Synthesis of New Pentathiepin and Dithiatriselenepin Fused to Ferrocene via Dithiametallacycles

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2,2-Dimethylferroceno[1,2-*d*][1,3,2]dithiastannole, a synthetic equivalent of unstable 1,2-ferrocenedithiol, was synthesized from *N*,*N*-dimethylsulfanoylferrocene by lithiation at the vicinal position, sulfurization, reduction, and protection with dichlorodimethylstannane. The dithiastannole, which has inherent low stability in organic solvents at ambient temperature, converted into diferroceno[1,2-*c*:1″,2″-*g*][1,2,5,6]tetrathiocin via 2,2-dimethyldiferroceno[1,2-*d*;1,2-*h*][1,3,6,7,2]tetrathiastannonin. The molecular structure of the tetrathiocin was determined by NMR, IR, mass spectra, elemental analysis, and X-ray crystallographic analysis. 2,2-Bis(η^5-pentamethylcyclopentadienyl)ferroceno-[1,2-*d*][1,3,2]dithiatitanole was synthesized from the tetrathiocin by the reduction and protection with bis(η^5-pentamethylcyclopentadienyl)titanium dichloride in moderate yield. In contrast to the dithiastannole, the dithiatitanole was thermally stable up to 300 °C in the solid-state. Transformations into ferroceno[1,2-*f*][1,2,3,4,5]pentathiepin and -[1,5,2,3,4]dithiatriselenepin were successfully carried out, namely by the reactions of the dithiatitanole with some electrophiles containing sulfur or selenium atom(s). The molecular structure of the ferrocenopentathiepin was determined by NMR, IR, mass spectra, elemental analysis, and X-ray crystallographic analysis. The structure of the ferrocenodithiatriselenepin was determined by ^{1}H and ^{13}C NMR, IR, mass spectra, and elemental analysis, and supported by the ^{77}Se NMR spectrum and theoretical calculations.

The synthesis and reactivity of compounds containing multi-sulfur linkages have been extensively studied in view of their biological activities and chemical properties.[1–12] In particular, pentathiepins have attracted much attention because of their remarkable stability, a high energy barrier for inversion of the chair-like polysulfide ring, and their potent biological activity.[9] Although many methods have been developed to prepare pentathiepins by using either elemental sulfur or other sulfur-transfer reagents, these methods often gave poor yields of the desired products, and required extreme precaution.[13–16] Recently, we have succeeded in the systematic and selective synthesis of cyclic polysulfides fused to the benzene ring derived from benzo[1,3,2]-dithiastannole and -dithiatitanole as synthetic equivalents of *ortho*-benzenedithiol.[17–24] However, there is a limited approach to the synthesis of cyclic polysulfide fused to a twin cyclopentadienyl ring of the ferrocene due to a synthetic limitation.[25,26] As one of the reasons, synthetic methods of 1,2-ferrocenedithiol, which is an effective precursor of cyclic polysulfides fused to ferrocene, have not been established due to the inherent instability. Therefore, it is necessary to establish systematic and selective syntheses of synthetic equivalents of 1,2-ferrocenedithiol. On the other hand, there is no report concerning the synthesis of ferrocene-fused cyclic seven-membered rings containing sulfur and/or selenium atoms, which have structural and electrochemical interest, or potent biological activity, in contrast to sulfur and selenium-containing five-membered ring systems.[17–19] In this paper, we report an efficient synthesis of ferroceno[1,2-*f*][1,2,3,4,5]pentathiepin and ferroceno[1,2-*f*]-[1,5,2,3,4]dithiatriselenepin bearing two sulfur and three selenium atoms derived from 2,2-dimethylferroceno[1,2-*d*]-[1,3,2]dithiastannole or 2,2-bis(η^5-pentamethylcyclopentadienyl)ferroceno[1,2-*d*][1,3,2]dithiatitanole as synthetic equivalents of unstable 1,2-ferrocenedithiol.

Results and Discussion

Synthesis of 2,2-Dimethylferroceno[1,2-*d*][1,3,2]dithiastannole 7. The *N*,*N*-dimethylsulfanoyl group, an *ortho*-directing group, should be capable of introducing a thiol group at the vicinal position. We utilized direct lithiation at the vicinal position of *N*,*N*-dimethylsulfanoylferrocene (**2**), and subsequent quenching of the resulting lithium salt with elemental sulfur, which was an efficient pathway for the formation of 1,2-disubstituted ferrocene derivatives from ferrocenesulfonyl chloride (**1**)[27,28] as the starting material. As shown in Scheme 1, compound **2** was obtained by a treatment of **1** with aqueous dimethylamine in 87% isolated yield.

The reaction of **2** with an equimolar amount of butyllithium in THF at 0 °C, followed by a treatment of deuterium oxide, gave 2-position deuterated derivative **2a** quantitatively, which was determined by the ^{1}H and ^{13}C NMR spectra. In particular, the triplet signal at 69.0 ppm of the ^{13}C NMR spectrum of **2a** in chloroform-*d* indicated the deuterated carbon atom. Based on the results, we carried out lithiation at vicinal position of **2** with butyllithium in THF, followed by sulfurization with elemental sulfur. After the usual work-up, the resulting mixture gave an oxidized product, 2,2″-bis(*N*,*N*-dimethylsulfanoylfer-

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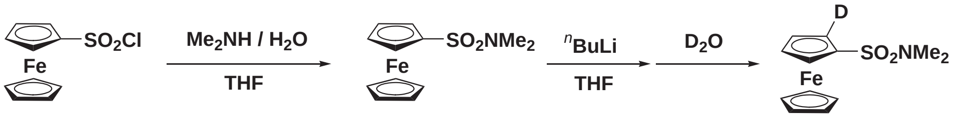
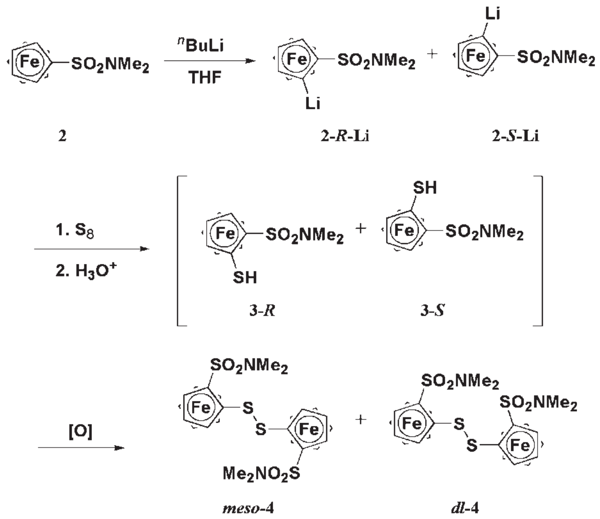


1 **2 (87%)** **2a**

Scheme 1.



