylsilane in diethyl ether at room temperature, the color of the reaction mixture remained deep red. The NMR spectra of the reaction mixture reveal the presence of only one species which can be assigned to the 1-silyl-substituted stannole anion **23** (Scheme 10). Trapping of **23** by methyl iodide, however, gave a complex mixture. The reaction of the stannole dianion **3** with 1 equiv. of chlorotriphenylstannane in diethyl ether at room temperature gave a dark-brown solution. The formation of the 1-stannyl-substituted stannole anion **24** was evidenced by a chemical trapping reaction. Addition of methyl iodide or chlorotriphenylstannane to the solution of **24** gave the 1-methyl-1-(triphenylstannyl)stannole **25** and the 1,1-bis(triphenylstannyl)stannole **26** in 47 and 39% yields, respectively (Scheme 10).



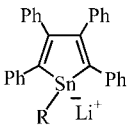
Scheme 10.

NMR Studies of the Newly Obtained Stannole Anions

The structure in solution of the stannole anions was characterized by ^1H , ^{13}C , ^{119}Sn and ^7Li NMR spectroscopy (Table 2). In the ^{119}Sn NMR spectra, there appears only one signal assignable to the 1-*tert*-butyl-substituted stannole anion **16** at $\delta = 30.4$ ppm, suggesting that the genera-

tion efficiency of **16** is relatively high, although the isolation of **16** by recrystallization was not successful. The resonance is at lower field than that of hexaphenylstannole (**4**) ($\delta = -88$ ppm) or pentaphenylstannole anion **1** ($\delta = -28.6$ ppm). The ^{119}Sn NMR signal of the stannyl anion ($t\text{Bu}_2\text{HSn-Sn}t\text{Bu}_2\text{Li}$) appears at low field ($\delta = 107.8$ ppm in $\text{D}_2\text{O}/\text{THF}$).^[21] Thus, the low-field shift of the stannole anion **16**

Table 2. Selected ^{13}C , ^{119}Sn and ^7Li NMR chemical shifts of stannole anions (ppm).

				
Compounds	$\delta(^{13}\text{C}_\alpha)$	$\delta(^{13}\text{C}_\beta)$	$\delta(^7\text{Li})$	$\delta(^{119}\text{Sn})$
1 (R = Ph)	176.47 ($J_{\text{C, Sn}} = 171$ Hz)	150.24	-0.64	-28.6
16 (R = <i>t</i> Bu)	170.66 ($J_{\text{C, Sn}} = 113$ Hz)	151.78	0.92	30.4
19 (R = Tip)	170.39 ($J_{\text{C, Sn}} = 90$ Hz)	148.97	0.95	-49.6
21 (R = $\text{Mes}_2\text{C}_6\text{H}_3$)	170.34	[a]	0.15	-50.2 (br)
22 (R = $\text{Tip}_2\text{C}_6\text{H}_3$)	170.33	[a]	0.61	-47.1
23 (R = $\text{Si}i\text{Pr}_3$)	156.01 ($J_{\text{C, Sn}} = 190$ Hz)	145.50	0.48	-218.5 ($J_{\text{Sn, Si}} = 380$ Hz)
24 (R = SnPh_3)	172.03 ($J_{\text{C, Sn}} = 150$ Hz)	148.85	-0.74, 0.62	-240.5 (ring) ($J_{\text{Sn, Sn}} = 3800$ Hz)

[a] Not identified.

can be explained by the substituent effect of the *tert*-butyl group on the tin atom. On the other hand, the ^{119}Sn NMR signals of the stannole anions **19**, **21** and **22**, bearing an aryl group on the tin atom are observed at $\delta = -49.6$ ($\text{Ar} = \text{Tip}$), -50.2 ($\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-Mes}_2$) and -47.1 ($\text{Ar}'' = \text{C}_6\text{H}_3\text{-2,6-Tip}_2$) ppm in the region similar to that of pentaphenylstannole anion **1**. Although the isolation of **19**, **21** and **22** by recrystallization was not successful, the ^{119}Sn NMR signals due to **19**, **21** and **22** were major in each reaction mixture. Thus, the generation efficiency of **19**, **21** and **22** was estimated to be relatively high. The signal assignable to 1-silyl-substituted stannole anion **23** was observed at $\delta = -218$ ppm with a coupling constant of 380 Hz resulting from a tin–silicon bond. The high-field resonance is characteristic of silyl-substituted stannanes.^[22] Although the isolation of **23** by recrystallization was not successful, the generation efficiency of **23** was estimated to be very high, judging from the clean ^{119}Sn , ^{13}C , and ^1H NMR spectra of the reaction mixture. The ^{119}Sn NMR spectrum of the 1-stannyl-substituted stannole anion **24** reveals two signals at $\delta = -98.7$ and -240.5 ppm, assignable to the triphenylstannyl and the stannole moieties, respectively. Each signal has a coupling constant of about 3800 Hz resulting from a tin–tin bond. Although hexaphenyldistannane was also generated in the reaction mixture as a minor product, probably because stannole dianion **3** functions as a reductant for triphenylstannyl chloride, the generation efficiency of **24** was estimated to be relatively high.

The ^{13}C NMR signals due to **16**, **19**, **23** and **24** could be assigned completely. In particular, a characteristic low-field signal assignable to the α -carbon atom in **16**, **19** and **24** was observed at $\delta \approx 170$ ppm with a large tin–carbon coupling constant of about 90–150 Hz, as was observed in the stannole dianion **3** and pentaphenylstannole anion **1**. Interestingly, the α -carbon atom of **23** ($\delta = 156.0$ ppm), assigned by a large tin–carbon coupling constant of about 190 Hz, appears at higher field than those of other stannole anions, probably due to the effect of the silyl group on the tin atom. The ^{13}C NMR signals due to the α -carbon atom of **21** and **22** could be observed at $\delta = 170.34$ ppm for **21** and $\delta = 170.33$ ppm for **22**. Other signals in the ^{13}C NMR spectra, however, are too complicated to be assigned, probably due to steric congestion around the tin atom. The ^7Li NMR signals of all the stannole anions are observed at $\delta \approx 0$ ppm.

