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Preparation and Structures of Chiral Mono and Bis *ortho*-Aminoalkyl-Substituted 1,1′-Trichalcogena[3]ferrocenophanes

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ABSTRACT: *We prepared a series of mono and bis ortho-aminoalkyl-substituted chiral trichalcogena[3]-ferrocenophanes by dilithiation of mono- and bis-aminoferrocenes and subsequent reaction with sulfur and selenium in moderate yields. The X-ray crystallographic analyses of triselena[3]ferrocenophanes revealed that the bridge selenium atom was directed toward to the ortho-substituent (endo). In the bis-type ferrocenophanes, bridge inversion was not detected by ^1H NMR because they would be homomeric.* Heteroatom Chem 17:118–124, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20189

INTRODUCTION

Chiral ferrocenes and half-metallocenes have been of interest especially in asymmetric catalysis as chiral ligands [1]. Ferrocenylphosphines have become a popular and effective ligands for transition metal complexes which catalyze asymmetric reactions with an often high enantioselectivity. Chiral ferrocenylchalcogenides (S, Se) would be alternative ligands for ferrocenylphosphine ligands. They were first applied to the palladium complex catalyzed Grignard cross-coupling reaction with alkyl chlorides, but the reaction was not successful, and the enantioselectivities were low [2]. Uemura and coworkers prepared chiral diferrocenyl dichalcogenides and applied them to rhodium and iridium catalyzed asymmetric hydrosilylations with ketones, in which an optically active secondary alcohol could be obtained up to 85% ee [3]. Recently, Dai and coworkers succeeded in the palladium catalyzed asymmetric allylic substitution of dimethyl malonate using the oxazoline derivatives of the ferrocenylchalcogenides, of which the ferrocenyl N, S- and N, Se-ligands work effectively to give the product in high enantioselectivities [4]. Planar chiral ferrocenyl S, P-ligands have also been shown as an effective ligand for the palladium catalyzed asymmetric allylic substitution [5]. We are interested in chiral trichalcogena[3]ferrocenophanes as potential chiral ferrocenyl ligands in asymmetric synthesis based on their unique structure [6], and prepared a series of compounds and examined their structures and catalytic ability in the benchmark asymmetric diethylzinc addition to benzaldehyde.

RESULTS AND DISCUSSION

We first prepared a series of mono *ortho*-substituted chiral trichalcogena[3]-ferrocenophanes **2a–b** (E = S) and **3a–b** (E = Se) by the dilithiation of (*R*)- or (*S*)-aminoferrocenes **1a–b** (R = Me, Ph) and subsequent reaction with sulfur and selenium (Scheme 1)

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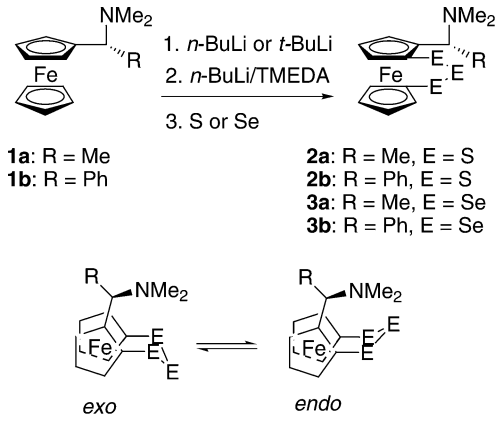


SCHEME 1

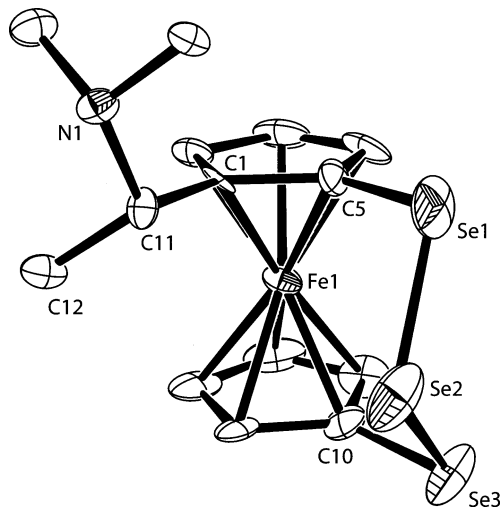


FIGURE 1 Structure of HCl salt of (*S,Rp*)-**3a** (HCl is deleted).

