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Silyl-Substituted Dithioles as Candidates for New Electron Donors

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Molecular orbital calculations revealed that the introduction of a silyl group onto the 2-position of 1,3-dithiole caused significant decrease of the ionization potential and that 2-silyl-1,3-dithioles served as a pseudo π-electron system. The silyl group could also be utilized as a bridge for linking π-electron systems to achieve artificial stacking. These concepts led us to the design and synthesis of silyl-substituted 1,3-benzodithioles as candidates for new electron donors. The oxidation potential of monosilyl-substituted 1,3-benzodithiole was found to be significantly less positive than that of the parent 1,3-benzodithiole. The introduction of the second silyl group caused further decrease of the oxidation potential. Compounds composed of two 1,3-benzodithiole units linked by a silyl group were also synthesized. These showed comparable oxidation potentials to those of the corresponding monomeric compounds. The effect of stannyl-substitution onto the 2-position of 1,3-dithiole was found to be larger than that of silyl-substitution. The effects of silyl- and stannyl-substitution for related systems such as thioanisole and 1,3-dithiane were also studied.

Since the electrical conductivity in the perylene-bromine complex was first reported,[1] significant interest in organic conducting materials (organic metals) has emerged among scientists in various fields. The finding of high electrical conductivity in the charge-transfer (CT) complex of tetrathiafulvalene (TTF) with tetracyanoquinodimethane (TCNQ)[2] was a highlight of this field and thereafter various derivatives of TTF have been synthesized and utilized as organic metals (Fig. 1). While the largest body of work on electron donors has been devoted to structural modifications of TTF,[3] very limited study was done to achieve the developments of new classes of donors, though such study is strongly needed.[4] During the course of our study directed toward identifying new electron donors utilizing unique electronic properties of silicon, we have recently reported the synthesis and the electrochemical behavior of silyl-substituted 1,3-dithioles as candidates for new electron donors.[5] In this paper we report the full details of this study.[5a]

Our approach towards a new class of electron donors is based on the following concepts.

(1) Silicon promotes the electron transfer from a heteroatom such as oxygen, nitrogen, and sulfur, at *β*-position (Fig. 2). Theoretical and experimental studies revealed that this effect was attributed to the rise of HOMO level by the interaction of a carbon–silicon σ orbital with a nonbonding p orbital of the heteroatom.[6] Such interaction also stabilizes the resulting radical cation and this stabilization also facilitates the electron transfer.

(2) Linking of donor π-systems with covalent bonds may be

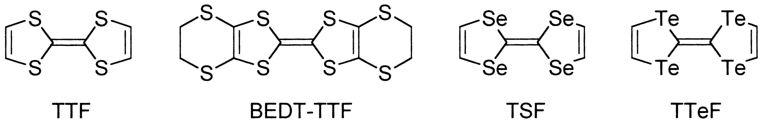


Fig. 1. TTF and its derivatives for organic metals.

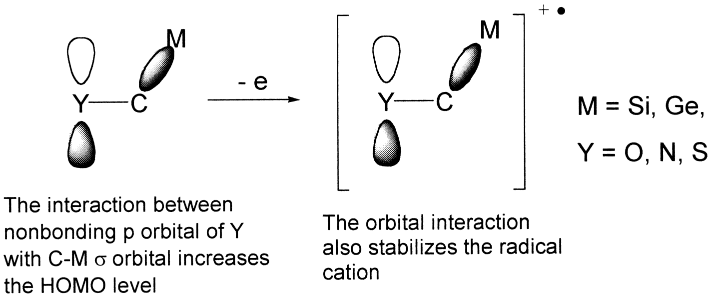


Fig. 2.

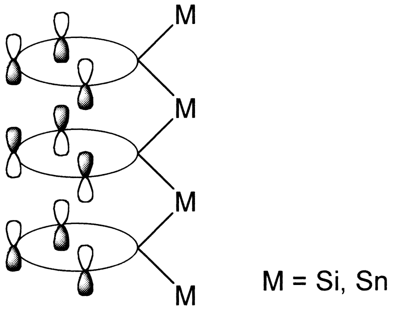


Fig. 3.

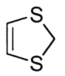
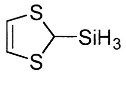
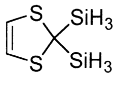
effective for the construction of artificial stackings.[7] It has been established that the high conductivity of organic metals is related to their crystal structures, in which the donors and the acceptors form segregated stacks with extensive π-electron overlap. Thus, achievement of the stacking of donor molecules to make columns in the CT complexes seems essential for the conductivity.[8] C–Si bonds which are longer than C–C bonds seem to be suitable for linking π-systems to achieve artificial stacking (Fig. 3).

Based on these concepts we envisioned that silicon could be utilized both for enhancing the electron-donating ability of π-systems containing heteroatoms and for linking the π-systems to construct artificial stacking.

Results and Discussion

Molecular Orbital Calculations. In the study directed toward a new class of electron donors utilizing the unique electronic property of group 14 elements, we focused our attention on 1,3-dithiole, which constitutes a half of TTF, as a core structure. Because ionization potential represents one of the most important properties of electron donors, the effect of silyl-substitution on the ionization potential of 1,3-dithiole was first examined using molecular orbital calculations. Ionization potentials based on the energy difference between the neutral molecule and the radical cation were calculated at MP2/3-21G* level (Table 1 and Fig. 4). The calculations indicated that the introduction of silicon onto the methylene carbon of 1,3-dithioles caused significant decrease of the ionization potential. This remarkable effect of silyl-substitution is attributed to the interaction between the carbon–silicon σ orbital and the p orbitals of the sulfur atoms in the radical cation. Because two sulfur atoms conjugate with the carbon-carbon double bond, the system serves as a pseudo π-system. It is noteworthy that the five-membered ring is almost flat in the cation radical (Fig. 4, **B′**) to ensure the effective conjugation in the ring (Fig. 4). The introduction of the second silyl group causes further decrease of the ionization potential. These results are consistent with the results of electrochemical studies on the oxidation potentials (vide infra). Because HOMO levels usually serve as effective indices of the ionization potentials, the HOMO levels of the neutral compounds were also determined by the calculations at HF/3-21G* level. Interestingly, the effect of silyl-substitution on the HOMO level was found to be quite different from that on the ionization potential. This is presumably attributed to the envelope-like conformation of the neutral molecules. In 2-silyl-1,3-dithiole the silyl group occupies the pseudo equatorial position (Fig. 4, **B**). Thus the interaction between the carbon–silicon σ orbital and the p orbitals of neighboring sulfur atoms is not effective in the neutral molecule because they are nearly perpendicular with each other. The envelope conformation of 1,3-dithiole moiety suggested by the calculation is consistent with the structure determined by the X-ray analysis (vide infra). The slight decrease of the HOMO level by the introduction of a silyl group indicates that the SiH_3 group is somewhat electron-withdrawing, although the detailed mechanism has not been clarified as yet. In 2,2-disilyl-1,3-dithiole, the second silyl group occupies the pseudo axial position (Fig. 4, **C′**) and the carbon–silicon σ orbital interacts effectively with the sulfur atoms to cause a very small increase of the HOMO level. Presumably the effect of the first silyl group and that of the second silyl group compensate each oth-