Conclusions

We have succeeded in an efficient synthesis of pentaphenylstannole anion **1** by the reaction of hexaphenylstannole (**4**) with 3 equiv. of lithium. The stannole anion **1** reacted with 1,*n*-dihaloalkanes ($n = 1, 3, 4, 5$ and 6) to give the corresponding adducts, as do common organostannyl anions. On the other hand, 1,2-dihaloethanes reacted with **1** as one-electron oxidants. The UV/Vis spectra of the newly obtained bis(stannoles) reveal no significant interaction between the two stannole rings in solution. The synthesis of a variety of stannole anions from stannole dianion **3** could

be also achieved. The formation of the anions was clearly evidenced by NMR analysis and chemical trapping reactions. The ^7Li NMR signals of these stannole anions are observed at $\delta \approx 0$ ppm. The aromaticity of the newly obtained stannole anions can not be presently discussed by using ^7Li NMR spectroscopy because of the involvement of exchange of lithium cations as well as a small possibility of η^5 -coordination of a lithium cation to the stannole anion.

Experimental Section

General Procedures: All experiments were performed under argon using a usual glass apparatus or a glovebox. THF, diethyl ether and $[\text{D}_6]\text{benzene}$ were distilled from sodium/benzophenone or a potassium mirror. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra were recorded with a Bruker AM-400 or a Bruker DRX-400 spectrometer in CDCl_3 or a mixture of THF or diethyl ether and $[\text{D}_6]\text{benzene}$. ^{119}Sn (149 MHz) and ^7Li (156 MHz) NMR spectra were recorded with a Bruker DRX-400 spectrometer in CDCl_3 or a mixture of THF or diethyl ether and $[\text{D}_6]\text{benzene}$. Wet column chromatography (WCC) was carried out with Kanto silica gel 60N. Preparative gel permeation chromatography (GPC) was carried out with an LC-918 (Japan Analytical Ind. Co., Ltd.) with JAIGEL-1H and -2H columns with chloroform as the eluent. All melting points were determined with a Mitamura Riken Kogyo MEL-TEMP apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University.

Synthesis of 1,2,3,4,5-Pentaphenylstannole Anion (1) from 1,1,2,3,4,5-Hexaphenylstannole (4): A THF (4 mL) solution of hexaphenylstannole (**4**) (370 mg, 0.59 mmol) was treated with lithium (10 mg, 1.45 mmol) at room temperature. After the reaction mixture was stirred for 6 h, an aliquot (1.0 mL) of the reaction mixture was placed in an NMR tube with $[\text{D}_6]\text{benzene}$ (0.2 mL) and the tube was degassed by freeze-pump-thaw cycles and sealed. **1:** ^1H NMR ($\text{THF}/\text{C}_6\text{D}_6$): $\delta = 6.45\text{--}6.49$ (m, 2 H), $6.55\text{--}6.58$ (m, 2 H), $6.61\text{--}6.67$ (m, 7 H), $6.70\text{--}6.74$ (m, 4 H), $6.75\text{--}6.78$ (m, 6 H), $6.86\text{--}6.90$ (m, 3 H), $7.71\text{--}7.74$ (m, 1 H) ppm. ^{13}C NMR ($\text{THF}/\text{C}_6\text{D}_6$): $\delta = 121.36$ (d), 123.51 (d), 124.10 (d), 126.44 (d), 126.56 (d), 126.59 (d), 128.54 (d), 131.58 (d), 138.66 (d), 145.59 (s), 150.24 (s), 150.66 (s, $J_{\text{C,Sn}} = 33$ Hz), 161.96 (s), 176.47 (s, $J_{\text{C,Sn}} = 171$ Hz) ppm. ^{119}Sn NMR ($\text{THF}/\text{C}_6\text{D}_6$): $\delta = -28.6$ ppm. ^7Li NMR ($\text{THF}/\text{C}_6\text{D}_6$): $\delta = -0.64$ ppm.

Reaction of Pentaphenylstannole Anion 1 with Methyl Iodide: To a THF (5 mL) solution of **1** prepared from **4** (148 mg, 0.235 mmol) and lithium (4 mg, 0.61 mmol) was added an excess amount of methyl iodide (1.0 mL, 1.61 mmol) at room temperature. After removal of volatile substances, the residue was subjected to column chromatography (hexane/ethyl acetate, 10:1) to afford 1-methyl-1,2,3,4,5-pentaphenylstannole (**6**) (80 mg, 0.13 mmol, 55%). **6:** M.p. $139\text{--}140^\circ\text{C}$ (decomp.) ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$). ^1H NMR (CDCl_3): $\delta = 0.86$ (s, $J_{\text{H,Sn}} = 56$ Hz, 3 H), $6.79\text{--}6.88$ (m, 8 H), $6.94\text{--}7.06$ (m, 12 H), $7.34\text{--}7.41$ (m, 3 H), $7.51\text{--}7.67$ (m, 2 H) ppm. ^{13}C NMR (CDCl_3): $\delta = -9.06$ (q), 125.19 (d), 125.77 (d), 127.30 (d), 127.80 (d), 128.76 (d), 129.15 (d), 129.20 (d), 130.29 (d), 136.45 (d), 139.50 (s), 140.71 (s), 142.55 (s), 143.62 (s), 154.59 (s) ppm. ^{119}Sn NMR (CDCl_3): $\delta = -38.8$ ppm. $\text{C}_{38}\text{H}_{34}\text{Sn}$ (609.42): calcd. C 74.10, H 4.97; found C 73.84, H 4.96.

Reaction of Pentaphenylstannole Anion 1 with Chlorotriphenylstannane: To a THF (4 mL) solution of **1** prepared from **4** (178 mg, 0.28 mmol) and lithium (6 mg, 0.85 mmol) was added chlorotri-