[7]. The dilithiation was carried out by the reported method stepwise using *n*-BuLi (or *t*-BuLi for **1b**) and TMEDA, and the reaction of the resulting 1,1′-dilithioferrocene with sulfur and selenium powder at room temperature for 12–15 h afforded **2a–b** and **3a–b** in moderate yields (39–52%), respectively. ^{1}H NMR spectrum of **2a** (R = Me, E = S) was identical to that of the previously reported compound with two CH_3 signals (1.17 and 1.25 ppm) and two NMe_2 signals (2.06 and 2.18 ppm) having the ratio of major to minor of 70:30 [8]. The spectral observations are rationalized in terms of a bridge inversion isomerization, namely the bridge sulfur atom faced outward (*exo*) and inward (*endo*) to the *ortho*-substituent [9]. **2b** (R = Ph, E = S) was revealed to exist as almost a 50:50 mixture of the two conformers by the ^{1}H and ^{13}C NMR measurements; two NMe_2 signals appear evenly at 2.06 and 2.11 ppm at 25°C. In a previous NMR study on the conformation of **2a** in solution, the major conformer was assigned as *exo* and the high ratio of the conformers could be rationalized by the steric effect of the methyl group [10]. The lower ratio of the two conformers in **2b** was unexpected because the phenyl group would be more sterically demanding, and the ratio would be higher.

In the ^{1}H NMR spectrum of the selenium analog **3a** (R = Me, E = Se), CH_3 and NMe_2 signals appeared as broad singlets at 25°C, and each broad signal was separated into two singlets at low temperature (below 0°C): CH_3 signals, 1.05 (major) and 1.23 (minor); NMe_2 signals, 2.03 (major) and 2.22 (minor). The X-ray diffraction analysis of the HCl salt of (*S,Rp*)-**3a**, which could be obtained as a single crystal, revealed that the bridge selenium atom faced *endo* to the *ortho*-aminoalkyl group (Fig. 1). The structure of (*S,Rp*)-**3b** (R = Ph, E = Se) was shown in Fig. 2, which suggests that the bridge selenium atom also faced *endo* to the *ortho*-substituent. Tables 1 and 2 summarize the selected bond lengths and angles of (*S,Rp*)-**3a**·HCl and (*S,Rp*)-**3b**, respectively. From these structural analytical results, the bridge selenium atom of triselena[3]ferrocenophanes tends to face *endo* to *ortho*-substituent [11].

We could obtain a series of 1,1′-bis *ortho*-substituted chiral trichalcogena[3]ferrocenophanes **5a–b** (E = S) and **6a–b** (E = Se) by dilithiation of the (*R,R*)-bis(amino)ferrocenes **4a–b** (R = Me, Ph) and subsequent reaction with sulfur and selenium in moderate yields (30–57%) by a method similar to the preparation of the above **2a–b** and **3a–b** (Scheme 2) [12]. In these bis-type compounds, bridge inversion isomers were not detected by ^{1}H NMR because they would be homomeric. The *ortho* position to the