Table 1. Ionization Potentials of Silyl-Substituted Dithioles Obtained by Molecular Orbital Calculations

Compound	Ionization potential/eV[a]	HOMO level/eV	
	MP2/3-21G*	HF/3-21G*	PM3
	7.23	−8.04	−9.06
	6.97	−8.06	−8.69
	6.80	−7.98	−8.41

a) Adiabatic ionization potentials were calculated based on the difference in total energy between the neutral molecule and the radical cation, geometries of which are fully optimized.

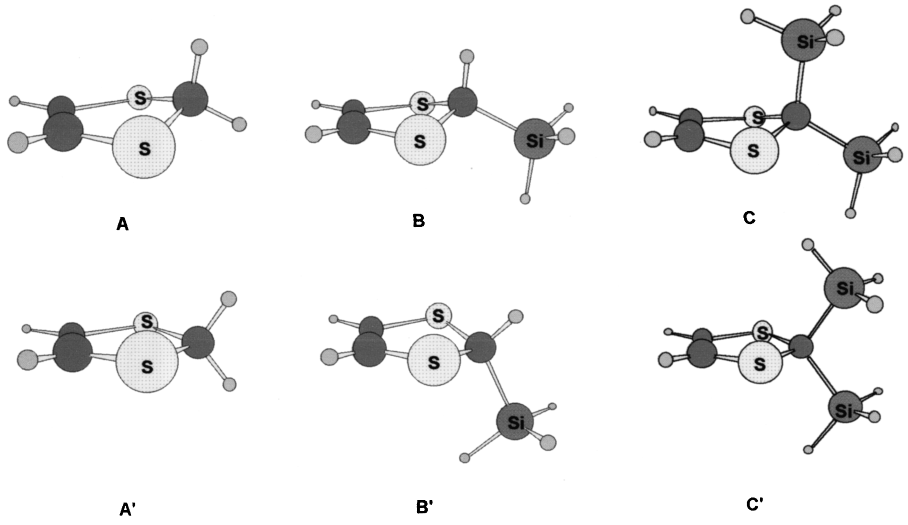
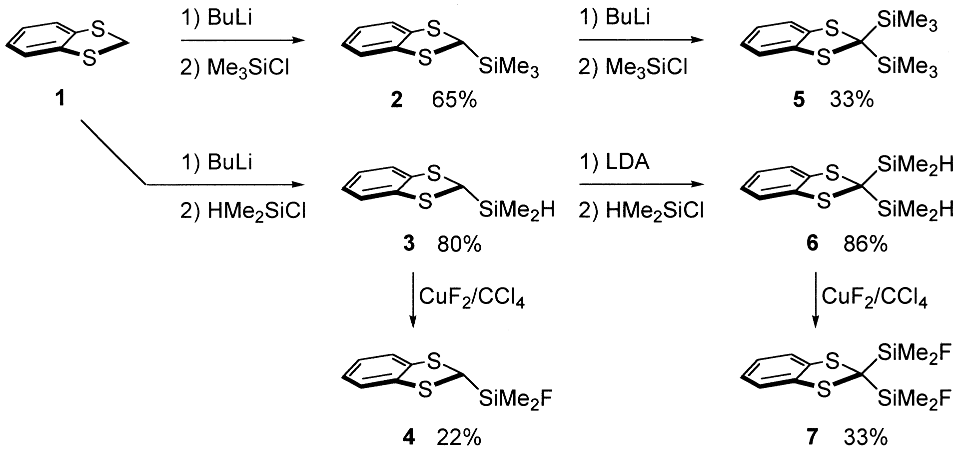


Fig. 4. Structures of neutral molecules of 1,3-dithiole (**A**), 2-silyl-1,3-dithiole (**B**), 2,2-disilyl-1,3-dithiole (**C**) and their radical cations (**A′**, **B′**, and **C′**) obtained by ab initio molecular orbital calculations (MP2/3-21G*).

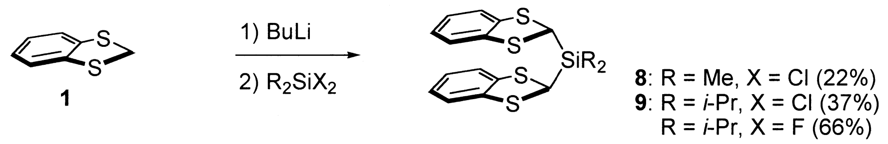
er. Based on these results, we can conclude that the HOMO levels obtained by HF/3-21G* calculations do not serve as good indices of the ionization potentials. The results of the semi-empirical calculations are interesting. The HOMO levels obtained by PM3 calculations correlate well with the ionization potentials based on the energy difference between the neutral molecule and the radical cation obtained by MP2/3-21G* calculations. This is presumably because the geometry optimization with PM3 calculations gives flat structures of neutral silyl-substituted 1,3-dithioles, in which the carbon–silicon σ orbtial interacts effectively with the p orbitals of the neighboring sulfur atoms. Therefore, the HOMO levels obtained by PM3 calculations seem to serve as good indices of the ionization potentials, although the structures of the neutral molecules are not correct.