phenylstannane (202 mg, 0.52 mmol) at $-100\text{ }^{\circ}\text{C}$. After being warmed to room temperature, the reaction mixture was stirred overnight. After removal of volatile substances, the residue was chromatographed (hexane/ethyl acetate, 10:1) to give 1,2,3,4,5-pentaphenyl-1-(triphenylstannyl)stannole (**7**) (169 mg, 0.19 mmol, 66%). **7**: M.p. $189\text{ }^{\circ}\text{C}$ (decomp.). ^1H NMR (CDCl_3): $\delta = 6.73\text{--}6.84$ (m, 8 H), $6.85\text{--}6.92$ (m, 6 H), $6.94\text{--}7.00$ (m, 6 H), $7.25\text{--}7.38$ (m, 12 H), $7.40\text{--}7.53$ (m, 8 H) ppm. ^{13}C NMR (CDCl_3): $\delta = 125.18$ (d), 125.79 (d), 127.30 (d), 127.77 (d), 128.76 (d), 128.92 (d), 128.96 (d), 129.00 (d), 129.15 (d), 129.54 (d, $J_{\text{C},\text{Sn}} = 21\text{ Hz}$), 130.35 (d), 137.38 (d, $J_{\text{C},\text{Sn}} = 9$, 41 Hz), 136.15 (s), 140.80 (s), 142.57 (s), 146.97 (s), 154.23 (s) ppm. ^{119}Sn NMR (CDCl_3): $\delta = -125.0$ ($^1J_{\text{Sn},\text{Sn}} = 3573\text{ Hz}$), -111.5 ($^1J_{\text{Sn},\text{Sn}} = 3573\text{ Hz}$) ppm. $\text{C}_{52}\text{H}_{40}\text{Sn}_2$ (902.32): calcd. C 69.22, H 4.47; found C 68.81, H 4.36.

Reaction of Pentaphenylstannole Anion 1 with Dichloromethane: To a THF (5 mL) solution of **1** prepared from **4** (250 mg, 0.40 mmol) and lithium (7 mg, 1.05 mmol) was added excess dichloromethane (5 mL, 79 mmol) at room temperature. After removal of volatile substances, the residue was chromatographed (hexane/ethyl acetate, 10:1) to give bis(1,2,3,4,5-pentaphenyl-1-stannacyclopentadienyl)methane (**8**) (88 mg, 0.079 mmol, conv. 79%). The starting **4** was recovered in 50% yield. **8**: M.p. $226\text{--}228\text{ }^{\circ}\text{C}$ (decomp.) ($\text{CH}_2\text{Cl}_2 + \text{EtOH}$). ^1H NMR (CDCl_3): $\delta = 1.14$ (s, $J_{\text{H},\text{Sn}} = 64\text{ Hz}$, 2 H), $6.71\text{--}6.77$ (m, 16 H), $6.90\text{--}6.95$ (m, 24 H), $7.28\text{--}7.33$ (m, 6 H), $7.42\text{--}7.52$ (m, 4 H) ppm. ^{13}C NMR (CDCl_3): $\delta = -15.37$ (t, $J_{\text{C},\text{Sn}} = 253$, 256 Hz), 125.30 (d), 125.82 (d), 127.25 (d), 127.90 (d), 128.82 (d, $J_{\text{C},\text{Sn}} = 39\text{ Hz}$), 129.15 (d), 129.35 (d, $J_{\text{C},\text{Sn}} = 22\text{ Hz}$), 130.38 (d), 136.28 (d, $J_{\text{C},\text{Sn}} = 41\text{ Hz}$), 140.36 (s, $J_{\text{C},\text{Sn}} = 18\text{ Hz}$), 140.68 (s, $J_{\text{C},\text{Sn}} = 70\text{ Hz}$), 142.05 (s, $J_{\text{C},\text{Sn}} = 47\text{ Hz}$), 143.47 (s), 154.53 (s, $J_{\text{C},\text{Sn}} = 89\text{ Hz}$) ppm. ^{119}Sn NMR (CDCl_3): $\delta = -29.5$ ($^2J_{\text{Sn},\text{Sn}} = 284\text{ Hz}$) ppm. $\text{C}_{69}\text{H}_{52}\text{Sn}_2$ (1118.61): calcd. C 74.09, H 4.69; found C 74.20, H 4.57.

Reaction of Pentaphenylstannole Anion 1 with 1,3-Dibromopropane: 1,3-Dibromopropane (0.03 mL, 0.30 mmol) was added to a THF (5 mL) solution of **1** prepared from **4** (350 mg, 0.56 mmol) and lithium (11 mg, 1.64 mmol) at room temperature. After removal of volatile substances, the residue was subjected to GPC to afford 1,3-bis(1,2,3,4,5-pentaphenyl-1-stannacyclopentadienyl)propane (**9**) (104 mg, 0.091 mmol, 33%). **9**: M.p. $90\text{--}95\text{ }^{\circ}\text{C}$ (decomp.). ^1H NMR (CDCl_3): $\delta = 1.65\text{--}1.86$ (m, 4 H), $2.10\text{--}2.35$ (m, 2 H), $6.73\text{--}6.85$ (m, 16 H), $6.85\text{--}7.00$ (m, 24 H), $7.27\text{--}7.36$ (m, 6 H), $7.40\text{--}7.60$ (m, 4 H) ppm. ^{13}C NMR (CDCl_3): $\delta = 13.13$ (t, $^1J_{\text{C},\text{Sn}} = 340$, 356 Hz, $^3J_{\text{C},\text{Sn}} = 70\text{ Hz}$), 24.63 (t, $^2J_{\text{C},\text{Sn}} = 21\text{ Hz}$), 125.14 (d), 125.72 (d), 127.26 (d), 127.83 (d), 128.78 (d), 129.05 (d, $J_{\text{C},\text{Sn}} = 21\text{ Hz}$), 129.09 (d), 130.30 (d), 136.75 (d, $J_{\text{C},\text{Sn}} = 38\text{ Hz}$), 139.26 (s), 140.66 (s, $J_{\text{C},\text{Sn}} = 63\text{ Hz}$), 142.72 (s, $J_{\text{C},\text{Sn}} = 45\text{ Hz}$), 144.02 (s, $J_{\text{C},\text{Sn}} = 391$, 409 Hz), 154.75 (s, $J_{\text{C},\text{Sn}} = 79\text{ Hz}$) ppm. ^{119}Sn NMR (CDCl_3): $\delta = -49.9$ ppm. $\text{C}_{71}\text{H}_{56}\text{Sn}_2$ (1146.67): calcd. C, 74.37, H 4.92; found C 74.07, H 4.92.