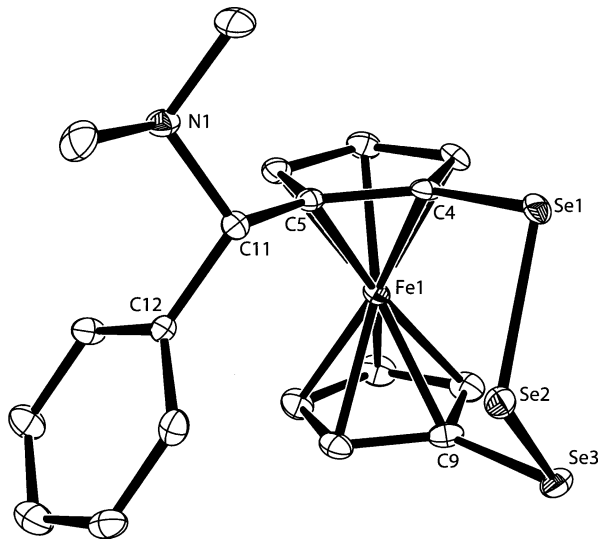
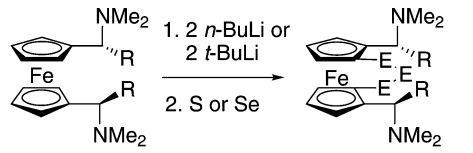


FIGURE 2 Structure of (*S,Rp*)-**3b**.



4a: R = Me
4a: R = Ph

5a: R = Me, E = S
5b: R = Ph, E = S
6a: R = Me, E = Se
6b: R = Ph, E = Se

SCHEME 2

trichalcogena bridge was substituted heteroannularly and in the opposite side to each other by the two same aminoalkyl groups. The ^{1}H NMR and ^{13}C NMR spectra of both **5a** and **5b** had two NMe_2 signals (singlet in ^{1}H NMR), showing that the NMe_2 group was unequal due to the direction of the bridge sulfur atom, which affected the chemical shifts of the groups. Figure 3 shows the X-ray diffraction analysis of the HCl salt of (*R,R,Sp,Sp*)-**5a** (*R* = Me, *E* = S), and Table 3 summarizes its selected bond lengths and angles. Crystallographic data of trichalcogenal (3) ferrocenophanes, **3a, 3b**, and **5a** are shown in Table 4.

We tested the ligand and catalytic ability of ferrocenophanes **2–3** and **5–6** (Fc^*E_3) to the benchmark asymmetric diethylzinc addition to benzaldehyde [13].These results are summarized in Table 5. The reaction was usually carried out in toluene at room temperature for 18 h using 1 mmol of benzaldehyde, 2 mmol of diethylzinc, and 5 mol% of Fc^*E_3

TABLE 1 Selected Bond Lengths and Bond Angles of (*S,Rp*)-**3a**·HCl

Bond Length (Å)		*Bond Angle (°)*	
C(11)–N(1)	1.51	N(1)–C(11)–C(1)	113.0
C(1)–C(11)	1.47	C(1)–C(11)–C(12)	112.6
C(11)–C(12)	1.55	Se(2)–Se(1)–C(5)	103.5
Se(1)–C(5)	1.88	Se(3)–Se(2)–Se(1)	102.4
Se(1)–Se(2)	2.35	C(10)–Se(3)–Se(2)	99.5
Se(2)–Se(3)	2.31		
Se(3)–C(10)	1.90		

TABLE 2 Selected Bond Lengths and Bond Angles of (*S,Rp*)-**3b**

Bond Length (Å)		*Bond Angle (°)*	
C(11)–N(1)	1.49	N(1)–C(11)–C(5)	108.9
C(5)–C(11)	1.51	C(12)–C(11)–C(5)	107.6
C(11)–C(12)	1.52	Se(2)–Se(1)–C(4)	100.8
Se(1)–C(4)	1.89	Se(3)–Se(2)–Se(1)	100.91
Se(1)–Se(2)	2.34	C(9)–Se(3)–Se(2)	100.4
Se(2)–Se(3)	2.33		
Se(3)–C(9)	1.89		