Synthesis. As model compounds for electron donors based on our hypothesis, we designed a series of silicon-substituted 1,3-benzodithioles and related compounds (**2–13**). Silyl-substituted 1,3-benzodithioles were synthesized in a procedure shown in Scheme 1. 1,3-Benzodithiole (**1**)[9] was easily deprotonated with butyllithium in THF at about −23 °C.[10] Treatment of the resulting anion with chlorotrimethylsilane and chlorodimethylsilane gave 2-trimethylsilyl-1,3-benzodithiole (**2**) and 2-dimethylsilyl-1,3-benzodithiole (**3**), respectively. The second silyl group was introduced by the deprotonation of **2** with butyllithium followed by the reaction with chlorotrimethylsilane to give 2,2-bis(trimethylsilyl)-1,3-benzodithiole (**5**). Compound **6** was obtained by the deprotonation of **3** with lithium diisopropylamide (LDA) and successive reaction with chlorodimethylsilane. Hydrosilanes **3** and **6** were converted into the corresponding fluorosilanes **4** and **7** by CuF_2-mediated fluorination.[11]

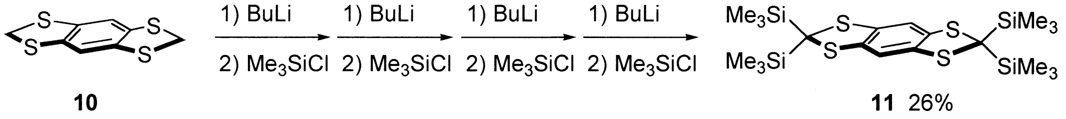
Silyl-linked 1,3-benzodithioles **8** and **9** were prepared as follows. Deprotonation of 1,3-benzodithiole (**1**), followed by the treatment with dichlorodimethylsilane, gave the desired silyl-linked compound **8** only in very poor yield. Although the use of dichlorodiisopropylsilane gave a better result, the yield was still low. The use of difluorodiisopropylsilane, however, led to the formation of the desired silyl-linked compound **9** in satisfactory yield (Scheme 2).



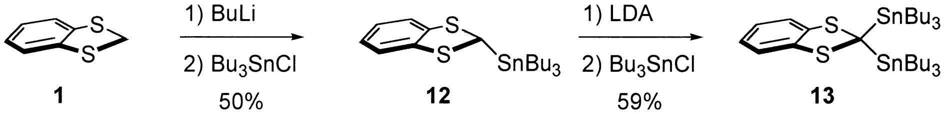
Scheme 1. Synthesis of silyl-substituted 1,3-benzodithioles.



Scheme 2. Synthesis of silyl-linked 1,3-benzodithioles.



Scheme 3. Synthesis of **11**.



Scheme 4. Synthesis of stannyl-substituted 1,3-benzodithioles.

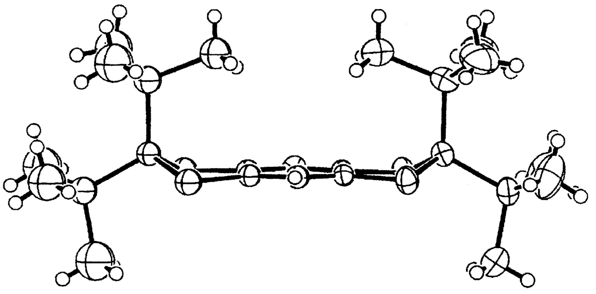


Fig. 5. X-ray crystal structure of **11**.

The synthesis of silyl-substituted benzo[1,2-*d*:4,5-*d*′]bis[1,3]dithiole **11** was simple and straightforward. Deprotonation of benzo[1,2-*d*:4,5-*d*′]bis[1,3]dithiole (**10**)[12] with 1.0 mol amt. of butyllithium, followed by the treatment with 1.0 mol amt. of chlorotrimethylsilane, gave the monosilylated compound together with small amounts of 2,2-bis-, 2,6-bis-, and 2,2,6-tris-silylated compounds, although they were not fully characterized. Repetition of the sequence of deprotonation and silylation in one-pot led to the formation of **11**, which was purified with flash chromatography followed by recrystallization (Scheme 3). X-ray crystal structure analysis revealed that the structure of **11** is non-planar and that the 1,3-dithiole rings constitute envelope-like conformations, as shown in Fig. 5, although ^{1}H NMR spectroscopy indicated that four Me_3Si groups are equivalent in solution.

Tin-substituted 1,3-benzodithioles **12** and **13** were also synthesized in a similar manner. As shown in Scheme 4, deprotonation of 1,3-benzodithiole with butyllithium followed by the reaction with tributylchlorostannane gave the monostannylated compound **12**, which was deprotonated with LDA. The resulting anion was allowed to react with tributylchlorostannane to give the distannylated compound **13**.

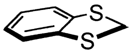
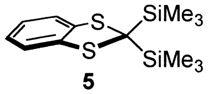
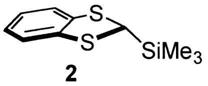
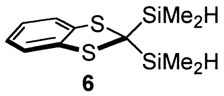
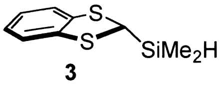
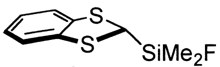
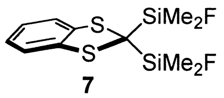
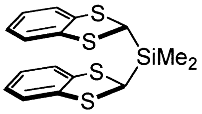
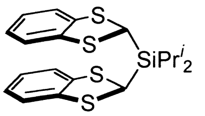
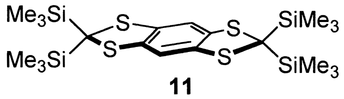
Electrochemistry. The oxidation potentials of silyl-substituted 1,3-benzodithiole derivatives were determined with rotating disk electrode voltammetry (Table 2). The oxidation potential of 2-trimethylsilyl-1,3-benzodithiole (**2**) was found to be less positive than that of 1,3-benzodithiole (**1**); this result is consistent with the ionization potentials obtained by the molecular orbital calculations. The oxidation potential of 2,2-bis(trimethylsilyl)-1,3-benzodithiole (**5**) was less positive than **2**, indicating that the introduction of the second silyl group caused a further decrease of the oxidation potential. As can be seen from the oxidation potentials of **3**, **4**, **6**, and **7**, the substituents on silicon slightly affect the electron donating ability.[11]

The electrochemical behavior of the silyl-linked 1,3-benzodithioles **8** and **9** was studied and the oxidation potentials are listed in Table 2. The value of compound **8** was found to be slightly more positive than that of the corresponding monomeric silyl-substituted 1,3-benzodithiole **2**. The effect of stacking of two benzodithiole rings, which might enhance the electron donating ability of **8**, was not observed. The reason for the slight increase of the oxidation potential is not clear at present. The introduction of more bulky substituents such as isopropyl groups on silicon, which might increase the population of the stacking conformer, did not change the oxidation potential remarkably (compound **9**). Therefore, the electrochemical study did not give any evidence for the stacking of two benzodithiole rings.