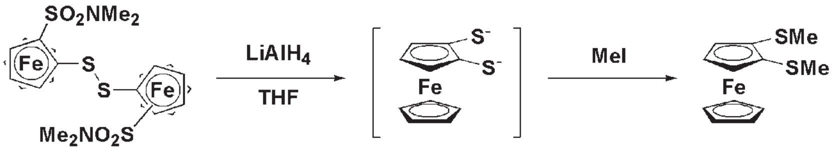
Scheme 2.

rocenyl) 1,1″-disulfide (**4**), in quantitative yield (Scheme 2). It was difficult to isolate the desired **3** as a thiol form by the usual work-up under air. Disulfide **4** was obtained as a diastereomeric mixture (***meso*-4** and ***dl*-4**) that possessed planar chirality due to two different substituents on the cyclopentadienyl ring of each ferrocene moiety.[29]

Although reduction of the *N*,*N*-dimethylsulfanoyl group of **4** has not been achieved by NaBH$_4$, i-Bu$_2$AlH, or SmI$_2$ (see experimental section), the reduction with LiAlH$_4$ in THF under reflux conditions proceeded easily to give the corresponding ferrocene-1,2-dithiolate dianion (**5**). As shown in Scheme 3, the reaction of **4** with LiAlH$_4$ in THF under reflux for 48 h, followed by the treatment of iodomethane as a model reaction, gave 1,2-bis(methylthio)ferrocene (**6**) in 55% isolated yield, which clearly indicated that the reduction was carried out under the reaction conditions. Then, the reduction of the diastereomeric mixture of **4** with LiAlH$_4$ and a subsequent addition of dichlorodimethylstannane in THF afforded a mixture of 2,2-dimethylferroceno[1,2-*d*][1,3,2]dithiastannole (**7**) and 2,2-dimethyldiferroceno[1,2-*d*;1,2-*h*][1,3,6,7,2]tetrathiastannonin (**8**) in 25 and 5% yields, respectively (Scheme 4).

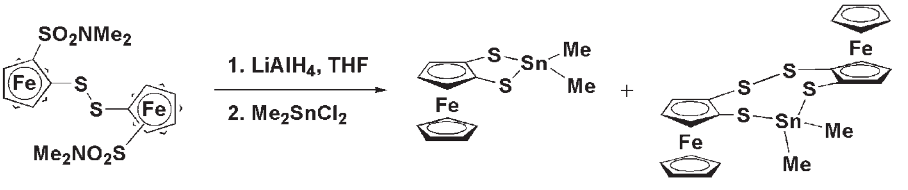
Dithiastannole **7** and tetrathiastannonin **8** were identified by the ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopies. In the ^{1}H NMR spectra of **7** and **8**, the signals of the α- and β-protons of the substituted cyclopentadienyl groups were 4.27 and 4.07 ppm for **7**, and 4.44, 4.62, and 4.34 ppm for **8**, respectively. Moreover, the signals of the two methyl groups of the tin atoms of **7** and **8** in the ^{1}H and ^{13}C NMR spectra were detected as a set of singlets and a singlet, respectively. In the ^{13}C NMR spectra of **7** and **8**, there were three and five signals for the substituted cyclopentadienyl rings, respectively. These spectral features clearly indicated that **7** and **8** had C_s and C_2 symmetric conformation in solution, respectively. The ^{119}Sn NMR spectra of **7** and **8** appeared at 256.9 and 135.4 ppm as singlet peaks, respectively. The former was in the range of typical values for the reported benzo[1,2-*d*][1,3,2]dithiastannoles,[17–24,30–33] and the latter was similar to that for the reported large-membered dithiastannacycle.[34] The structure of **8** was supported by not only the spectroscopic data, but also the formation of tetrathiocin **11** (vide infra).

Reaction of 7 with Sulfur Dichloride. According to previously reported reactions of benzo[1,2-*d*][1,3,2]dithiastannoles with electrophiles containing sulfur atoms,[17,19,24] we carried out a reaction of **7** with sulfur dichloride in order to investigate the reactivity of **7**. After the preparation of **7** by using the above-mentioned method, the treatment of **7** with a large



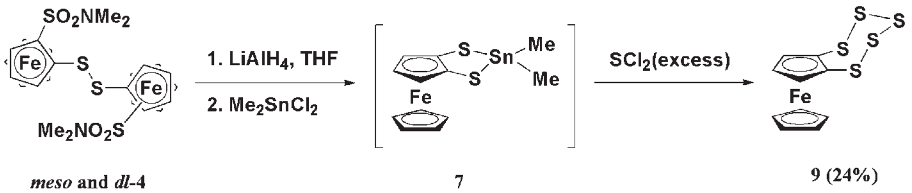
***meso* and *dl*-4** **5** **6 (55%)**

Scheme 3.



***meso* and *dl*-4** **7 (25%)** **8 (5%)**

Scheme 4.



Scheme 5.

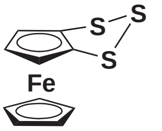


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Chart 1.

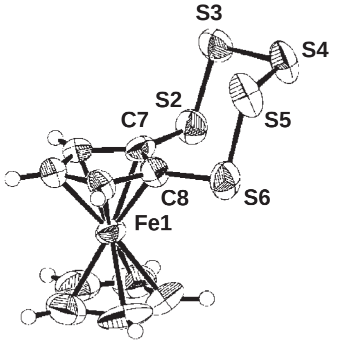


Fig. 1. ORTEP drawing of pentathiepin **9**. Thermal ellipsoids are drawn at the 50% probability.

excess of sulfur dichloride in THF afforded ferroceno[1,2-*f*]-[1,2,3,4,5]pentathiepin (**9**) in 24% isolated yield as orange crystals (Scheme 5). Pentathiepin **9** was stable toward moisture and air in the solid-state, and did not decompose at all in chloroform solution under daylight or irradiation with a high-pressure mercury lamp. In this reaction, we could not observe the formation of ferroceno[1,2-*d*][1,2,3]trithiole (**10**) (Chart 1). These results indicated that the formation of trithiole **10** might be thermodynamically disadvantageous, rather than that of **9**. We performed theoretical calculations in order to study the thermal stabilities of **9** and **10** (vide infra).

The structure of pentathiepin **9** has been sufficiently characterized by physical and spectroscopic means, and its solid-state structure was confirmed by X-ray crystallographic analysis (Fig. 1 and Table 1). In the ^{1}H NMR spectrum, there were a pair of doublets and a triplet at 4.53 and 4.42 ppm assigned to the α- and β-cyclopentadienyl ring protons, respectively, and a singlet signal at 4.32 ppm for the unsubstituted cyclopentadienyl protons. The ^{13}C NMR spectrum of **9** showed resonances at 70.0, 71.1, and 75.4 ppm, assignable to unsubstituted carbon atoms, and at 93.3 ppm, assignable to the *ipso*-cyclopentadienyl carbon atom fused to the sulfur ring. These spectral features should imply that pentathiepin **9** has a C_2 symmetry in solution. The remarkably large downfield shift for the *ipso*-carbon atom of **9** might reflect a deshielding effect of the neighboring sulfur atom.[35]

Table 1. Crystal Data of **9**

Empirical formula	$C_{10}H_8FeS_5$
Formula weight	344.32
Crystal system	monoclinic
Space group	$P2_1$ (#4)
a/Å	8.6743(7)
b/Å	7.5798(8)
c/Å	10.4960(9)
β/°	110.762(6)
V/Å^3	645.29(10)
Z	2
D_{calcd}/g cm^{-3}	1.772
μ(Cu Kα)/cm^{-1}	166.57
Total reflections	2472
Independent refrections	1257
R	0.070
Rw	0.097
GOF	1.10

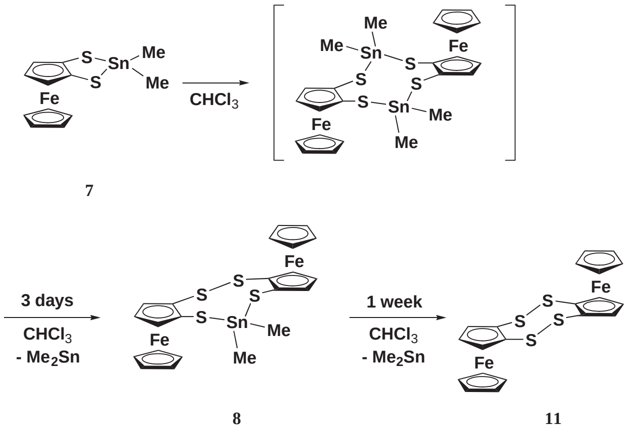
In the solid-state, the S–C–C–S torsion angle of **9** was 1(1)°, the plane of which was located coplanar with the cyclopentadienyl ring, while two sulfur atoms at the 2- and 4-positions were deviated from this plane (the S–S–C–C torsion angles are 75.9(8) and −77.6(8)°, respectively) to avoid the ferrocene moiety. The S–S–S–S torsion angles of 76.6(3) and −76.0(2)° are in good agreement with those of previously reported pentathiepins fused to five-membered heteroaromatic rings (Table 2).[16,36] Accordingly, the inherent thermal stability of pentathiepin **9** might be attributed to the chair conformation due to avoidance of the repulsion of lone-pair electrons among the neighboring sulfur atoms.