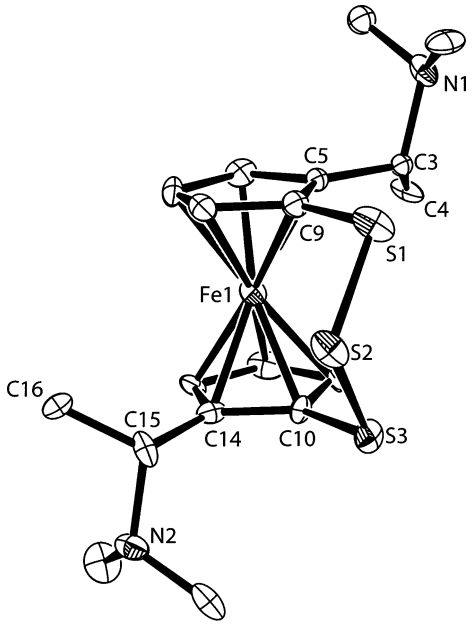


FIGURE 3 Structure of HCl salt of **5a** (HCl and H_2O are deleted).

to benzaldehyde. The zinc–chalcogen complex was assumed to be generated as a catalyst by the reaction with diethylzinc. The enantiomeric excess of the product was determined by GC with a chiral capillary column. As shown in the table, **2a,b, 3a,b, 5a,b**, and **6a,b** gave low yields with low ee% values. The use of the bis-type ferrocenophanes **5b** and **6b** gave somewhat higher ee values among the ferrocenophane derivatives although they were still unsatisfactory results. The *E–E* (*E* = S, Se) bond fission by diethylzinc to generate a zinc–chalcogen complex took place doubtfully, and this may cause the low enantioselectivities. **6a** was then first converted into the corresponding 1,1′-diselenol $Fc^*(SeH)_2$ by reduction with $LiAlH_4$ or DIBAH before the addition of diethylzinc and it would react with diethylzinc to generate the

TABLE 3 Selected Bond Lengths and Bond Angles of **5a**·2HCl·2H_2O

Bond Length (Å)		*Bond Angle (°)*	
C(3)–N(1)	1.50	N(1)–C(3)–C(4)	109.0
C(3)–C(5)	1.50	C(14)–C(15)–N(2)	109.0
C(3)–C(4)	1.51	C(14)–C(15)–C(16)	115.0
C(14)–C(15)	1.53	S(2)–S(1)–C(9)	101.9
C(15)–C(16)	1.53	S(3)–S(2)–S(1)	104.7
N(2)–C(15)	1.54	C(10)–S(3)–S(2)	104.3
S(1)–C(9)	1.77		
S(1)–S(2)	2.06		
S(2)–S(3)	2.06		
Se(3)–C(10)	1.75		

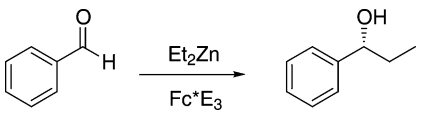
TABLE 4 Crystallographic Data of Compounds **3a, 3b**, and **5a**

Compound	*(S,Rp)*-**3a**-*HCl*	*(S,Rp)*-**3b**	*(R,R,Sp,Sp)*-**5a**·*2HCl·2H*$_2$*O*
Molecular formula	$C_{14}H_{18}NClFeSe_3$	$C_{19}H_{19}NFeSe_3$	$C_{18}H_{32}N_2O_2S_3Cl_2Fe$
Formula weight	528.48	554.09	531.40
Crystal dimensions (mm × mm × mm)	0.90 × 0.30 × 0.20	0.30 × 0.10 × 0.10	0.30 × 0.15 × 0.10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$	$P2_1$
Detector position (mm)	45.01	44.97	44.98
Pixel size (mm)	0.137	0.137	0.137
a (Å)	13.837(4)	12.090(4)	10.773(5)
b (Å)	7.374(2)	9.387(3)	8.612(4)
c (Å)	17.580(5)	16.376(5)	13.072(6)
β (°)	111.5520(11)	104.773(5)	98.264(5)
V (Å^3)	1668.3(8)	1797.0(10)	1200.2(9)
Z	4	4	2
D_{calc} (g/cm^3)	2.104	2.048	1.470
μ cm^{-1})	69.16	75.98	11.28
F(0 0 0)	1016.00	1072.00	556.00
Final *R* indices ($I > 3\sigma(I)$)	$R_1 = 0.030$, $wR_2 = 0.037$	$R_1 = 0.036$, $wR_2 = 0.083$	$R_1 = 0.065$, $wR_2 = 0.066$

zinc–selenium complex. However, the enantioselectivity hardly improved although the yield of the product was higher than that without them.