The oxidation potentials of benzo[1,2-*d*:4,5-*d*′]bis[1,3]dithiole (**10**) and 2,2,6,6-tetrakis(trimethylsilyl)benzo[1,2-*d*:4,5-*d*′]bis[1,3]dithiole (**11**), in which two 1,3-dithiole units are connected to a benzene ring, were also determined with rotating disk electrode voltammetry. The oxidation potential of **11** was much less positive than that of **10**, indicating the remarkable effect of silyl-substitution. Presumably, the four carbon–silicon σ orbitals interact effectively with the neighboring p orbitals of the sulfur atoms in the radical cation. This result coincides with the effect of silyl-substitution on benzodithiole.

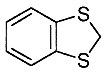
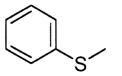
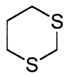
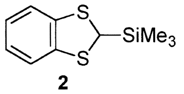
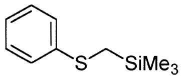
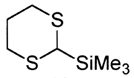
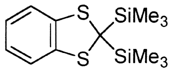
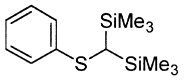
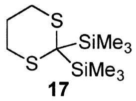
It is interesting to compare the effect of silicon for the oxidation of the benzodithiole system with that for the oxidation of other systems such as thioanisole and 1,3-dithiane. As

Table 2. Oxidation Potentials of Silyl-Substituted 1,3-Benzodithioles and Related Compounds

Compound	Ed/V	Compound	Ed/V
 **1**	$1.07^{a)}$	 **5**	$0.63^{a)}$
 **2**	$0.80^{a)}$	 **6**	$0.65^{a)}$
 **3**	$0.77^{a)}$		
 **4**	$0.90^{a)}$	 **7**	$0.81^{a)}$
 **8**	$0.85^{a)}$	 **10**	$1.04^{b)}$
 **9**	$0.82^{a)}$	 **11**	$0.64^{b)}$

a) Determined by rotating disk electrode voltammetry with a glassy carbon working electrode in 0.1 M $LiClO_4/CH_3CN$ vs SCE. b) Determined by rotating disk electrode voltammetry with a glassy carbon working electrode in 0.1 M Bu_4NClO_4/CH_2Cl_2 vs Ag/AgCl.

Table 3. Oxidation Potentials of Silyl-Substituted 1,3-Benzodithioles, Thioanisole, and 1,3-Dithianes

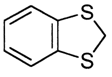
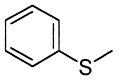
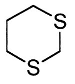
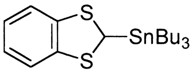
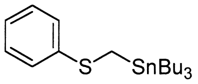
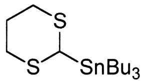
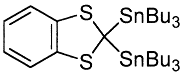
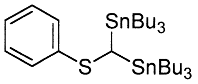
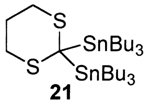
Compound	$Ed/V^{a)}$	Compound	$Ed/V^{a)}$	Compound	$Ep/V^{b)}$
	$1.07^{c)}$		$1.18^{c)}$		$1.18^{d)}$
 **2**	$0.80^{c)}$	 **14**	$1.13^{c)}$	 **16**	$0.99^{d)}$
 **5**	$0.63^{c)}$	 **15**	$1.04^{c)}$	 **17**	$0.70^{d)}$

a) Decomposition potential determined by rotating disk electrode voltammetry. b) Peak potential determined by cyclic voltammetry. c) Present work (in 0.1 M $LiClO_4/CH_3CN$ vs SCE). d) Ref. 13 (in 0.1 M $LiClO_4/CH_3CN$ vs $Ag/AgNO_3$).

shown in Table 3, the introduction of a silyl group onto the methyl carbon of thioanisole caused little decrease of the oxidation potential. This is probably because of the flexible conformation of (trimethylsilylmethylthio)benzene (**14**). The free rotation around the sulfur-carbon bond may disfavor the effective interaction between the carbon–silicon σ orbital with the p orbital of the sulfur. In the case of [bis(trimethylsilyl)methylthio]benzene (**15**), the conformation is still flexible and its oxidation potential was much higher than that of **5**.

The effect of mono-silyl-substitution for 1,3-dithiane was also smaller, as reported by Glass,[13] than that for 1,3-benzodithiole. Probably the fixed geometry of 2-trimethylsilyl-1,3-dithiane (**16**), in which the silyl group occupies the equatorial position, disfavors the interaction of the carbon–silicon σ orbital with the p orbitals of the sulfur atoms, because they are nearly in perpendicular orientation. The oxidation potential of 2,2-bis(trimethylsilyl)-1,3-dithiane (**17**) was, however, comparable to that of 2,2-bis(trimethylsilyl)-1,3-benzodithiole (**5**). The remarkable effect of the second silyl group is explained as follows. The second silyl group occupies the axial position in

Table 4. Oxidation Potentials of Stannyl-Substituted 1,3-Benzodithioles, Thioanisole, and 1,3-Dithianes

Compound	Ed/V[a)]	Compound	Ed/V[a)]	Compound	Ep/V[b)]
	1.07[c)]		1.18[c)]		1.18[d)]
 **12**	0.20[c)]	 **18**	0.68[c)]	 **20**	0.75[d)]
 **13**	−0.02[c)]	 **19**	0.47[c)]	 **21**	0.19[d)]

a) Decomposition potential determined by rotating disk electrode voltammetry. b) Peak potential determined by cyclic voltammetry. c) Present work (in 0.1 M $LiClO_4/CH_3CN$ vs SCE). d) Ref. 13 (in 0.1 M $LiClO_4/CH_3CN$ vs $Ag/AgNO_3$).

1,3-dithiane ring and this carbon–silicon σ orbital interacts effectively with the p orbitals of the sulfur atoms because they are almost in the same plane.

The oxidation potentials of stannyl-substituted 1,3-benzodithioles **12** and **13** were also determined with rotating disk electrode voltammetry. Table 4 included the oxidation potentials of stannyl-substituted 1,3-benzodithioles and some related compounds. The stannyl-substitution caused dramatic decrease of the oxidation potential. The larger effect of tin compared to that of silicon is attributed to the higher energy level of the carbon–tin σ orbital than that of the carbon–silicon σ orbital. The smaller energy gap between the carbon–tin σ orbital and the sulfur p orbitals gives rise to better orbital interaction.[6d] The effect of mono-stannyl-substitution in 1,3-benzodithiole was larger than that for thioanisole and 1,3-dithiane.[13] These results are quite similar to those for silicon cases. The introduction of the second stannyl group on 1,3-dithiane, however, caused a larger decrease of the oxidation potential than that for 1,3-benzodithiole. The axial carbon–tin bond in 1,3-dithiane interacts strongly with the sulfur p orbitals, which in turn favors the electron transfer.