Formation and Structural Characterization of Diferroceno[1,2-*c*:1″,2″-*g*][1,2,5,6]tetrathiocin 11. Although dithiastannole **7** was relatively stable at below 0 °C in chloroform, upon standing in the solution at room temperature for 3 days, dithiastannole **7** was gradually converted to more stable tetrathiastannonin **8** with dimerization involving elimination of the dimethylstannyl group. Further, tetrathiastannonin **8** in the solution converted completely into diferroceno-[1,2-*c*:1″,2″-*g*][1,2,5,6]tetrathiocin **11** within one week as a stable product with only a single diastereomer (Scheme 6).

The structure of tetrathiocin **11** has been sufficiently characterized by physical and spectroscopic data. In the ^{1}H NMR spectrum of **11**, there was a pair of doublets and a triplet at 4.50 and 4.42 ppm assignable to the α- and β-cyclopentadienyl protons, and a singlet at 4.17 ppm for the unsubstituted cyclopentadienyl ring protons. In the ^{13}C NMR spectrum of **11**, four peaks were found that could be assigned to the cyclopentadienyl carbon atoms. These results indicated that **11** should be a single diastereomer in solution. The molecular

Table 2. Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for Pentathiepin **9**

Bond lengths		Bond angles		Torsion angles	
S2–S3	2.057(4)	S2–S3–S4	104.7(2)	S2–S3–S4–S5	−76.0(2)
S3–S4	2.051(5)	S3–S4–S5	105.4(2)	S3–S4–S5–S6	76.6(3)
S4–S5	2.045(4)	S4–S5–S6	104.6(2)	S4–S3–S2–C7	88.1(3)
S5–S6	2.053(5)	S3–S2–C7	101.8(3)	S4–S5–S6–C8	−88.6(4)
S2–C7	1.75(1)	S5–S6–C8	101.8(4)	S3–S2–C7–C8	−77.6(8)
S6–C8	1.754(9)	S2–C7–C8	125.6(7)	S5–S6–C8–C7	75.9(8)
		S6–C8–C7	126.1(7)	S2–C7–C8–S6	1(1)



Scheme 6.

structure of **11** was determined by an X-ray crystallographic analysis (Fig. 2 and Table 3), which also revealed that the single diastereomer should be in an *anti*-conformation as two ferrocene units. It was found that a striking feature in the crystal structure of **11** was a chair conformation for the eight-membered ring. The C–S–S–C torsion angle of **11**, 102.2(6)°, was smaller than those of previously reported tetrathiocins fused to a benzene ring (Table 4).[20,37]

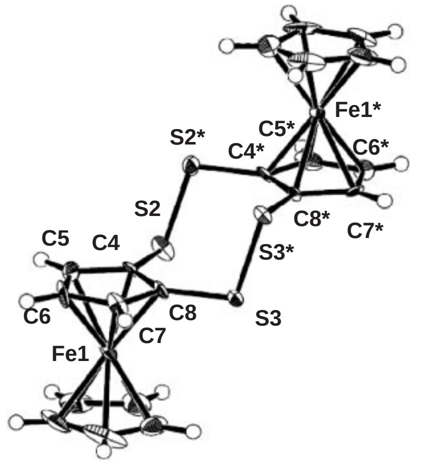


Fig. 2. ORTEP drawing of tetrathiocin **11**. Thermal ellipsoids are drawn at the 50% probability.

Moreover, it was found that the conversion from the mixture of dithiastannole **7** and tetrathiastannonin **8** to tetrathiocin **11** in chloroform-*d* solution was promoted by iodine within 10 min (Fig. 3), as judged by the ^{1}H NMR spectrum. On the other hand, tetrathiocin **11** was directly synthesized from disulfide **4** by a sequence of reduction, stannylation, and oxidation with iodine in 36% isolated yield, as shown in Scheme 7. Tetrathiocin **11** was available as a precursor of metallacycles to generate ferrocenedithiolate dianion derivative **5** by reduction with $LiAlH_4$.

Synthesis of 2,2-Bis(η^5-pentamethylcyclopentadienyl)ferroceno[1,2-*d*][1,3,2]dithiatitanole 12. Unfortunately, dithiastannole **7**, a synthetic equivalent of unstable 1,2-ferrocenedithiol, was not isolated as a stable form due to its tendency to intermolecular dimerization in an organic solution without metal protection. Thus, 2,2-bis(η^5-pentamethylcyclopentadienyl)ferroceno[1,2-*d*][1,3,2]dithiatitanole (**12**) was prepared by the reduction of tetrathiocin **11**, followed by titanylation with bis(η^5-pentamethylcyclopentadienyl)titanium dichloride as dark-green crystals in 42% isolated yield

Table 3. Crystal Data of **11**

Empirical formula	$C_{20}H_{16}Fe_2S_4$
Formula weight	496.28
Crystal system	tetragonal
Space group	$P4/ncc$ (#130)
a/Å	17.950(1)
c/Å	11.764(1)
V/Å^3	3790.2(6)
Z	8
D_{calcd}/g cm^{-3}	1.739
μ(Cu Kα)/cm^{-1}	163.97
Total reflections	2246
Independent refrections	2044
R	0.051
Rw	0.069
GOF	1.08

Table 4. Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for Tetrathiocin **11**

Bond lengths		Bond angles		Torsion angles	
S2–S2	2.073(4)	S2–S2–C4	103.2(3)	S2–S2–C4–C5	102.9(8)
S3–S3	2.076(4)	S3–S3–C8	103.0(3)	S2–S2–C4–C8	−80.1(8)
S2–C4	1.749(8)	S2–C4–C5	124.9(7)	S2–C4–C8–S3	1(1)
S3–C8	1.758(8)	S2–C4–C8	127.6(6)	C4–S2–S2–C4	102.2(6)

(Scheme 8).[17,18,38–42] In contrast to dithiastannole **7**, dithiatitanole **12** was thermally stable in the solid-state or in chloroform solution without any decomposition or dimerization at ambient temperature. The molecular structure of **12** was characterized by physical and spectroscopic means. In the ^{1}H NMR spectrum, two singlet signals assigned to the methyl protons were observed on each pentamethylcyclopentadienyl ring, which indicated that **12** had a C_s symmetry similar to dithiastannole **7**.