In this paper, we present the preparation of a series of chiral trichalcogena[3]-ferrocenophanes (E = S, Se) and discuss their structures on the basis of their NMR measurements and X-ray crystallographic analyses. Further studies on application of these compounds to ligands for a metal complex catalyzed asymmetric synthesis are now in progress.

TABLE 5 Diethylzinc Addition to Benzaldehyde Catalyzed by Fc*E_3[a]



Entry	*Fc* E*$_3$	*Yield (%)*	*ee (%) (config)*[b]
1	**2a**	70	2, *R*
2	**2b**	66	7, *R*
3	**3a**	81	6, *R*
4	**3b**	70	6, *R*
5	**5a**	47	4, *R*
6	**5b**	39	28, *R*
7	**5a**	46	14, *R*
8[c]	**6a**	99	12, *R*
9[c,d]	**6a**	99	36, *R*
10[d,e]	**6a**	84	16, *R*
11	**6b**	51	28, *R*

[a]Ferrocenophane (0.05 mmol), benzaldehyde (1.0 mmol), Et_2Zn (2.0 mmol), toluene (2 mL); room temperature, 18 h.
[b]Determined by GC with a chiral capillary column (Chiraldex GT-A).
[c]DIBAH (0.1 mmol) was added.
[d]In diethyl ether.
[e]$LiAlH_4$ (0.1 mmol) was added.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded using a Varian Mercury 300 NMR (300 MHz) spectrometer as solutions in $CDCl_3$. The chemical shifts are reported in δ units downfield from the internal reference, Me_4Si. Infrared spectra were obtained using a JASCO Herschel FT/IR-230A spectrometer. The HPLC analyses were carried out using a Hitachi L-7100 equipped with a UV detector using Daicel Chiralcel OB, OJ, and OD columns (0.46 mm, 25 cm) eluting with 2-propanol/*n*-hexane (1:9–1:99). The GC/MS analyses were carried out using a Hewlett–Packard 5980/5972 instrument equipped with a chiral capillary column (Asteck, Chiraldex G-TA) (0.25 mm, 30 m) (helium as carrier gas). The optical rotations were determined using a JASCO DIP-370. Column chromatography was performed on a Yamazen YFLC-254 and a Michael Miller column equipped with a UV detector using Merck silica gel 60. Preparative TLC was conducted using a 20 cm × 20 cm glass sheet coated with a 2 mm thick layer of Merck Kieselgel 60 PF_{254}. The optically active ferrocenes, **1a** (>99% ee), **1b** (98% ee), **4a** (>98% ee), and **4b** (>98% ee) were prepared by the reported methods [14].

Crystallographic Measurements

The diffraction data were collected at room temperature on a Rigaku AFC7R four-circle automated diffractometer with graphite monochromatized Mo-Kα radiation using the ω–2θ scan technique to a maximum 2θ value of 50° or 55°. The structure solution and refinements were carried out using

the teXsan and Crystal Structure crystallographic software packages. The positions of the nonhydrogen atoms were determined by Patterson methods (DIRDIF PATTY) or direct methods (SIR92) and expanded using Fourier techniques (DIRDIF94 or 99).