Reaction of Pentaphenylstannole Anion 1 with 1,4-Dibromobutane: 1,4-Dibromobutane (0.019 mL, 0.16 mmol) was added to a THF (3 mL) solution of **1** prepared from **4** (200 mg, 0.32 mmol) and lithium (6 mg, 0.89 mmol) at room temperature. After removal of volatile substances, the residue was subjected to GPC to afford 1,4-bis(1,2,3,4,5-pentaphenyl-1-stannacyclopentadienyl)butane (**10**) (66 mg, 0.057 mmol, 36%). **10**: M.p. $190\text{ }^{\circ}\text{C}$ (decomp.). ^1H NMR (CDCl_3): $\delta = 1.45\text{--}1.63$ (m, 4 H), $1.68\text{--}1.86$ (m, 4 H), $6.77\text{--}6.83$ (m, 16 H), $6.90\text{--}7.01$ (m, 24 H), $7.30\text{--}7.36$ (m, 6 H), $7.46\text{--}7.58$ (m, 4 H) ppm. ^{13}C NMR (CDCl_3): $\delta = 12.71$ (t, $^1J_{\text{C},\text{Sn}} = 369\text{ Hz}$), 30.92 (t, $^2J_{\text{C},\text{Sn}} = 56\text{ Hz}$, $^3J_{\text{C},\text{Sn}} = 24\text{ Hz}$), 125.13 (d), 125.73 (d), 127.27 (d), 127.81 (d), 128.77 (d), 129.09 (d, $J_{\text{C},\text{Sn}} = 20\text{ Hz}$), 129.09 (d), 130.32 (d), 136.71 (d, $J_{\text{C},\text{Sn}} = 38\text{ Hz}$), 139.58 (s), 140.73 (s, $J_{\text{C},\text{Sn}} = 63\text{ Hz}$),

142.84 (s, $J_{\text{C},\text{Sn}} = 45\text{ Hz}$), 144.21 (s, $J_{\text{C},\text{Sn}} = 390$, 408 Hz), 154.69 (s, $J_{\text{C},\text{Sn}} = 81\text{ Hz}$) ppm. ^{119}Sn NMR (CDCl_3): $\delta = -47.3$ ppm. $\text{C}_{72}\text{H}_{58}\text{Sn}_2$ (1160.70): calcd. C 74.51, H 5.04; found C 74.00, H 5.09.

Reaction of Pentaphenylstannole Anion 1 with 1,5-Dibromopentane: 1,5-Dibromopentane (0.046 mL, 0.35 mmol) was added to a THF (5 mL) solution of **1** prepared from **4** (430 mg, 0.68 mmol) and lithium (14 mg, 2.0 mmol) at room temperature. After removal of volatile substances, the residue was subjected to GPC to afford 1,5-bis(1,2,3,4,5-pentaphenyl-1-stannacyclopentadienyl)pentane (**11**) (152 mg, 0.13 mmol, 38%). **11**: M.p. $85\text{--}87\text{ }^{\circ}\text{C}$ (decomp.). ^1H NMR (CDCl_3): $\delta = 1.31\text{--}1.43$ (m, 2 H), $1.43\text{--}1.58$ (m, 4 H), $1.58\text{--}1.77$ (m, 4 H), $6.63\text{--}6.84$ (m, 16 H), $6.84\text{--}7.00$ (m, 24 H), $7.29\text{--}7.42$ (m, 6 H), $7.42\text{--}7.63$ (m, 4 H) ppm. ^{13}C NMR (CDCl_3): $\delta = 13.27$ (t, $^1J_{\text{C},\text{Sn}} = 355$, 372 Hz), 26.26 (t, $^3J_{\text{C},\text{Sn}} = 24\text{ Hz}$), 37.98 (t, $^2J_{\text{C},\text{Sn}} = 54\text{ Hz}$), 125.10 (d), 125.71 (d), 127.28 (d), 127.79 (d), 128.74 (d), 129.14 (d, $J_{\text{C},\text{Sn}} = 20\text{ Hz}$), 129.14 (d), 130.29 (d), 136.72 (d, $J_{\text{C},\text{Sn}} = 44\text{ Hz}$), 139.63 (s), 140.75 (s, $J_{\text{C},\text{Sn}} = 63\text{ Hz}$), 142.90 (s, $J_{\text{C},\text{Sn}} = 44\text{ Hz}$), 144.32 (s, $J_{\text{C},\text{Sn}} = 389$, 406 Hz), 154.63 (s, $J_{\text{C},\text{Sn}} = 79\text{ Hz}$) ppm. ^{119}Sn NMR (CDCl_3): $\delta = -46.5$ ppm. $\text{C}_{73}\text{H}_{60}\text{Sn}_2$ (1174.73): calcd. C 74.64, H 5.15; found C 74.59, H 5.15.

Reaction of Pentaphenylstannole Anion 1 with 1,6-Dibromohexane: 1,6-Dibromohexane (0.04 mL, 0.27 mmol) was added to a THF (4 mL) solution of **1** prepared from **4** (338 mg, 0.54 mmol) and lithium (11 mg, 1.59 mmol) at room temperature. After removal of volatile substances, the residue was subjected to GPC to afford 1,6-bis(1,2,3,4,5-pentaphenyl-1-stannacyclopentadienyl)hexane (**12**) (151 mg, 0.13 mmol, 47%). **12**: M.p. $75\text{--}80\text{ }^{\circ}\text{C}$ (decomp.). ^1H NMR (CDCl_3): $\delta = 1.15\text{--}1.30$ (m, 4 H), $1.51\text{--}1.75$ (m, 8 H), $6.70\text{--}6.86$ (m, 16 H), $6.86\text{--}7.05$ (m, 24 H), $7.26\text{--}7.35$ (m, 6 H), $7.45\text{--}7.63$ (m, 4 H) ppm. ^{13}C NMR (CDCl_3): $\delta = 13.63$ (t, $^1J_{\text{C},\text{Sn}} = 358$, 373 Hz), 26.78 (t, $^3J_{\text{C},\text{Sn}} = 24\text{ Hz}$), 33.45 (t, $^2J_{\text{C},\text{Sn}} = 50\text{ Hz}$), 125.08 (d), 125.70 (d), 127.28 (d), 127.78 (d), 128.74 (d), 129.05 (d, $J_{\text{C},\text{Sn}} = 20\text{ Hz}$), 129.05 (d), 130.29 (d), 136.71 (d, $J_{\text{C},\text{Sn}} = 45\text{ Hz}$), 139.71 (s), 140.77 (s, $J_{\text{C},\text{Sn}} = 63\text{ Hz}$), 142.89 (s, $J_{\text{C},\text{Sn}} = 45\text{ Hz}$), 144.41 (s, $J_{\text{C},\text{Sn}} = 388$, 407 Hz), 154.61 (s, $J_{\text{C},\text{Sn}} = 78\text{ Hz}$) ppm. ^{119}Sn NMR (CDCl_3): $\delta = -46.6$ ppm. $\text{C}_{74}\text{H}_{62}\text{Sn}_2$ (1188.76): calcd. C 74.77, H 5.26; found C 75.01, H 5.39.