Conclusion

The research reported above has demonstrated the potentiality of new electron donors based on *β*-effects of group 14 elements such as silicon and tin in electron transfer. The interaction of the carbon-group 14 element σ orbital with the neighboring p orbital of the heteroatom plays a crucial role to enhance the electron donating ability. Further work is in progress to synthesize various types of silicon- and tin-substituted π-systems to construct artificial stacking (Fig. 6), and to explore the unique properties of such electron donors.

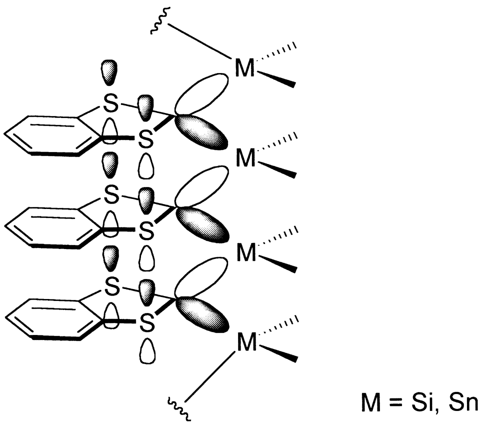


Fig. 6.

Experimental

General. Tetrahydrofuran (THF) was freshly distilled under argon from sodium benzophenone ketyl prior to use. Other reagents were commercially available and were used without further treatment. Flash chromatography was carried out using Kanto 60N silica gel. ^1H, ^{13}C, and ^{29}Si NMR spectra were measured on a Varian Gemini 2000 spectrometer at 300, 75, and 60 MHz, respectively. Infrared (IR) spectra were obtained on a Shimadzu FTIR-8100 spectrophotometer. Mass spectra were determined on a JEOL JMS-SX102A spectrometer. Melting points were measured by a Tanako micro melting point apparatus.

Molecular Orbital Calculations. The ab initio calculations were carried out using the GAUSSIAN 98 program (G98W)[14] at the HF/3-21G* and MP2/3-21G* level. The semi-empirical calculations were carried out using Chem 3D program. All geometries were fully optimized.

Electrochemistry. The oxidation potential measurements were carried out by using rotating disk electrode voltammetry with a Bioanalytical Systems BAS 100B and a Nikko Keisoku RDE-1, using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) reference in 0.1 M $LiClO_4/CH_3CN$ at 5000 rpm. The sweep rate was 10 mV/s.

Synthesis. 1,3-Benzodithiole (**1**),[9] benzo[1,2-*d*:4,5-*d*′]bis-[1,3]dithiole (**10**),[12] and (trimethylsilylmethylthio)benzene (**14**)[15] were synthesized in modified procedures reported in the literature.

2-Trimethylsilyl-1,3-benzodithiole (2): A solution of 1.50 M butyllithium in hexane (1.0 mL, 1.50 mmol) was added at 0 °C to a solution of compound **1** (220 mg, 1.43 mmol) in dry THF (3 mL) and the solution was stirred at 0 °C for 1.5 h. The organolithium compound thus obtained was added at −20 °C to another flask containing chlorotrimethylsilane (0.19 mL, 162 mg, 1.50 mmol) and THF (5 mL). After being stirred at −20 °C–rt for 3 h, the mixture was poured into water (20 mL) and extracted with *t*-butyl methyl ether (20 mL × 2). The ether phase was separated and dried over anhydrous magnesium sulfate. Evaporation of the solvent and subsequent purification of the residue by flash chromatography with hexane as the eluent afforded **2** as pale yellow needles (211 mg, 65%): Mp 67.0–68.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 9H), 4.52 (s, 1H), 6.96–7.20 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.6, 39.5, 122.1, 125.5, 140.1; ^{29}Si NMR (60 MHz, $CDCl_3$) δ 3.74; IR (KBr) 1561, 1441, 1431, 1260, 1123, 1109, 1030, 1013, 930, 845, 777, 758, 743, 702, 673, 637 cm^{-1}; UV–vis (CH_3CN, λ_{max}/nm) 393, 290, 281, 233, 215; LRMS (EI) *m/z* (%) 226 (M$^+$, 18), 212 (3), 183 (7), 168 (3), 153 (100), 108 (6), 82 (3), 73 (16), 69 (6), 58 (4); HRMS (EI) Calcd for $C_{10}H_{14}S_2Si$: (M$^+$), 226.0306. Found: *m/z* 226.0315. Found: C, 53.11; H, 6.08%. Calcd for $C_{10}H_{14}S_2Si$: C, 53.09; H, 6.24%.

2-Dimethylsilyl-1,3-benzodithiole (3): The title compound was synthesized in a similar manner to **2**. Pure compound **3** was obtained as pale yellow needles after purification by flash chromatography with hexane as the eluent (80%): Mp 55.0–56.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.33 (d, 6H, J = 3.9 Hz), 4.19–4.22 (m, 1H), 4.55 (d, 1H, J = 1.8 Hz), 6.97–7.21 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.3, 36.9, 122.1, 125.5, 139.7; ^{29}Si NMR (60 MHz, $CDCl_3$) δ −12.0; IR (KBr) 2153, 1561, 1441, 1281, 1253, 1123, 1109, 1017, 936, 787, 666, 631 cm^{-1}; LRMS (EI) *m/z* (%) 212 (M$^+$, 30), 211 (4), 183 (4), 168 (2), 153 (100), 121 (3), 109 (2), 91 (2), 77 (9), 59 (3); HRMS (EI) Calcd for $C_9H_{12}S_2Si$: (M$^+$), 212.0150. Found: *m/z* 212.0150. Found: C, 50.60; H, 5.71%. Calcd for $C_9H_{12}S_2Si$: C, 50.89; H, 5.69%.