General Procedure for the Preparation of Mono ortho-Substituted Chiral Trithia- and Triselena-[3]ferrocenophanes

In a two-neck round-bottom flask containing a magnetic stirring bar, **1a** (>99% ee) (1.65 g, 6.4 mmol) and dry diethyl ether (100 mL) were charged under the slight pressure of nitrogen. The flask was cooled in an ice bath, and a hexane solution of *n*-BuLi (1.5 M, 5 mL, 7.5 mmol) (*t*-BuLi for **1b**) was then added using a syringe through the septum with magnetic stirring. The ice bath was removed and the mixture was stirred at room temperature for 1 h, TMEDA (1.7 mL, 7.7 mmol) was then added to the mixture followed by adding *n*-BuLi (1.5 M, 5 mL, 7.5 mmol). After stirring for 5 h, sulfur (1.28 g, 40 mmol) or selenium powder (3.1 g, 40 mmol) was added all at once and the solution was stirred overnight (15–18 h). The reaction was quenched with water, and the solution was then extracted with three 20 mL portions of ethyl acetate. The combined extracts were washed (brine), dried (K_2CO_3), filtered, and the solvent was removed on a rotary evaporator leaving a yellow residue. Purification of the residue by column chromatography (silica gel, hexane/ethyl acetate/triethyl amine = 100:1:0.03) gave the optically active mono-*ortho*-substituted trithia- or triselena[3]ferrocenophane.

(R,Sp)-(1-Dimethylamino)ethyl-2-(1,2,3-trithia)-[3]ferrocenophane **2a**. Yellow brown oil. Yield, 52%. $[\alpha]_D^{25} = +6.4$ ($c = 1.0$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): major isomer, δ 1.18 (d, 3H, $J = 6.9$ Hz), 2.07 (s, 6H), 3.45–3.6 (m, 1H), 3.5–5.1 (m, 7H): minor isomer (distinguished signals) δ 1.26 (d, 3H, $J = 7.2$ Hz), 2.19 (s, 6H). ^{13}C NMR ($CDCl_3$): major isomer, δ 13.2 (CH_3), 40.3 (NCH_3), 55.7 (CHN), 68.0, 68.1, 69.1, 69.3, 71.3, 71.4, 79.1, 86.4, 90.4, 98.5: minor isomer (distinguished signals) δ 16.8 (CH_3), 41.3 (NCH_3), 54.5 (CHN), 67.3, 68.3, 70.5, 70.9, 78.3, 82.2, 88.5, 91.3, 92.6. HRMS calcd for $C_{14}H_{18}FeNS_3$ [M + H] 351.9951, found 352.0044.

(R,Sp)-(1-Dimethylamino)benzyl-2-(1,2,3-trithia)-[3]ferrocenophane **2b**. Yellow brown oil. Yield, 30%. $[\alpha]_D^{25} = +53.0$ ($c = 0.35$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): major isomer, δ 2.06 (s, 6H), 2.56 (s, 1H, one of Cp-H), 3.3–4.8 (m, 6H), 4.80 (s, 1H, PhC*H*), 7.2–7.6 (m, 5H): minor isomer (distinguished signals) δ 2.11 (s), 2.44 (s, one of Cp-H), 4.56 (s, PhC*H*). ^{13}C NMR ($CDCl_3$): major isomer, δ 44.9 (NCH_3), 67.8 (CHN), 68.7, 69.4, 69.9, 71.4, 71.6, 72.3, 78.1, 89.9, 90.2, 92.1, 127.8, 128.2, 128.7, 142.7: minor isomer (distinguished signals) δ 44.4, 67.7 (NCH_3), 68.2, 68.8, 69.7, 70.4, 71.5, 72.4, 83.9, 89.6, 90.3, 100.5, 128.4, 128.9, 143.4. HRMS calcd for $C_{19}H_{20}FeNS_3$ [M +H] 414.0107, found 414.0303.