Reaction of Pentaphenylstannole Anion 1 with 1,2-Dichloroethane: Excess 1,2-dichloroethane (2 mL, 32 mmol) was added to a THF (4 mL) solution of **1** prepared from **4** (252 mg, 0.40 mmol) and lithium (9 mg, 1.30 mmol) at room temperature. After volatile substances were removed, the residue was washed with hexane to give 1,1'-bistannole **2**^[8,9] (298 mg, 0.27 mmol, 71%).

Reaction of Pentaphenylstannole Anion 1 with 1,2-Dibromoethane: Excess 1,2-dibromoethane (0.5 mL, 5.8 mmol) was added to a THF (5 mL) solution of **1** prepared from **4** (303 mg, 0.48 mmol) and lithium (11 mg, 1.59 mmol) at room temperature. After volatile substances were removed, the residue was washed with hexane to give 1,1'-bistannole **2**^[8,9] (196 mg, 0.18 mmol, 74%).

Formation of 2 by Oxidation of Pentaphenylstannole Anion 1: A THF (7 mL) solution of **1** prepared from **4** (408 mg, 0.65 mmol) and lithium (12 mg, 1.69 mmol) was exposed to air for a few minutes. After volatile substances were removed, the residue was washed with hexane to give 1,1'-bistannole **2**^[8,9] (120 mg, 0.11 mmol, conv. 70%). The starting **4** was recovered in 20% yield.

Reaction of Pentaphenylstannole Anion 1 with Di-tert-butylchlorostannane: A THF (4 mL) solution of **1** prepared from **4** (250 mg, 0.40 mmol) and lithium (8 mg, 1.16 mmol) was added to a THF (2 mL) solution of di-tert-butylchlorostannane (121 mg, 0.40 mmol) at $-100\text{ }^{\circ}\text{C}$. The reaction mixture was warmed to room

temperature and stirred overnight. After removal of volatile substances, the residue was subjected to GPC to afford di-*tert*-butylbis(1,2,3,4,5-pentaphenyl-1-stannacyclopentadienyl)stannane (**14**) (109 mg, 0.08 mmol, conv. 49%). The starting **4** was recovered in 16% yield. **14**: M.p. 138–140 °C (decomp.). ^1H NMR (CDCl_3): δ = 1.15 (s, $J_{\text{H},\text{Sn}}$ = 7, 77 Hz, 18 H), 6.72–6.83 (m, 24 H), 6.91–6.94 (m, 16 H), 7.25–7.34 (m, 6 H), 7.52–7.66 (m, 4 H) ppm. ^{13}C NMR (CDCl_3): δ = 33.33 (q, $J_{\text{C},\text{Sn}}$ = 10 Hz), 35.31 (s, $J_{\text{C},\text{Sn}}$ = 31 Hz), 125.10 (d), 125.64 (d), 127.19 (d), 127.60 (d), 128.68 (d, $J_{\text{C},\text{Sn}}$ = 11 Hz), 128.96 (d, $J_{\text{C},\text{Sn}}$ = 44 Hz), 129.59 (d, $J_{\text{C},\text{Sn}}$ = 20 Hz), 130.93 (d), 137.40 (d, $J_{\text{C},\text{Sn}}$ = 41 Hz), 140.99 (s), 141.16 (s, $J_{\text{C},\text{Sn}}$ = 54 Hz), 142.73 (s, $J_{\text{C},\text{Sn}}$ = 47 Hz), 148.60 (s, $J_{\text{C},\text{Sn}}$ = 16 Hz), 154.25 (s, $J_{\text{C},\text{Sn}}$ = 71 Hz) ppm. ^{119}Sn NMR (CDCl_3): δ = –103.2 ($^1J_{\text{Sn},\text{Sn}}$ = 329 Hz), –44.8 ($^1J_{\text{Sn},\text{Sn}}$ = 329 Hz) ppm. $\text{C}_{76}\text{H}_{68}\text{Sn}_3$ (1337.54): calcd. C 68.25, H 5.12; found C 68.23, H 5.11.

Reaction of 1-*tert*-Butylstannole Anion 16 with Methyl Iodide: A diethyl ether (5 mL) solution of stannole dianion **3** prepared from hexaphenylstannole **4** (270 mg, 0.43 mmol) and lithium (15 mg, 2.18 mmol) was added to a diethyl ether (2 mL) solution of *tert*-butyl chloride (0.05 mL, 0.46 mmol) was added at room temperature. After being stirred for 30 min, the mixture was treated with methyl iodide (0.03 mL, 0.07 mmol). After filtration of materials insoluble in dichloromethane, the filtrate was recrystallized from dichloromethane and methanol to give 1-*tert*-butyl-1-methyl-2,3,4,5-tetraphenylstannole (**15**)^[17] (130 mg, 0.24 mmol, 55%). **15**: M.p. 75–80 °C (decomp.) (CH_2Cl_2 + MeOH). ^1H NMR (CDCl_3): δ = 0.60 (s, $J_{\text{H},\text{Sn}}$ = 51 Hz, 3 H), 1.22 (s, $J_{\text{H},\text{Sn}}$ = 74 Hz, 9 H), 6.77–6.79 (m, 4 H), 6.83–6.85 (m, 4 H), 6.93–6.98 (m, 8 H), 7.04–7.08 (m, 4 H) ppm. ^{13}C NMR (CDCl_3): δ = –10.57 (q), 29.90 (s), 30.68 (q), 124.86 (d), 125.58 (d), 127.18 (d), 127.74 (d), 129.09 (d), 130.44 (d), 141.01 (s), 143.62 (s), 145.41 (s), 154.47 (s) ppm. ^{119}Sn NMR (CDCl_3): δ = 5.1 ppm. $\text{C}_{33}\text{H}_{32}\text{Sn}$ (547.35): calcd. C 72.42, H 5.89; found C 72.43, H 5.51.