2-Fluorodimethylsilyl-1,3-benzodithiole (4): To a suspension of $CuF_2{\cdot}2H_2O$ (275 mg, 2.0 mmol) in CCl_4 (5 mL) was added a solution of **3** (106 mg, 0.5 mmol) in CCl_4 (2 mL). The mixture was stirred at room temperature for 24 h. The solids were removed by filtration and the filtrate was evaporated. Flash chromatography of the residue with hexane as the eluent gave **4** (25.3 mg, 22%) as pale yellow needles: Mp 66.5–67.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.45 (d, 6H, $J_{H\text{–}F}$ = 7.5 Hz), 4.51 (s, 1H), 6.99–7.21 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.0 (d, $J_{C\text{–}F}$ = 13.7 Hz), 36.9 (d, $J_{C\text{–}F}$ = 15.9 Hz), 122.2, 125.7, 138.8; ^{29}Si NMR (60 MHz, $CDCl_3$) δ 24.46 (d, $J_{Si\text{–}F}$ = 290.4 Hz); IR (KBr) 1655, 1561, 1441, 1262, 1125, 1015, 941, 887, 808, 762, 743, 664 cm^{-1}; LRMS (EI) *m/z* (%) 230 (M$^+$, 76), 215 (7), 187 (4), 168 (9), 153 (100), 140 (39), 108 (15), 96 (11), 77 (62), 69 (20), 63 (10). Found: C, 46.75; H, 4.72; F, 8.02%. Calcd for $C_9H_{11}FS_2Si$: C, 46.92; H, 4.81; F, 8.25%.

2,2-Bis(trimethylsilyl)-1,3-benzodithiole (5): The title compound was synthesized in a similar manner to **2** by using compound **2** as the starting material. Pure compound **5** was obtained as colorless needles after purification by flash chromatography with hexane as the eluent (33%): Mp 67.0–67.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.20 (s, 18H), 6.91–7.00 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.2, 35.7, 121.1, 125.3, 140.7; ^{29}Si NMR (60 MHz, $CDCl_3$) δ 6.56; IR (KBr) 2951, 1565, 1445, 1406, 1248, 1115, 1034, 1015, 930, 781, 743, 714, 673, 631, 619 cm^{-1}; UV–vis (CH_3CN, λ_{max}/nm) 321, 244; LRMS (EI) *m/z* (%) 298 (M$^+$, 16), 283 (5), 225 (100), 210 (19), 183 (15), 177 (3), 151 (9), 91 (3), 73 (48); HRMS (EI) Calcd for $C_{13}H_{22}S_2Si_2$: (M$^+$), 298.0701. Found: *m/z* 298.0716. Found: C, 52.12; H, 7.67%. Calcd for $C_{13}H_{22}S_2Si_2$: C, 52.29; H, 7.43%.

2,2-Bis(dimethylsilyl)-1,3-benzodithiole (6): The title compound was synthesized in a similar manner to **5**. Pure compound **6** was obtained as pale yellow oil after purification by flash chromatography with hexane as the eluent (86%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (d, 12H, J = 3.3 Hz), 4.13–4.16 (m, 2H), 6.91–7.09 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9, 32.4, 121.7, 125.6, 140.0; ^{29}Si NMR (60 MHz, $CDCl_3$) δ −9.89; IR (neat) 2959, 2901, 2855, 2126, 1891, 1566, 1509, 1443, 1250, 1115, 1030, 1013, 793, 739, 698, 673, 662, 633 cm^{-1}; LRMS (EI) *m/z* (%) 270 (M$^+$, 35), 255 (6), 211 (100), 196 (49), 183 (95), 177 (25), 151 (37), 137 (10), 121 (18), 91 (10), 77 (9), 59 (54); HRMS (EI) Calcd for $C_{11}H_{18}S_2Si_2$: (M$^+$), 270.0388. Found: *m/z* 270.0392. Found: C, 48.56; H, 6.95%. Calcd for $C_{11}H_{18}S_2Si_2$: C, 48.83; H, 6.71%.

2,2-Bis(fluorodimethylsilyl)-1,3-benzodithiole (7): The title compound was synthesized in a similar manner to **4**. Pure compound **7** was obtained as yellow oil after purification by flash chromatography with hexane as the eluent (33%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.46 (d, 12H, $J_{H\text{–}F}$ = 8.1 Hz), 6.95–7.10 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.9 (d, $J_{C\text{–}F}$ = 13.7 Hz), 31.5, 121.9, 126.1, 139.1; ^{29}Si NMR (60 MHz, $CDCl_3$) δ 23.90 (d, $J_{Si\text{–}F}$ = 294.0 Hz); IR (neat) 2979, 1904, 1561, 1445, 1431, 1406, 1279, 1260, 1248, 1115, 1030, 1011, 787, 745, 668, 644 cm^{-1}; LRMS (EI) *m/z* (%) 306 (M$^+$, 20), 229 (100), 210 (11), 183 (3), 153 (7), 77 (9); HRMS (EI) Calcd for $C_{11}H_{16}F_2S_2Si_2$: (M$^+$), 306.0200. Found: *m/z* 306.0214.

Bis(1,3-benzodithiol-2-yl)dimethylsilane (8): A solution of 1.50 M butyllithium in hexane (0.99 mL, 1.49 mmol) was added at 0 °C to a solution of compound **1** (230 mg, 1.49 mmol) in dry THF (5 mL) and the solution was stirred at 0 °C for 1.5 h. Dichlorodimethylsilane (0.090 mL, 96 mg, 0.74 mmol) was added to the reaction mixture at −78 °C. After being stirred at −78 °C–rt for 5 h, the mixture was poured into water (10 mL) and extracted with *t*-butyl methyl ether (10 mL × 2). The ether phase was separated and dried over anhydrous magnesium sulfate. Evaporation of the solvent and subsequent purification of the residue by flash chromatography with hexane as the eluent afforded **8** as colorless needles (60 mg, 22%): Mp 132.0–133.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.43 (s, 6H), 4.66 (s, 2H), 6.98–7.21 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.3, 36.9, 122.2, 125.7, 139.2; ^{29}Si NMR (60 MHz, $CDCl_3$) δ 3.93; IR (KBr) 1561, 1443, 1431, 1254, 1111, 1015, 932, 833, 797, 750, 671 cm^{-1}; UV–vis (CH_3CN, λ_{max}/nm) 300, 238; LRMS (EI) *m/z* (%) 364 (M$^+$, 11), 211 (5), 183 (31), 153 (100), 121 (10), 108 (5), 77 (21), 69 (5); HRMS (EI) Calcd for $C_{16}H_{16}S_4Si$: (M$^+$), 363.9904. Found: *m/z* 363.9902. Found: C, 52.25; H, 4.41%. Calcd for $C_{16}H_{16}S_4Si$: C, 52.70; H, 4.42%.