(R,Sp)-(1-Dimethylamino)ethyl-2-(1,2,3-triselena)-[3]ferrocenophane **3a**. Brown oil. Yield, 44%. $[\alpha]_D^{25} = +165.0$ ($c = 0.20$, $CHCl_3$). ^{1}H NMR (CD_2Cl_2, 300 MHz, −20°C): major isomer, δ 1.02 (d, 3H, $J = 6.8$ Hz), 2.00 (s, 6H), 3.52 (q, 1H), 3.75 (s, 1H), 3.84 (s, 1H), 3.94 (s, 1H), 4.16 (s, 1H), 4.28 (s, 1H), 4.37 (s, 2H): minor isomer (distinguished signals) δ 1.21 (d, $J = 6.8$ Hz), 2.17 (s). ^{13}C NMR (CD_2Cl_2): major isomer, δ 7.5 (CH_3), 38.4 (NCH_3), 56.4 (CHN), 66.9, 67.0, 68.2, 69.0, 69.7, 70.2, 81.0, 86.2, 89.9, 98.2: minor isomer (distinguished signals) δ 39.8 (NCH_3). HRMS calcd for $C_{14}H_{18}FeNSe_3$ [M + H] 493.8301, found 493.8815. The crystals of HCl salt of (*S,Rp*)-**3a** suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$–hexane. CCDC 274903.

(R,Sp)-(1-Dimethylamino)benzyl-2-(1,2,3-triselena)-[3]ferrocenophane **3b**. Brown solid; mp 103–104°C. Yield, 34%. $[\alpha]_D^{25} = +89.0$ ($c = 0.27$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): all signals are broadened. δ 2.06 (s, 6H), 2.51 (s, 1H), 3.3–4.8 (m, 7H), 7.2–7.6 (m, 5H). HRMS calcd for $C_{19}H_{20}FeNSe_3$ [M + H] 555.8459, found 555.9293. The crystals of (*S,Rp*)-**3b** suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$–hexane. CCDC 274904.

General Procedure for the Preparation of Bis ortho-Substituted Chiral Trithia- and Triselena-ferrocenophanes

In a two-neck round-bottom flask containing a magnetic stirring bar, **4a** (98% ee) (1.64 g, 5.0 mmol) and dry diethyl ether (100 mL) were charged under the slight pressure of nitrogen. The flask was cooled in an ice bath, and a hexane solution of *n*-BuLi (1.5 M, 13 mL, 20 mmol) (*t*-BuLi for **4b**) was then added using a syringe through the septum with magnetic stirring. The ice bath was removed, and the mixture was stirred at room temperature for 6 h. Sulfur (1.0 g, 31 mmol) or selenium powder (2.31 g, 30 mmol) was added all at once, and the solution was stirred overnight (15–18 h). The reaction was quenched with water, and the solution was then extracted with three 20-mL portions of ethyl acetate. The combined extracts were washed (brine), dried

(K_2CO_3), filtered, and the solvent was removed on a rotary evaporator leaving a yellow residue. Purification of the residue by column chromatography (silica gel, hexane/ethyl acetate/triethyl amine = 1:1:0.03) gave the optically active bis-*ortho*-substituted trithia- or triselenaferrocenophane.

(R,R,Sp,Sp)-1,1′-Bis(1-dimethylamino)ethyl-2-(1,-2,3-trithia)[3]ferrocenophane **5a**. Yellow brown solid; mp 129–130°C. Yield, 57%. $[\alpha]_D^{25} = +61$ ($c = 0.10$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.17 (d, 6H, $J = 6.9$ Hz), 2.06 (s, 6H), 2.12 (s, 6H), 3.43(q, 1H, $J = 6.9$ Hz), 3.55 (s, 1H), 3.59 (q, 1H, $J = 6.9$ Hz), 3.93 (s, 1H), 4.24 (s, 1H), 4.28 (s, 1H), 4.40 (s, 1H), 4.47 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 13.4 (CH_3), 17.2, 40.8 (CH_3), 41.7(NCH_3), 54.9 (CHN), 56.3 (CHN), 67.8, 69.0, 69.3, 70.6, 71.3, 82.9, 86.5, 89.1 93.6, 98.6. HRMS calcd for $C_{18}H_{27}FeN_2S_3$ [M + H] 423.0686, found 423.2571. The crystals of the HCl salt of **5a** suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$–hexane. CCDC 274905.