Reactions of 12 with Electrophiles Containing Sulfur Atom(s). Transformation into heterocycles containing group 16 elements fused to a ferrocene was carried out by our original methods,[17–19,21,22,24,29,31–33] namely, by the reactions of dithiatitanole **12** with electrophiles containing sulfur atom(s). We performed the reaction of dithiatitanole **12** with an equimolar amount of thionyl chloride or sulfur dichloride (Scheme 9). The ring transformation reactions of **12** with several S_1 sources are summarized in Table 5.

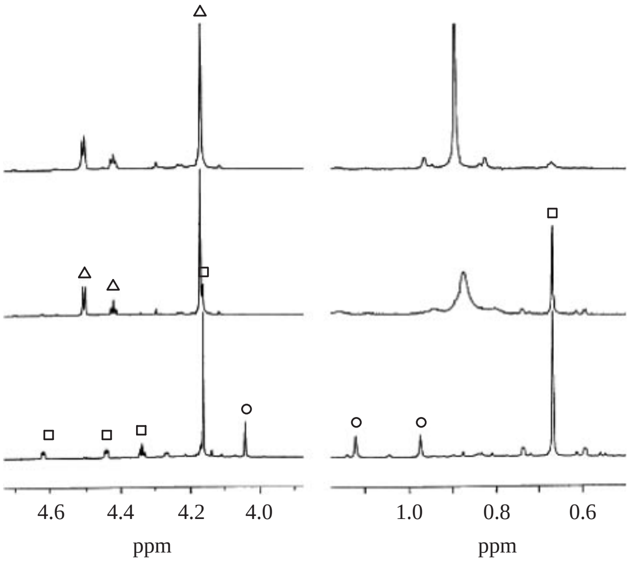
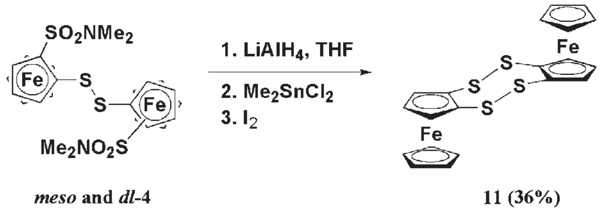


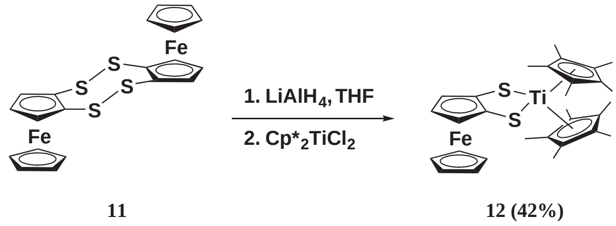
Fig. 3. Partial ^{1}H NMR spectra of low (left) and high field regions (right) of reaction of stannacycles with iodine in chloroform-*d* before the reaction (bottom), after the reaction for 5 min (middle), 10 min (top). Stannole **7** (open circles), stannonin **8** (open squares), and tetrathiocin **11** (open triangles) were observed.

In the case of thionyl chloride, tetrathiocin **11** was unexpectedly obtained as a main product in moderate yield. It is considered to be due to thionyl chloride acting as an oxidizing reagent of dithiatitanole **12**. Similar reactions of dithiatitanoles to tetrathiocins have been reported.[43] Upon the treatment of **12** with sulfur dichloride, pentathiepin **9** was obtained together with tetrathiocin **11**, while trithiole **10** was not obtained. Interestingly, pentathiepin **9** was formed quantitatively based on the number of sulfur atoms using sulfur dichloride, as shown in Table 5. These results implied that all sulfur atoms of the employed sulfur dichloride in these reactions should be consumed in the formation of the seven-membered polysulfide ring of **9**. The reaction might proceed until the formation of pentathiepin **9**, possessing a stable ring size, rather than trithiole **10**.

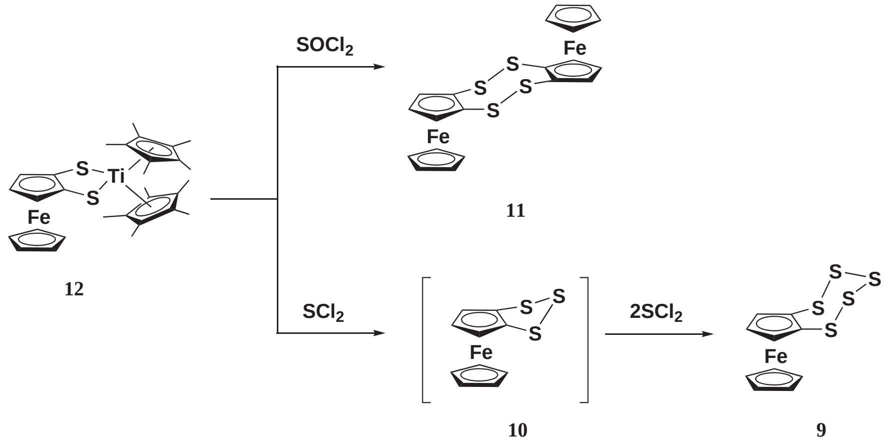
In addition, we performed a desulfurization reaction of **9** using triphenylphosphine in order to synthesize trithiole **10** by means of a ring-contraction reaction of the seven-membered polysulfide linkage of **9**. The treatment of **9** with two equimolar amounts of triphenylphosphine in toluene solution under reflux for 3 h afforded unreacted **9** and tetrathiocin **11** in 61 and 33% isolated yields, respectively (Scheme 10). By using ten



Scheme 7.



Scheme 8.

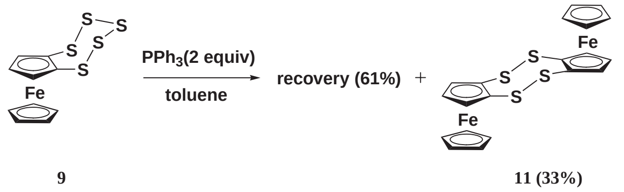


Scheme 9.

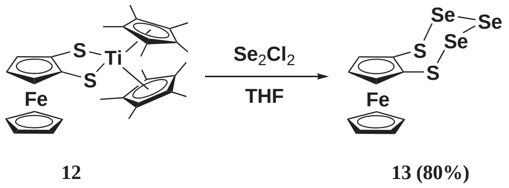
Table 5. Reactions of **12** with $SOCl_2$ or SCl_2

Reagent	Solvent	$T/°C$	Isolated yield/%	
			9	**11**
$SOCl_2$ (1.1 equiv)	THF	−78	no reaction	
$SOCl_2$ (1.1 equiv)	THF	0	trace	50
$SOCl_2$ (1.2 equiv)	THF	rt	trace	62
$SOCl_2$ (1.1 equiv)	CH_2Cl_2	0	trace	69
SCl_2 (1.1 equiv)	THF	0	36 (95)[a)]	37
SCl_2 (excess)	THF	0	50	0
SCl_2 (1.1 equiv)	CH_2Cl_2	0	38 (quant)[a)]	30

a) Yields are based on SCl_2 in the parentheses.



Scheme 10.



Scheme 11.