Bis(1,3-benzodithiol-2-yl)diisopropylsilane (9): This compound was synthesized similarly to **8** in 37% (dichlorodiisopropylsilane) and 66% (difluorodiisopropylsilane) yields. Purification by flash chromatography with hexane as the eluent afforded compound **9** as yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (d, 12H, J = 7.5 Hz), 1.49–1.57 (m, 2H), 4.96 (s, 2H), 6.99–7.25 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.2, 18.6, 35.5, 122.2, 125.6, 139.4; ^{29}Si NMR (60 MHz, $CDCl_3$) δ 3.57; IR (neat) 2944, 2865, 1561, 1458, 1441, 1260, 1121, 1011, 922, 882, 808, 741, 675, 631 cm^{-1}; LRMS (EI) *m/z* (%) 420 (M$^+$, 6), 284 (3), 211 (8), 183 (19), 153 (100), 140 (24), 121 (9), 77 (28), 69 (12); HRMS (EI) Calcd for $C_{20}H_{24}S_4Si$: (M$^+$), 420.0530. Found: *m/z* 420.0543.

2,2,6,6-Tetrakis(trimethylsilyl)benzo[1,2-*d*:4,5-*d′*]bis[1,3]-dithiole (11): To a solution of **10** (230 mg, 1.00 mmol) in THF (4 mL) was added butyllithium (1.56 M in hexane, 0.64 mL, 1.00 mmol) at 0 °C and the mixture was stirred at this temperature for 0.5 h. Chlorotrimethylsilane (0.127 mL, 1.00 mmol) was added at −23 °C, and the mixture was stirred at this temperature for 20 min and then warmed to 0 °C. Butyllithium (1.56 M in hexane, 0.64 mL, 1.00 mmol) was added at 0 °C, and the mixture was stirred at this temperature for 0.5 h. Chlorotrimethylsilane (0.127 mL, 1.00 mmol) was added at −23 °C, and the mixture was stirred at this temperature for 10 min. Butyllithium (1.56 M in hexane, 0.64 mL, 1.00 mmol) was added at −23 °C, and the mixture was stirred at this temperature for 0.5 h. Chlorotrimethylsilane (0.127 mL, 1.00 mmol) was added at −23 °C, and the mixture was stirred at this temperature for 15 min. Butyllithium (1.56 M in hexane, 0.64 mL, 1.00 mmol) was added at −23 °C, and the mixture was stirred at this temperature for 0.5 h. Chlorotrimethylsilane (0.127 mL, 1.00 mmol) was added at −23 °C, and the mixture was stirred at this temperature for 15 min and then warmed to room temperature. The reaction mixture was then partitioned between brine and ether. The organic phase was separated and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified via flash chromatography (N_2 flash) followed by recrystallization (CH_2Cl_2/CH_3CN) to obtain the title compound (135 mg, 26%): Mp 189.5–193.0 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 0.19 (s, 36H), 6.38 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ −1.3, 37.5, 114.1, 138.6; IR (KBr) 2953, 1317, 1252, 858 cm^{-1}. HRMS (EI) Calcd for $C_{20}H_{38}S_4Si_4$: (M^+), 518.0934. Found: *m/z* 518.0916. Found: C, 46.00; H, 7.46%. Calcd for $C_{20}H_{38}S_4Si_4$: C, 46.28; H, 7.38%.

Crystallographic Analysis of 11. Crystal data: $C_{20}H_{38}S_4Si_4$, M_r =518.1 g mol^{-1}, colorless prismatic crystals, crystal size 0.40 × 0.30 × 0.50 mm, a = 12.521(1) Å, b = 12.521(1) Å, c = 18.622(3) Å, tetragonal, space group $P\bar{4}2_1c$ [No. 114], Rigaku AFC5 diffractmeter, λ= 0.71069 Å, scan mode $\omega-2\theta$, 2005 measured reflections (+h, +k, +l) [[sinq/l]$_{max}$ = 0.65–1 1327 observed reflections [$I > 2\sigma(I)$], structure solved by direct methods, final refinement least squares. R = 0.053, R_w = 0.043.

2-Tributylstannyl-1,3-benzodithiole (12): A solution of 1.50 M butyllithium in hexane (2.70 mL, 4.05 mmol) was added at 0 °C to a solution of compound **1** (595 mg, 3.86 mmol) in dry THF (5 mL) and the solution was stirred at 0 °C for 1.5 h. The anion thus obtained was added at −20 °C to another flask containing tributylchlorostannane (1.10 mL, 1.32 g, 4.05 mmol) and THF (3 mL). After being stirred at −20 °C–rt for 3 h, the mixture was poured into water (10 mL) and extracted with *t*-butyl methyl ether (10 mL × 2). The ether phase was separated and dried over anhydrous magnesium sulfate. Evaporation of the solvent and subsequent purification of the residue by flash chromatography with hexane as the eluent afforded compound **12** as colorless oil (856 mg, 50%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 9H, J = 7.5 Hz), 1.16 (t, 6H, J = 7.8 Hz), 1.34 (q, 6H, J = 7.5 Hz), 1.56–1.64 (m, 6H), 4.43 (s, 1H), 6.97–7.27 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.3, 13.6, 27.2, 28.9, 31.0, 121.8, 125.1, 141.3; IR (neat) 2957, 2926, 2870, 2851, 1563, 1464, 1439, 1377, 1109, 1075, 741, 693, 673 cm^{-1}; UV–vis (CH_3CN, λ_{max}/nm) 393, 230; LRMS (FAB) *m/z* (%) 443 (M^+, 6), 291 (29), 261 (5), 235 (30), 209 (11), 183 (9), 179 (55), 153 (100), 121 (4). Found: C, 51.76; H, 7.32%. Calcd for $C_{19}H_{32}S_2Sn$: C, 51.48; H, 7.28%.

2,2-Bis(tributylstannyl)-1,3-benzodithiole (13): A solution of 1.50 M butyllithium in hexane (0.66 mL, 0.99 mmol) was added at −78 °C to a solution of diisopropylamine (0.14 mL, 100 mg, 0.99 mmol) in dry THF (5 mL) and the solution was stirred at −78 °C for 30 min. A solution of compound **12** (411 mg, 0.93 mmol) in THF (2 mL) was added and the solution was stirred at −78–−10 °C for 2 h. Tributylchlorostannane (0.32 mL, 383 mg, 1.18 mmol) was added at −78 °C and the mixture was stirred at −78 °C–rt for 3 h. Work-up as usual and subsequent purification by flash chromatography with hexane as the eluent afforded product **13** as yellow oil (402 mg, 59%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 18H, J = 7.2 Hz), 0.93–0.99 (m, 12H), 1.23–1.35 (m, 12H), 1.44–1.52 (m, 12H), 6.91–7.17 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.4, 13.6, 27.5, 29.2, 121.7, 125.3, 143.0; IR (neat) 2957, 2923, 2853, 1665, 1522, 1464, 1439, 1416, 1375, 1075, 961, 743, 673 cm^{-1}; UV-vis (CH_3CN, λ_{max}/nm) 332, 254. Found: C, 50.56; H, 7.71%. Calcd for $C_{31}H_{58}S_2Sn_2$: C, 50.84; H, 7.98%.