Preparation of 1-*tert*-Butylstannole Anion 16: A diethyl ether (0.7 mL) solution of stannole dianion **3** prepared from hexaphenylstannole **4** (58 mg, 0.09 mmol) with lithium (5 mg, 0.72 mmol) was added to a diethyl ether (2 mL) solution of *tert*-butyl chloride (0.01 mL, 0.09 mmol) at room temperature. The resulting bright-red solution was degassed by freeze-pump-thaw cycles and sealed. **16**: ^1H NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): δ = 1.25 (s, 9 H), 6.61–6.78 (m, 12 H), 6.80–6.83 (m, 4 H), 6.88–6.90 (m, 4 H) ppm. ^{13}C NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): δ = 28.64 (s), 33.71 (q), 122.22 (d), 124.04 (d), 126.80 (d), 127.07 (d), 129.35 (d), 131.59 (d), 145.05 (s), 150.35 (s), 151.78 (s), 170.66 (s, $J_{\text{C},\text{Sn}}$ = 113 Hz) ppm. ^{119}Sn NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): δ = 30.4 ppm. ^7Li NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): δ = 0.92 ppm.

Formation of 17 by Oxidation of 1-*tert*-Butylstannole Anion 16: A diethyl ether (4 mL) solution of stannole dianion **3** prepared from hexaphenylstannole **4** (197 mg, 0.31 mmol) with lithium (21 mg, 3.03 mmol) was added to a diethyl ether (2 mL) solution of *tert*-butyl chloride (0.04 mL, 0.34 mmol) at room temperature. After being stirred for 30 min, the resulting bright-red solution was exposed to air for a few minutes. After filtration of materials insoluble in dichloromethane, the filtrate was recrystallized from dichloromethane and methanol to give bi(1-*tert*-butyl-2,3,4,5-tetraphenyl-1-stannacyclopentadienyl) (**17**)^[9] (45 mg, 0.042 mmol, 27%).

Reaction of Stannole Dianion 3 with Bromobenzene: A diethyl ether (7 mL) solution of stannole dianion **3** prepared from hexaphenylstannole **4** (404 mg, 0.64 mmol) and lithium (53 mg, 7.57 mmol) was added to a diethyl ether (2 mL) solution of bromobenzene (0.067 mL, 0.64 mmol) at room temperature. After being stirred for 5 h, the resulting solution was exposed to air for a few minutes.

After filtration of materials insoluble in dichloromethane, a complex mixture (293 mg) was obtained.

Preparation of 1-(2,4,6-Triisopropylphenyl)stannole Anion 19: A diethyl ether (10 mL) solution of stannole dianion **3** prepared from hexaphenylstannole **4** (707 mg, 1.12 mmol) with lithium (77 mg, 11.1 mmol) was added to a diethyl ether (3 mL) solution of 1-bromo-2,4,6-triisopropylbenzene (317 mg, 1.12 mmol) at room temperature. After being stirred overnight, the resulting deep-red solution was degassed by freeze-pump-thaw cycles and sealed. In a glovebox, after filtration of insoluble materials, the filtrate was concentrated. The residue was washed with hexane to give 1-lithio-1-(2,4,6-triisopropylphenyl)-2,3,4,5-tetraphenylstannole (**19**). **19**: ^1H NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): δ = 1.12–1.17 (m, 18 H), 2.66–2.80 (sept, $J_{\text{H},\text{H}}$ = 7 Hz, 2 H), 2.88–2.98 (sept, $J_{\text{H},\text{H}}$ = 7 Hz, 1 H), 6.55–6.61 (m, 2 H), 6.61–6.67 (m, 2 H), 6.67–6.77 (m, 8 H), 6.77–6.85 (m, 10 H) ppm. ^{13}C NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): δ = 24.25 (q), 25.84 (q), 34.82 (d), 40.93 (d), 122.24 (d), 122.43 (d), 124.22 (d), 124.45 (d), 126.80 (d), 127.04 (d), 127.39 (d, $J_{\text{C},\text{Sn}}$ = 14 Hz), 128.53 (d), 128.74 (d, $J_{\text{C},\text{Sn}}$ = 14 Hz), 131.47 (d), 138.60 (d, $J_{\text{C},\text{Sn}}$ = 47 Hz), 144.74 (s), 148.97 (s), 149.69 (s, $J_{\text{C},\text{Sn}}$ = 35 Hz), 152.23 (s, $J_{\text{C},\text{Sn}}$ = 15 Hz), 156.47 (s, $J_{\text{C},\text{Sn}}$ = 150 Hz), 161.61 (s), 170.39 (s, $J_{\text{C},\text{Sn}}$ = 90 Hz) ppm. ^{119}Sn NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): δ = –49.6 ppm. ^7Li NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): δ = 0.95 ppm. The elemental analysis of **19** could not be carried out because of its extremely high reactivity toward water and oxygen.

Reaction of Stannole Anion 19 with Methyl Iodide: A diethyl ether (4 mL) solution of stannole dianion **3** prepared from hexaphenylstannole **4** (150 mg, 0.24 mmol) and lithium (16 mg, 2.29 mmol) was added to a diethyl ether (2 mL) solution of 1-bromo-2,4,6-triisopropylbenzene (66 mg, 0.23 mmol) at room temperature. After being stirred for 4 h, the mixture was treated with methyl iodide (0.1 mL, 1.61 mol). After removal of volatile substances, materials insoluble in dichloromethane were removed by filtration. The residue was subjected to GPC to afford 1-methyl-2,3,4,5-tetraphenyl-1-(2,4,6-triisopropylphenyl)stannole (**18**) (48 mg, 0.07 mmol, 29%). **18**: M.p. 188 °C (decomp.). ^1H NMR (CDCl_3): δ = 0.96 (s, $J_{\text{H},\text{Sn}}$ = 55 Hz, 3 H), 1.05 (d, $J_{\text{H},\text{H}}$ = 7 Hz, 12 H), 1.24 (d, $J_{\text{H},\text{H}}$ = 7 Hz, 6 H), 2.86 (sept, $J_{\text{H},\text{H}}$ = 7 Hz, 1 H), 2.97 (sept, $J_{\text{H},\text{H}}$ = 7 Hz, 2 H), 6.73–6.84 (m, 4 H), 6.84–6.95 (m, 12 H), 6.95–7.05 (m, 6 H) ppm. ^{13}C NMR (CDCl_3): δ = –3.04 (q, $J_{\text{C},\text{Sn}}$ = 323 Hz), 23.88 (q), 24.93 (q), 34.14 (d), 38.13 (d, $J_{\text{C},\text{Sn}}$ = 33 Hz), 121.50 (d, $J_{\text{C},\text{Sn}}$ = 49 Hz), 124.90 (d), 125.49 (d), 127.07 (d), 127.62 (d), 128.93 (d, $J_{\text{C},\text{Sn}}$ = 20 Hz), 130.30 (d), 137.17 (s), 140.93 (s, $J_{\text{C},\text{Sn}}$ = 63 Hz), 143.12 (s, $J_{\text{C},\text{Sn}}$ = 45 Hz), 147.09 (s, $J_{\text{C},\text{Sn}}$ = 406 Hz), 150.12 (s, $J_{\text{C},\text{Sn}}$ = 10 Hz), 153.08 (s, $J_{\text{C},\text{Sn}}$ = 84 Hz), 155.92 (s, $J_{\text{C},\text{Sn}}$ = 43 Hz) ppm. ^{119}Sn NMR (CDCl_3): δ = –66.0 ppm. $\text{C}_{44}\text{H}_{46}\text{Sn}$ (693.60): calcd. C 76.20, H 6.69; found C 76.19, H 6.71.