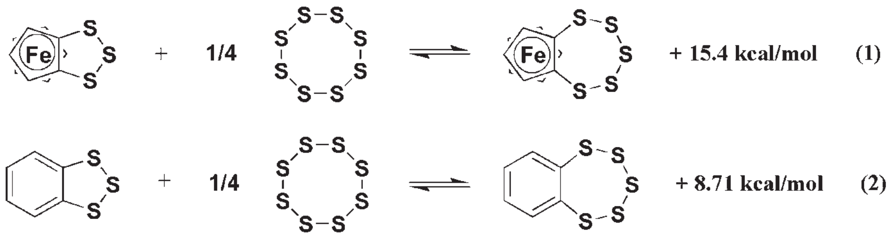


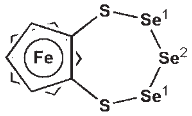
Fig. 4. Homodesmotic reactions (1) between forroceno[1,2-*f*][1,2,3,4,5]pentathiepin and ferroceno[1,2-*d*][1,2,3]trithiole, (2) between benzo[1,2-*f*][1,2,3,4,5]pentathiepin and benzo[1,2-*d*][1,2,3]trithiole.

equimolar amounts of triphenylphosphine in this reaction, tetrathiocin **11** was obtained solely in 76% isolated yield. In sharp contrast to previous reports concerning the formation of benzo[1,2-*d*][1,2,3]trithioles, the formation of ferroceno-[1,2-*d*][1,2,3]trithiole (**10**) was not observed in this reaction. These results indicate that the formation of trithiole **10** should be thermodynamically unfavorable, rather than that of **9**.

In order to investigate the thermal stabilities of ferrocenotrithiole **10** and ferrocenopentathiepin **9**, we performed theoretical calculations of the enthalpy of formation energy using a homodesmotic reaction of the ferrocene derivatives together with well-known benzene derivatives (Fig. 4). As shown in Eq. 1, the homodesmotic reaction of a ferrocene derivative showed an exothermic reaction ($\Delta H = -15.4$ kcal/mol) and, therefore, ferrocenopentathiepin **9** is more thermodynamically stable than ferrocenotrithiole **10**. In the cases of polysulfides fused to a benzene ring (Eq. 2), the homodesmotic reaction was also an exothermic reaction with $\Delta H = -8.71$ kcal/mol. These homodesmotic reactions would imply that their equilibrium constants were estimated to be 1.9×10^{11} for Eq. 1 and 2.4×10^{6} for Eq. 2. The thermodynamic stability of **9** bearing a seven-membered polysulfide ring was supported by not only the experimental results, but also by theoretical calculations of the difference in these equilibrium constants.

Reactions of 12 with Diselenium Dichloride. There were no seven-membered heterocycles containing both sulfur and selenium atoms fused to aromatic rings. Therefore, we tried to synthesize a new seven-membered ring system fused to a ferrocene by the reaction of dithiatitanole **12** with electrophiles containing selenium atom(s). The treatment of dithiatitanole **12** with diselenium dichloride gave ferroceno[1,2-*f*]-[1,5,2,3,4]dithiatriselenepin (**13**) having two sulfur and three selenium atoms in 80% isolated yield (Scheme 11). The structure has been sufficiently characterized by physical and spectroscopic data. The patterns of the signals in the ^{1}H and ^{13}C NMR spectra of **13** were similar to those of pentathiepin **9**. Moreover, the ^{77}Se NMR spectrum provided pertinent information on the new seven-membered ring framework of dithiatriselenepin **13**. In the ^{77}Se NMR spectrum, there were two singlet signals at 856.8 and 884.1 ppm in tetrahydrofuran-d_8, of which the ratio of the intensities was 2:1. The former should be assigned to the selenium at the 2- and 4-positions, and the latter should be assigned to the selenium at the 3-position in the seven-membered ring framework of **13**. In the mass spectrum of **13**, it was found that a molecular ion peak was found at m/z 486 (M^+, $C_{10}H_8FeS_2{}^{78}Se^{80}Se_2$), together with significant peaks at m/z 328 $[M^+ - ({}^{78}Se^{80}Se)]$ and 248 $[M^+ - ({}^{78}Se^{80}Se_2)]$, representing the loss of two and three selenium atoms, respectively. The pattern of the fragments of **13** was similar to that of pentathiepin **9**, that is, in the mass spectrum of **9** a molecular ion peak was found at m/z 344 (M^+, $C_{10}H_8FeS_5$) and subsequent peaks at m/z 280 ($M^+ - S_2$) and

Table 6. Experimental and Calculated ^{77}Se NMR Chemical Shift Values (ppm) of **13**

		Exptl		Calcd$^{c)}$
	Se^1:	858.1$^{a)}$	856.8$^{b)}$	788
	Se^2:	880.0$^{a)}$	884.1$^{b)}$	824

a) The NMR spectra were measured in $CDCl_3$ and using Me_2Se as a external standard. b) The NMR spectra were meaured in THF-d_8 using Me_2Se as a external standard. c) The calculated chemical shifts were difference of Se magnetic shielding tensor of **13** calculated by GIAO-B3LYP/3-21G(d)//B3LYP/3-21G(d).

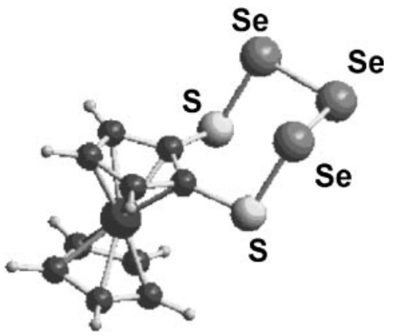


Fig. 5. Optimized structure of **13** calculated at RB3LYP/3-21G(d) level.

248 ($M^+ - S_3$).

In order to study the electronic structure of **13** in detail, DFT calculations were carried out. The electronic structure was optimized and characterized by frequency computations, and wave function stability checks at the RB3LYP/3-21G(d) level. The ferrocene fragment of the optimized structure of **13** was similar to that of the solid-state structure of pentathiepin **9** by X-ray crystallographic analysis (Fig. 5). The S–C–C–S torsion angles of **13** were 0.0°, the plane of which was coplanar with the cyclopentadienyl ring. Furthermore, the selenium atoms at the 2- and 4-positions were deviated from the plane; the Se–S–C–C torsion angles are ±81.5°. The Se–Se–Se–S torsion angles are ±75.2°. In addition, in order to computationally evaluate the ^{77}Se NMR spectrum of **13**, the chemical shifts were calculated by density functional theory (Table 6). The calculated chemical shifts obtained by using the GIAO method were smaller than the experimental values, but reproduced the same trend. These experimental and theoretical results clearly demonstrate the formation of a new seven-membered ring, comprised of two sulfur and three selenium atoms, fused to a ferrocene.

Electrochemical Study. The solution redox properties of pentathiepin **9**, tetrathiocin **11**, and dithiatriselenepin **13** were studied by cyclic voltammetry. Cyclic voltammograms were measured in acetonitrile or benzonitrile containing 0.1 M (1 M = 1 mol dm^{-3}) n-Bu_4NClO_4 as a supporting electrolyte, of which the redox potentials are summarized in Table 7. The cyclic voltammogram of tetrathiocin **11** containing two ferrocene units showed two distinct reversible anodic steps ($E^1{}_{1/2} = +0.35$, $E^2{}_{1/2} = +0.53$ V) derived from the corresponding ferrocenium cations separated by the disulfide fragments of **11**. The cyclic voltammograms of pentathiepin **9** and dithiatriselenepin **13** showed a well-defined reversible redox wave derived from the corresponding ferrocenium cation ($E_{1/2} = +0.55$ V and $E_{1/2} = +0.49$ V for **9** and **13**, respectively), which were similar to those of previously reported ferrocenophanes.[44]

Table 7. Redox Potentials$^{c)}$

Compound	E_{pa}/V	E_{pc}/V	$E_{1/2}$/V
9$^{a)}$	+0.59	+0.52	+0.55
11$^{b)}$	+0.42	+0.28	+0.35
	+0.59	+0.46	+0.53
13$^{a)}$	+0.53	+0.44	+0.49

a) Concentration, 2 mM sample MeCN/0.1 M n-Bu_4NClO_4; scan rate = 100 mV s^{-1}. b) Concentration, 2 mM sample PhCN/0.1 M n-Bu_4NClO_4; scan rate = 2000 mV s^{-1}. c) Working electrode, glassy-carbon; reference electrode, Ag/0.01 M $AgNO_3$; counter electrode, Pt.