[Bis(trimethylsilyl)methylthio]benzene (15): A solution of 1.6 M butyllithium in hexane (1.7 mL, 2.7 mmol) was added at 0 °C to a solution of compound **14** (430 mg, 2.2 mmol) in dry THF (10 mL). After being stirred at 0 °C for 30 min, the solution was allowed to warm up to room temperature and stirred for further 2 h. Chlorotrimethylsilane (0.40 mL, 340 mg, 3.1 mmol) was added at −78 °C and the mixture was stirred at −78 °C–rt for 3 h. The product was partitioned between saturated brine and ether. The organic phase was separated and dried over anhydrous magnesium sulfate. Evaporation of the solvent and subsequent purification by flash chromatography with hexane as the eluent afforded compound **15** as colorless oil (573 mg, 97%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 18H), 1.58 (s, 1H), 7.11–7.17 (m, 2H), 7.25–7.37 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.2, 18.6, 124.8, 127.6, 128.6, 140.3; ^{29}Si NMR (60 MHz, $CDCl_3$) δ 3.26; IR (neat) 2953, 2899, 1582, 1478, 1439, 1250, 1086, 1024, 995, 843, 770, 737, 689 cm^{-1}; LRMS (EI) *m/z* (%) 268 (M^+, 25), 253 (25), 195 (3), 177 (14), 165 (41), 151 (10), 135 (20), 129 (7), 118 (6), 85 (7), 73 (100), 59 (8); HRMS (EI) Calcd for $C_{13}H_{24}SSi_2$: (M^+), 268.1137. Found: *m/z* 268.1120. Found: C, 58.25; H, 8.73%. Calcd for $C_{13}H_{24}SSi_2$: C, 58.14; H, 9.01%.

(Tributylstannylmethylthio)benzene (18): A solution of 1.63 M butyllithium in hexane (13.8 mL, 22.5 mmol) was added at 0 °C to a solution of thioanisole (2.0 mL, 2.12 g, 17.1 mmol) in dry ether (30 mL). The solution was refluxed under stirring overnight then cooled to 0 °C. Chlorotributylstannane (6.7 mL, 8.04 g, 24.7 mmol) was added in one portion and the mixture was refluxed for 4 h. After being cooled to room temperature, the reaction mixture was partitioned between saturated brine and ether. The organic phase was separated and dried over anhydrous magnesium sulfate. Evaporation of the solvent and subsequent purification of the residue by flash chromatography with hexane as the eluent gave compound **18** as colorless oil (5.25 g, 74%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, 9H, J = 7.2 Hz), 1.13–1.19 (m, 6H), 1.43–1.55 (m, 6H), 1.65–1.75 (m, 6H), 2.29 (s, 2H, J_{Sn-H} = 40.8 Hz), 7.19–7.21 (m, 2H), 7.37–7.43 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.8, 9.6, 13.6, 27.2, 28.9, 124.1, 125.1, 128.4, 142.5; IR (neat) 2957, 2920, 2870, 2858, 1586, 1478, 1464, 1439, 1377, 1075, 1024, 737, 689 cm^{-1}; LRMS (EI) *m/z* (%) 414 (M^+, 12), 412 (8), 410 (5), 357 (100), 355 (75), 353 (40), 291 (51), 289 (37), 287 (22), 235 (73), 197 (33), 179 (92), 177 (83), 175 (53), 123 (43), 121 (28), 119 (20), 91 (59), 77 (6); HRMS (EI) Calcd for $C_{19}H_{34}SSn$: (M^+), 414.1403. Found: *m/z* 414.1393. Found: C, 55.18; H, 8.38%. Calcd for $C_{19}H_{34}SSn$: C, 55.22; H, 8.29%.

[Bis(tributylstannyl)methilthio]benzene (19): A solution of 1.63 M butyllithium in hexane (4.67 mL, 7.61 mmol) was added at −78 °C to a solution of diisopropylamine (1.07 mL, 0.77 g, 7.61 mmol) in THF (15 mL) and the solution was stirred at −78 °C for 30 min. A solution of compound **18** (3.13 g, 7.57 mmol) in THF (20 mL) was added and the solution was stirred at −78–−10 °C for 3 h. Tributylchlorostannane (2.1 mL, 2.52 g, 7.74 mmol) was added at −78 °C and the mixture was stirred at −78 °C for 1.5 h and at room temperature overnight. Work-up as usual and subsequent purification by flash chromatography with hexane/ethyl acetate (99 : 1, v/v) as the eluent gave compound **19** as colorless oil (2.61 g, 49%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82–1.17 (m, 30H), 1.25–1.35 (m, 12H), 1.37–1.58 (m, 12H), 2.30 (s, 1H, $J_{\text{Sn–H}}$ = 36.9 Hz), 7.07–7.12 (m, 2H), 7.25–7.32 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 3.0, 11.1, 13.6, 27.5, 29.1, 124.5, 126.8, 128.4, 143.2; IR (neat) 2957, 2924, 2872, 2853, 1583, 1478, 1464, 1420, 1375, 1073, 1024, 961, 735, 689, 664 cm^{-1}; LRMS (EI) *m/z* (%) 704 (M^+, 9), 702 (11), 700 (9), 647 (22), 645 (28), 643 (24), 591 (21), 589 (27), 587 (24), 533 (3), 475 (2), 413 (3), 356 (53), 354 (40), 352 (21), 291 (37), 289 (28), 287 (17), 243 (68), 229 (93), 227 (68), 225 (41), 179 (100), 177 (83), 175 (52), 153 (6), 123 (30), 91 (36), 69 (33), 57 (23); HRMS (EI) Calcd for $C_{31}H_{60}SSn_2$: (M^+), 704.2460. Found: *m/z* 704.2435 Found: C, 52.76; H, 8.76%. Calcd for $C_{31}H_{60}SSn_2$: C, 53.02; H, 8.61%.

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