Oxidation of Stannole Anion 19: A diethyl ether (4 mL) solution of stannole dianion **3** prepared from hexaphenylstannole **4** (310 mg, 0.49 mmol) and lithium (32 mg, 4.61 mmol) was added to 1-bromo-2,4,6-triisopropylbenzene (139 mg, 0.49 mmol) at room temperature. After being stirred for 8 h, the resulting solution was exposed to air for a few minutes. After filtration of materials insoluble in diethyl ether, a complex mixture (410 mg) was obtained.

Preparation of 1-[2,6-Bis(2,4,6-trimethylphenyl)phenyl]stannole Anion 21: A diethyl ether (7 mL) solution of stannole dianion **3** prepared from hexaphenylstannole **4** (770 mg, 1.22 mmol) and lithium (86 mg, 12.3 mmol) was added to a diethyl ether (3 mL) solution of 1-iodo-2,6-bis(2,4,6-trimethylphenyl)benzene^[23] (450 mg, 1.09 mmol) at room temperature. After being stirred for 3 d, the resulting deep-red solution was degassed by freeze-pump-thaw cycles and sealed. After removal of insoluble materials by filtration,

the filtrate was concentrated in a glovebox to give 1-[2,6-bis(2,4,6-trimethylphenyl)phenyl]-1-lithio-2,3,4,5-tetraphenylstannole (**21**). The ^1H and ^{13}C NMR signals due to **21** are too complicated to be assigned probably because of steric congestion. However, in the ^{13}C NMR spectrum, the signal assignable to the α -carbon atom was observed at $\delta = 170.34$ ppm. **21**: ^{119}Sn NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = -50.2$ ppm. ^7Li NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = 0.15$ ppm. The elemental analysis of **21** could not be carried out because of its extremely high reactivity toward water and oxygen.

Preparation of 1-[2,6-Bis(2,4,6-triisopropylphenyl)phenyl]stannole Anion 22: A diethyl ether (5 mL) solution of stannole dianion **3** from hexaphenylstannole **4** (319 mg, 0.50 mmol) and lithium (35 mg, 5.07 mmol) was added to a diethyl ether (2 mL) solution of 1-iodo-2,6-bis(2,4,6-triisopropylphenyl)benzene^[24] (230 mg, 0.48 mmol) at room temperature. After being stirred for 3 d, the resulting deep-red solution was degassed by freeze-pump-thaw cycles and sealed. After removal of insoluble materials by filtration, the filtrate was concentrated in a glovebox to give 1-[2,6-bis(2,4,6-triisopropylphenyl)phenyl]-1-lithio-2,3,4,5-tetraphenylstannole (**22**). The ^1H and ^{13}C NMR signals for **22** are too complicated to be assigned probably because of steric congestion. However, in the ^{13}C NMR spectrum, the signal assignable to the α -carbon atom was observed at $\delta = 170.33$ ppm. **22**: ^{119}Sn NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = -47.1$ ppm. ^7Li NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = 0.61$ ppm. The elemental analysis of **22** could not be carried out because of its extremely high reactivity toward water and oxygen.

Preparation of 1-Triisopropylsilylstannole Anion 23: Chlorotriisopropylsilane (0.025 mL, 0.12 mmol) was added to a diethyl ether (1 mL) solution of stannole dianion **3** (54 mg, 0.11 mmol) at room temperature in a glovebox. After being stirred overnight, the reaction mixture was concentrated in a glovebox to give 1-lithio-2,3,4,5-tetraphenyl-1-(triisopropylsilyl)stannole (**23**). **23**: ^1H NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = 1.20$ – 1.46 (m, 3 H), 6.61 – 6.64 (m, 4 H), 6.64 – 6.75 (m, 6 H), 6.81 – 6.89 (m, 10 H) ppm. The signals due to the methyl protons of the triisopropylsilyl groups are overlapped with those of the methyl protons of diethyl ether. ^{13}C NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = 15.52$ (q), 20.29 (d, $J_{\text{C},\text{Sn}} = 13$ Hz), 124.78 (d), 125.47 (d), 127.35 (d), 127.59 (d), 130.59 (d), 130.94 (d), 142.77 (s, $J_{\text{C},\text{Sn}} = 37$ Hz), 145.50 (s, $J_{\text{C},\text{Sn}} = 40$ Hz), 155.04 (s, $J_{\text{C},\text{Sn}} = 46$ Hz), 156.01 (s, $J_{\text{C},\text{Sn}} = 190$ Hz) ppm. ^{119}Sn NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = -218.5$ ($^1J_{\text{Sn},\text{Si}} = 380$ Hz) ppm. ^7Li NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = 0.48$ ppm. The elemental analysis of **23** could not be carried out because of its extremely high reactivity toward water and oxygen.

Reaction of the 1-Triisopropylsilylstannole Anion 23 with Methyl Iodide: In a glovebox, a diethyl ether (3 mL) solution of stannole dianion **3** (94 mg, 0.19 mmol) and chlorotriisopropylsilane (0.041 mL, 0.19 mmol) was stirred at room temperature overnight and the resulting mixture was treated with methyl iodide (0.1 mL, 1.61 mmol). After removal of materials insoluble in diethyl ether, a complex mixture (101 mg) was obtained.