Conclusion

We succeeded in the synthesis of 2,2-dimethylferroceno[1,2-*d*][1,3,2]dithiastannole (**7**) and 2,2-bis(η^5-pentamethylcyclopentadienyl)ferroceno[1,2-*d*][1,3,2]dithiatitanole (**12**) as synthetic equivalents of unstable 1,2-ferrocenedithiol by efficient lithiation at vicinal position reactions of *N*,*N*-dimethylsulfanoylferrocene (**2**). Although dithiastannole **7** could not be isolated as a stable form due to its inherent instability, dithiatitanole **12** was stable under air without any decomposition in solution at ambient temperature. The treatment of **7** with sulfur dichloride gave ferroceno[1,2-*f*][1,2,3,4,5]pentathiepin (**9**) as the sole product without the formation of ferroceno[1,2-*d*][1,2,3]trithiole (**10**). The reaction of **12** with sulfur dichloride and diselenium dichloride afforded ferroceno[1,2-*f*]dithiatrichalcogenepin, **9** and **13**, as stable compounds in good yields, respectively. Dithiatitanole **12** has been proven to be a very useful intermediate in the synthesis of a variety of sulfur and/or selenium-containing heterocycles fused to ferrocene.

Experimental

General. Melting and decomposition points were determined on a Mel-Temp capillary tube apparatus, and were uncorrected. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra were measured on a Bruker AC-400 spectrometer using chloroform-*d* as a solvent with Me_4Si as the internal standard. ^{77}Se (76 MHz) and ^{119}Sn (149 MHz) NMR spectra used Me_2Se and Me_4Sn as the external standards, respectively. IR spectra were recorded on a JASCO FT-7300 spectrometer. Mass spectra were determined on a Hitachi M-2000 spectrometer operating at 70 eV in the EI mode. Elemental analyses were carried out by using a Yanagimoto MT-5 CHN corder and determined on the Division of Elemental Analysis in Iwate

University. Cyclic voltammetry was carried out by using a Cypress Systems CS-1090 galvanostat/potentiostat and three electrodes system, an auxiliary electrode of a platinum wire, a working electrode of a glassy carbon, and an Ag/0.01 M $AgNO_3$ reference electrode. The measurements were carried out in acetonitrile or benzonitrile solution containing 0.1 M n-Bu_4NClO_4 as a supporting electrolyte with scan rates in a range of 100–2000 mV s^{-1} under an argon atmosphere at ambient temperature. All solvents used in the reactions were purified by the general methods. All reactions were carried out under a nitrogen atmosphere, but the work-up was performed in air. Silica-gel column chromatography was performed with a Wakogel C-200. Ferrocenesulfonyl chloride was prepared according to the reported method.[27,28]

Computational Methods. All calculations were carried out with the Gaussian 98 program.[45] The geometries were optimized with the restricted Becke hybrid (B3LYP) methods. The zero-point vibrational energies were computed at the same level, and were not scaled. All stationary points were characterized by harmonic analysis. The magnetic shielding tensor of the selenium atom was evaluated by using the gauge invariant atomic orbital (GIAO) approach. The theoretical ^{77}Se NMR chemical shifts were obtained from the difference in the magnetic shielding tensors of the selenium atoms between optimized ferroceno[1,2-*f*]-[1,5,2,3,4]dithiatriselenepin and dimethylselenide.

Synthesis of *N*,*N*-Dimethylsulfanoylferrocene (2). To a stirred solution of ferrocenesulfonyl chloride (**1**, 9.022 g, 37.17 mmol) in THF (300 mL) at room temperature was added an aqueous dimethylamine solution (10 mL of a 9.87 M solution, 97.8 mmol). The mixture was stirred at room temperature for 15 h. After the reaction mixture was dried over anhydrous magnesium sulfate, the solvent was evaporated under reduced pressure. The residue was recrystallized from dichloromethane and hexane to afford *N*,*N*-dimethylsulfanoylferrocene (**2**, 9.527 g, 32.5 mmol, 87%): yellow crystals; mp 156.0–156.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 6H, $N(CH_3)_2$), 4.40 (brt, 2H, C_5H_4), 4.42 (s, 5H, C_5H_5), 4.59 (brt, 2H, C_5H_4); ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.9, 69.0, 70.5, 70.6, 82.1; IR (KBr) ν 3449, 3104, 1339, 1185, 1136, 951, 711, 607, 485 cm^{-1}; MS (70 eV) m/z 293 (M^+); Anal. Calcd for $C_{12}H_{15}FeNO_2S$: C, 49.16; H, 5.16%. Found: C, 49.00; H, 5.25%.

Synthesis of 2,2″-Bis(*N*,*N*-dimethylsulfanoylferrocenyl) 1,1″-Disulfide (4). To a stirred solution of *N*,*N*-dimethylsulfanoylferrocene (**2**, 3.179 g, 10.67 mmol) in THF (150 mL) was added butyllithium (4.8 mL of a 2.66 M hexane solution, 12.77 mmol) at 0 °C under an N_2 atmosphere. After stirring at 0 °C for 1 h, elemental sulfur (0.396 g, 12.35 mmol) was added to the mixture. The resulting mixture was stirred at room temperature for 2 h, and was stirred for 20 min under O_2 atmosphere. The mixture was poured into ice water, acidified by aqueous hydrochloric acid, and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; chloroform) to give a diastereomeric mixture of 2,2″-bis(*N*,*N*-dimethylsulfanoylferrocenyl) 1,1″-disulfide (**4**, 3.501 g, 5.39 mmol, quant.): yellow crystals; mp >350 °C; IR (KBr) ν 1339, 1191, 1155, 659, 713, 614, 505 cm^{-1}; MS (70 eV) m/z 648 (M^+); Anal. Calcd For $C_{24}H_{28}Fe_2N_2O_4S_4$: C, 44.46; H, 4.35; N, 4.32%. Found: C, 44.80; H, 4.66; N, 4.37%; major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (s, 12H, $N(CH_3)_2$), 4.41 (s, 10H, C_5H_5), 4.56 (brt, 2H, C_5H_3), 4.65 (brs, 2H, C_5H_3), 4.86 (brs, 2H, C_5H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.9, 71.4, 72.1, 72.7, 76.7, 83.3, 84.3; minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 12H, $N(CH_3)_2$), 4.44 (s, 10H, C_5H_5), 4.46 (brs, 2H, C_5H_3), 4.70 (brt, 2H, C_5H_3), 4.73 (brs, 2H, C_5H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.5, 70.4, 72.0, 72.7, 76.5, 83.2, 85.0.

Reduction of 2,2″-Bis(*N*,*N*-dimethylsulfanoylferrocenyl) 1,1″-Disulfide (4) Using Lithium Alminium Hydride. Lithium tetrahydridoaluminate (76 mg, 2.0 mmol) was added to a stirred solution of **4** (185 mg, 0.285 mmol) in THF (20 mL) at 0 °C. After the mixture was stirred under reflux for 48 h, it was cooled to 0 °C. Iodomethane (1.0 mL, 16 mmol) was added into the mixture at 0 °C, and the reaction mixture was allowed to warm to room temperature. After the mixture was poured into water, it was washed with aqueous sodium thiosulfate. The mixture was extracted with dichloromethane, and the organic layer was dried over anhydrous magnesium sulfate. After removing the solvent under reduced pressure the residue was purified by column chromatography (silica gel; hexane:ethyl acetate = 1:1) to afford 1,2-bis(methylthio)-ferrocene (90 mg, 0.32 mmol, 55%): orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 6H, SCH_3), 4.19 (s, 5H, C_5H_5), 4.21 (brt, 1H, C_5H_3), 4.38 (brd, 2H, C_5H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.0, 67.9, 70.7, 72.1, 86.3; IR (KBr) ν 3094, 2918, 1423, 1106, 1001, 820, 520 cm^{-1}; MS (70 eV) m/z 278 (M^+); Anal. Calcd for $C_{12}H_{14}FeS_2$: C, 51.81; H, 5.07%. Found: C, 51.87; H, 5.17%.

Reduction of 2,2″-Bis(*N*,*N*-dimethylsulfanoylferrocenyl) 1,1″-Disulfide (4) Using Diisobutylhydridoaluminium. A solution of diisobutylhydridoaluminium in toluene (2.50 mL of 1.0 M solution, 2.50 mmol) was added to a stirred solution of **4** (231 mg, 0.356 mmol) in THF (30 mL) at 0 °C. After the mixture was stirred under reflux for 8 h, it was cooled to 0 °C. Iodomethane (1.0 mL, 16 mmol) was added to the mixture at 0 °C and the reaction mixture was allowed to warm at room temperature. After the mixture was poured into water, it was washed with aqueous sodium thiosulfate. The resulting mixture was extracted with dichloromethane. Then, the organic layer was dried over anhydrous magnesium sulfate and the solvent evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; hexane:ethyl acetate = 1:1) to give 1-(*N*,*N*-dimethylsulfanoyl)-2-methylthioferrocene (119 mg, 0.351 mmol, 49%): yellow powder; mp 111.0–112.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H, SCH_3), 2.72 (s, 6H, $N(CH_3)_2$), 4.40 (brt, 1H, C_5H_3), 4.42 (s, 5H, C_5H_3), 4.50 (br, 1H, C_5H_3), 4.64 (br, 1H, C_5H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 18.6, 37.8, 68.9, 70.6, 71.5, 72.2, 82.7, 87.0; IR (KBr) ν 1337, 1199, 1145, 952, 612, 486 cm^{-1}; MS (70 eV) m/z 339 (M^+); Anal. Calcd for $C_{13}H_{17}FeNO_2S_2$: C, 46.03; H, 5.05; N, 4.13%. Found: C, 45.93; H, 5.15; N, 4.14%.

Synthesis of Stannacycles 7 and 8. Lithium tetrahydridoaluminate (0.653 g, 17.2 mmol) was slowly added to a stirred solution of 2,2″-bis(*N*,*N*-dimethylsulfanoylferrocenyl) 1,1″-disulfide (**4**, 1.118 g, 1.72 mmol) in THF (70 mL) at 0 °C. After the mixture was stirred under reflux for 8 h, it was cooled to room temperature. The reaction mixture was poured into a solution of dichlorodimethylstannane (3.778 g, 17.2 mmol) in THF (200 mL) at 0 °C. After the reaction mixture was stirred for 30 min at room temperature, it was poured into water and acidified with aqueous hydrochloric acid until pH = 3–4. The resulting mixture was extracted with dichloromethane, dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; chloroform:ethyl acetate = 10:1) to give a mixture (0.118 g, 0.43 mmol, 30%) of 2,2-dimethylferroceno[1,2-*d*][1,3,2]dithiastannole (**7**) and 2,2-dimethyldiferroceno[1,2-*d*;1,2-*h*][1,3,6,7,2]tetrathiastannonin

(**8**). The ratio of dithiastannole and tetrathiastannonin was 5:1 as judged by the ^{1}H NMR spectrum.

2,2-Dimethylferroceno[1,2-*d*][1,3,2]dithiastannole (7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 3H, $SnCH_3$), 1.12 (s, 3H, $SnCH_3$), 4.04 (s, 5H, C_5H_5), 4.07 (A_2B, $J = 2.7$ Hz, 1H, C_5H_3), 4.27 (A_2B, $J = 2.7$ Hz, 2H, C_5H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 3.0, 3.9, 66.1, 66.7, 72.2, 91.0; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ 256.9.

2,2-Dimethyldiferroceno[1,2-*d*;1,2-*h*][1,3,6,7,2]tetrathiastannonin (8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67 (s, 6H, $Sn(CH_3)_2$), 4.16 (s, 10H, C_5H_5), 4.34 (brt, 2H, C_5H_3), 4.44 (brs, 2H, C_5H_3), 4.62 (brs, 2H, C_5H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.2, 70.0, 71.4, 75.7, 76.0, 83.6, 86.3; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ 134.4.

Reaction of 7 with SCl_2. Lithium tetrahydridoaluminate (5.036 g, 132.7 mmol) was slowly added to a stirred solution of 2,2″-bis(*N*,*N*-dimethylsulfanoylferrocenyl) 1,1″-disulfide (**4**, 8.602 g, 13.27 mmol) in THF (120 mL) at 0 °C. After the mixture was stirred under reflux for 96 h, it was cooled to room temperature. The reaction mixture was poured into a solution of dichlorodimethylstannane (29.150 g, 132.7 mmol) in THF (100 mL) at 0 °C. After the reaction mixture was stirred for 30 min at room temperature, it was poured into water. The resulting mixture was extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. Sulfur dichloride (5.00 mL, 79.6 mmol) was added to the residue in THF (80 mL) at 0 °C. After the reaction mixture was stirred at room temperature for 2 h, it was poured into water. The resulting mixture was extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; hexane) to give ferroceno[1,2-*f*][1,2,3,4,5]pentathiepin (**9**, 1.100 g, 3.195 mmol, 24%): orange crystals; mp. 128.5–129.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (s, 5H, C_5H_5), 4.42 (A_2B, $J = 2.7$ Hz, 1H, C_5H_3), 4.53 (A_2B, $J = 2.7$ Hz, 2H, C_5H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 70.0, 71.1, 75.4, 93.3; IR (KBr) ν 3590, 1712, 1362, 1222, 755, 530 cm^{-1}; MS (70 eV) *m*/*z* 344 (M^+); Anal. Calcd for $C_{10}H_8FeS_5$: C, 34.88; H, 2.34%. Found: C, 34.61; H, 2.38%.

Synthesis of Diferroceno[1,2-*c*:1″,2″-*g*][1,2,5,6]tetrathiocin (11). Lithium tetrahydridoaluminate (3.222 g, 84.90 mmol) was slowly added to a stirred solution of 2,2″-bis(*N*,*N*-dimethylsulfanoylferrocenyl) 1,1″-disulfide (**4**, 4.235 g, 6.53 mmol) in THF (200 mL) at 0 °C. After the mixture was stirred under reflux for 40 h, it was cooled to room temperature. The reaction mixture was poured into a solution of dichlorodimethylstannane (8.725 g, 39.72 mmol) in THF (300 mL) at 0 °C. After the reaction mixture was stirred for 30 min at room temperature, it was poured into water and acidified with aqueous hydrochloric acid until pH = 1. The resulting mixture was extracted with ether. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (neutral silica gel; chloroform:hexane = 1:1) to give a mixture of dithiastannole **7** and tetrathiastannoin **8** (2.090 g) as an orange solid. Iodine (0.773 g, 5.78 mmol) was added to the orange solid in chloroform (150 mL), and the reaction mixture was stirred at room temperature for 12 h. The mixture was washed with aqueous sodium thiosulfate, dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; chloroform) to give diferroceno[1,2-*c*:1″,2″-*g*][1,2,5,6]tetrathiocin (**11**, 1.170 g, 2.36 mmol, 36%): orange crystals; mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (s, 10H, C_5H_5), 4.42 (A_2B, $J = 2.7$ Hz, 2H, C_5H_3), 4.50 (A_2B, $J = 2.7$ Hz, 4H, C_5H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 69.8, 70.8, 76.3, 89.1; IR (KBr) ν 3449, 2362, 1194, 1107, 1001, 819, 515, 458 cm^{-1}; MS (70 eV) *m*/*z* 496 (M^+); Anal. Calcd for $C_{20}H_{16}Fe_2S_4$: C, 48.40; H, 3.25%. Found: C, 48.13; H, 3.28%.