Preparation of 1-Triphenylstannylstannole Anion 24: Chlorotriphenylstannane (55 mg, 0.16 mmol) was added to a diethyl ether (2 mL) solution of stannole dianion **3** (70 mg, 0.14 mmol) at room temperature in a glovebox. After being stirred overnight, the reaction mixture was concentrated in a glovebox to give 1-lithio-2,3,4,5-tetraphenyl-1-(triphenylstannyl)stannole (**24**). **24**: ^1H NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = 6.55$ – 6.80 (m, 16 H), 6.80 – 6.94 (m, 4 H), 6.94 – 7.06 (m, 9 H), 7.35 – 7.46 (m, 6 H) ppm. ^{13}C NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = 122.48$ (d), 124.10 (d), 126.73 (d), 126.82 (d), 127.09 (d), 127.71 (d), 129.58 (d), 131.76 (d), 138.51 (d, $J_{\text{C},\text{Sn}} = 37$, 188 Hz), 144.83 (s), 148.85 (s), 149.70 (s), 151.99 (s), 172.03 (s, $J_{\text{C},\text{Sn}} = 148$ Hz) ppm. ^{119}Sn NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = -98.7$ ($^1J_{\text{Sn},\text{Sn}} = 3801$ Hz), -240.5 ($^1J_{\text{Sn},\text{Sn}}$

$= 3801$ Hz) ppm. ^7Li NMR ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$): $\delta = -0.74$, 0.62 ppm. The elemental analysis of **24** could not be carried out because of its extremely high reactivity toward water and oxygen.

Reaction of 1-(Triphenylstannyl)stannole Anion 24 with Methyl Iodide: A diethyl ether (2 mL) solution of the stannole dianion **3** (102 mg, 0.21 mmol) and chlorotriphenylstannane (80 mg, 0.21 mmol) was stirred in a glovebox at room temperature for 2 h, and the resulting mixture was treated with methyl iodide (0.1 mL, 1.61 mmol). After removal of volatile substances, insoluble inorganic salts were filtered off. The residue was subjected to GPC to afford 1-methyl-2,3,4,5-tetraphenyl-1-(triphenylstannyl)-stannole (**25**) (80 mg, 0.097 mmol, 47%). **25**: M.p. 143°C (decomp.). ^1H NMR (CDCl_3): $\delta = 0.89$ (s, $J_{\text{H},\text{Sn}} = 15$, 53 Hz, 3 H), 6.70 – 6.80 (m, 8 H), 6.88 – 6.97 (m, 12 H), 7.25 – 7.34 (m, 9 H), 7.34 – 7.49 (m, 6 H) ppm. ^{13}C NMR (CDCl_3): $\delta = -7.59$ (q, $J_{\text{C},\text{Sn}} = 59$ Hz), 125.08 (d), 125.70 (d), 127.26 (d), 127.78 (d), 128.67 (d), 128.79 (d, $J_{\text{C},\text{Sn}} = 11$ Hz), 129.39 (d, $J_{\text{C},\text{Sn}} = 21$ Hz), 130.34 (d), 137.34 (d, $J_{\text{C},\text{Sn}} = 8$, 41 Hz), 139.13 (s, $J_{\text{C},\text{Sn}} = 55$ Hz), 140.86 (s, $J_{\text{C},\text{Sn}} = 5$, 58 Hz), 142.77 (s, $J_{\text{C},\text{Sn}} = 47$ Hz), 147.78 (s), 153.50 (s, $J_{\text{C},\text{Sn}} = 21$ Hz) ppm. ^{119}Sn NMR (CDCl_3): $\delta = -87.3$ (s, $^1J_{\text{Sn},\text{Sn}} = 3532$ Hz), -127.4 (s, $^1J_{\text{Sn},\text{Sn}} = 3532$ Hz) ppm. $\text{C}_{47}\text{H}_{38}\text{Sn}_2$ (840.25): calcd. C 67.18, H 4.56; found C 66.90, H 4.49.

Reaction of the 1-(Triphenylstannyl)stannole Anion 24 with Chlorotriphenylstannane: A diethyl ether (2 mL) solution of the stannole dianion **3** (107 mg, 0.22 mmol) and chlorotriphenylstannane (168 mg, 0.44 mmol) was stirred in a glovebox at room temperature for 30 min. The color of the reaction mixture changed from dark red to yellow. After removal of volatile substances, insoluble inorganic salts were filtered off. The residue was subjected to GPC to afford 2,3,4,5-tetraphenyl-1,1-bis(triphenylstannyl)stannole (**26**) (100 mg, 0.085 mmol, 39%). **26**: M.p. 175 – 177°C (decomp.). ^1H NMR (CDCl_3): $\delta = 6.48$ – 6.56 (m, 4 H), 6.66 – 6.75 (m, 8 H), 6.80 – 6.88 (m, 2 H), 6.88 – 7.00 (m, 6 H), 7.11 – 7.35 (m, 30 H) ppm. ^{13}C NMR (CDCl_3): $\delta = 124.91$ (d), 125.64 (d), 127.21 (d), 127.62 (d), 128.65 (d), 127.86 (d), 128.78 (d, $J_{\text{C},\text{Sn}} = 11$ Hz), 129.59 (d, $J_{\text{C},\text{Sn}} = 15$ Hz), 137.33 (d, $J_{\text{C},\text{Sn}} = 8$, 42 Hz), 139.06 (s, $J_{\text{C},\text{Sn}} = 11$, 54 Hz), 141.05 (s, $J_{\text{C},\text{Sn}} = 50$ Hz), 142.93 (s, $J_{\text{C},\text{Sn}} = 45$ Hz), 150.22 (s, $J_{\text{C},\text{Sn}} = 12$ Hz), 153.74 (s, $J_{\text{C},\text{Sn}} = 19$, 63 Hz) ppm. ^{119}Sn NMR (CDCl_3): $\delta = -115.7$ ($^1J_{\text{Sn},\text{Sn}} = 2159$ Hz, $^2J_{\text{Sn},\text{Sn}} = 615$ Hz), -219.8 ($^1J_{\text{Sn},\text{Sn}} = 2159$ Hz) ppm. The elemental analysis of **26** could not be carried out because of its instability. For the ^1H , ^{13}C , and ^{119}Sn NMR spectra of **26**, see Supporting Information.

Supporting Information (see footnote on the first page of this article): All NMR spectroscopic data of compounds, **1**, **16**, **19**, **21**, **22**, **23**, **24**, and **26**. Experimental details for control experiment of the reduction of 1,1'-bistannole **1** with lithium to give stannole anion **1** and dianion **3**.

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