Synthesis of 2,2-Bis(η^5-pentamethylcyclopentadienyl)ferroceno[1,2-*d*][1,3,2]dithiatitanole (12). Lithium tetrahydridoaluminate (1.389 g, 36.60 mmol) was added to a stirred solution of diferroceno[1,2-*c*:1″,2″-*g*][1,2,5,6]tetrathiocin (**11**, 1.043 g, 2.10 mmol) in THF (200 mL) at 0 °C. After the mixture was stirred under reflux for 1.5 h, it was cooled to room temperature. The reaction mixture was poured into a solution of bis(η^5-pentamethylcyclopentadienyl)titanium dichloride (5.170 g, 13.28 mmol) in THF (350 mL) at 0 °C. After the reaction mixture was stirred for 30 min at room temperature, it was poured into water. The mixture was extracted with ether, dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; chloroform:hexane = 1:1) to give 2,2-bis(η^5-pentamethylcyclopentadienyl)ferroceno[1,2-*d*][1,3,2]dithiatitanole (**12**, 0.991 g, 1.75 mmol, 42%): dark-green crystals; mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (s, 15H, $TiC_5(CH_3)_5$), 2.08 (s, 15H, $TiC_5(CH_3)_5$), 3.76 (A_2B, $J = 2.3$ Hz, 1H, C_5H_3), 4.12 (s, 5H, C_5H_5), 4.24 (A_2B, $J = 2.3$ Hz, 2H, C_5H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 12.6, 65.6, 67.6, 70.4, 102.7, 122.8, 124.1; IR (KBr) ν 3448, 2895, 1638, 1445, 1377, 1103, 1017, 999, 811, 541, 525, 486, 468 cm^{-1}; MS (70 eV) *m*/*z* 566 (M^+); Anal. Calcd for $C_{30}H_{38}FeS_2Ti$: C, 63.61; H, 6.76%. Found: C, 63.66; H, 6.88%.

Reaction of 12 with $SOCl_2$. To a stirred solution of 2,2-bis(η^5-pentamethylcyclopentadienyl)ferroceno[1,2-*d*][1,3,2]dithiatitanole (**12**, 0.073 g, 0.13 mmol) in THF (30 mL) was added thionyl chloride (0.40 mL of a 0.35 M THF solution, 0.14 mmol) at 0 °C under an N_2 atmosphere. After stirring for 15 min, it was poured into ice water and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; chloroform:hexane = 1:1) to give diferroceno[1,2-*c*:1″,2″-*g*][1,2,5,6]tetrathiocin (**11**, 0.016 g, 0.032 mmol, 50%).

Reaction of 12 with SCl_2. To a stirred solution of 2,2-bis(η^5-pentamethylcyclopentadienyl)ferroceno[1,2-*d*][1,3,2]dithiatitanole (**12**, 0.055 g, 0.097 mmol) in THF (30 mL) was added sulfur dichloride (0.14 mL of a 0.76 M THF solution, 0.11 mmol) at 0 °C under an N_2 atmosphere. After stirring for 10 min, it was poured into ice water and extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; chloroform:hexane = 1:1) to give ferroceno[1,2-*f*][1,2,3,4,5]pentathiepin (**9**, 0.012 g, 0.035 mmol, 36%).

Synthesis of Ferroceno[1,2-*f*][1,2,3,4,5]pentathiepin (9) from Titanole. To a stirred solution of 2,2-bis(η^5-pentamethylcyclopentadienyl)ferroceno[1,2-*d*][1,3,2]dithiatitanole (**12**, 0.066 g, 0.12 mmol) in THF (30 mL) was added sulfur dichloride (70.0 µL, 1.11 mmol) at 0 °C under an N_2 atmosphere. After stirring for 10 min, the mixture was poured into ice water and extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; hexane) to give ferroceno[1,2-*f*][1,2,3,4,5]-pentathiepin (**9**, 0.020 g, 0.058 mmol, 50%).

Reactions of 9 with PPh_3. A typical run is as follows: to a stirred solution of ferroceno[1,2-*f*][1,2,3,4,5]pentathiepin (**9**, 0.033 g, 0.096 mmol) in toluene (10 mL) was added triphenylphosphine (0.050 g, 0.19 mmol). The mixture was stirred under reflux for 3 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; chloroform:hexane = 1:1) to give compound **9** (0.020 g, 0.058 mmol, 61%) and diferroceno-[1,2-*c*:1″,2″-*g*][1,2,5,6]tetrathiocin (**11**, 8.0 mg, 0.016 mmol, 33%).

Synthesis of Ferroceno[1,2-*f*][1,5,2,3,4]dithiatriselenepin (13). To a stirred solution of 2,2-bis(η^5-pentamethylcyclopentadienyl)ferroceno[1,2-*d*][1,3,2]dithiatitanole (**12**, 0.050 g, 0.088 mmol) in THF (30 mL) was added diselenium dichloride (50 µL, 0.63 mmol) at 0 °C under an N_2 atmosphere. After stirring for 15 min, the reaction mixture was poured into ice water and acidified with aqueous hydrochloric acid. The resulting red solid was separated by filtration, and the filtrate was extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; hexane) to give ferroceno[1,2-*f*][1,5,2,3,4]dithiatriselenepin (**13**, 0.034 g, 0.070 mmol, 80%): red crystals; mp. 115.0–115.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (s, 5H, C_5H_5), 4.50 (A_2B, $J =$ 2.7 Hz, 1H, C_5H_3), 4.54 (A_2B, $J = 2.7$ Hz, 2H, C_5H_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 70.6, 71.3, 76.9, 92.7; ^{77}Se NMR (76 MHz, THF-d_8) δ 856.8, 884.1; IR (KBr) ν 3906, 3082, 1194, 1105, 998, 818, 514, 461 cm^{-1}; MS (70 eV) m/z 486 (M^+, $C_{10}H_8FeS_2{}^{78}Se^{80}Se_2$); Anal. Calcd for $C_{10}H_8FeS_2Se_3$: C, 24.76; H, 1.66%. Found: C, 24.94; H, 1.84%.

X-ray Crystal Structure Analyses of 9 and 11. The intensity data of **9** and **11** were collected on a Rigaku AFC7R diffractometer employing Cu Kα radiation using the $\omega/2\theta$ scan technique. The structures were determined by direct methods (SIR92)[46] and expanded using Fourier technique (DIRDIF94).[47] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. All calculations were performed using the teXsan[48] crystallographic software package of Molecular Structure Corporation.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-192870 for compound No. **9** and CCDC-192869 for compound No. **11**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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