(R,R,Sp,Sp)-1,1′-Bis[(1-dimethylamino)benzyl]-2-(1,2,3-trithia)[3]ferrocenophane **5b**. Yellow brown solid; mp 44–45°C. Yield, 48%. $[\alpha]_D^{25} = +61$ ($c = 0.11$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.00 (s, 6H), 2.03 (s, 6H), 2.60 (t, 1H, $J = 1.1$ Hz), 3.33 (t, 1H, $J = 2.5$ Hz), 3.38 (t, 1H, $J = 2.5$ Hz), 3.51 (t, 1H, $J = 1.1$ Hz), 3.53 (s, 1H), 3.81 (s, 1H), 4.34 (t, 1H, $J = 1.1$ Hz), 4.55 (t, 1H, $J = 1.1$ Hz), 7.2–7.4 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 44.0 (NCH_3), 44.8 (NCH_3), 68.2, 68.9, 70.2, 70.7, 71.2, 72.3, 82.9, 89.2, 89.4, 92.8, 99.1, 127.7, 127.8, 128.2, 128.3, 128.4, 128.7, 129.0, 141.7, 143.6. HRMS calcd for $C_{28}H_{30}FeN_2S_3$ [M + H] 547.0999, found 547.1600.

(R,R,Sp,Sp)-1,1′-Bis[(1-dimethylamino)ethyl]-2-(1,2,3-triselena)[3]ferrocenophane **6a**. Brown solid; mp 94–95°C. Yield, 44%. $[\alpha]_D^{25} = +190$ ($c = 0.11$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.18 (d, 6H, $J = 6.8$ Hz), 2.14 (s, 12H), 3.5–3.6 (m, 2H), 3.7–3.8 (s, 2H), 4.19 (br s, 2H), 4.16 (br s, 2H). HRMS calcd for $C_{18}H_{27}FeN_2Se_3$ [M + H] 564.937, found 565.0068.

(R,R,Sp,Sp)-1,1′-Bis[(1-dimethylamino)benzyl]-2-(1,2,3-triselena)[3]ferrocenophane **6b**. Brown solid; mp 59–60°C. Yield, 30%. $[\alpha]_D^{25} = +103$ ($c = 0.117$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.04 (s, 6H), 3.0–4.5 (m, 8H), 7.2–7.4 (m, 10H). HRMS calcd for $C_{28}H_{30}FeN_2Se_3$ [M + H] 688.9353, found 689.0688.

General Procedure for the Diethylzinc Addition to Benzaldehyde

The following provides a typical experimental procedure for the diethylzinc addition to benzaldehyde. In a 50 mL schlenk tube containing a magnetic stirring bar, **6a** (35 mg, 0.05 mmol) and dry toluene (2.0 mL) were charged under the slight pressure of nitrogen. A hexane solution of diethylzinc (1.0 M, 2.0 mL, 2.0 mmol) was then added using a syringe through the septum with magnetic stirring at 0°C. The resulting mixture was stirred at 0°C for 1 h, and then benzaldehyde (106 mg, 1.0 mmol) was added to the mixture. The resulting solution was stirred at 0°C for 18 h. The reaction was quenched with 0.5 M HCl and the aqueous layer was extracted with three 20-mL portions of ethyl acetate, the aminoferrocene was extracted into the acidic aqueous layer. The combined extracts were washed (brine) and dried ($MgSO_4$). The yield of the product, i.e., 1-phenyl-1-propanol and its enantiomeric excess (ee%) was determined by GC using a chiral capillary column (Chiraldex G-TA, 20 m).

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[10] We could obtain the X-ray crystallographic structure of the HCl salt of **2a**, which showed that the bridge sulfur atom was oriented to *exo*. This result was consistent with the previous NMR study in solution [9a].

[11] Whether the *ortho*-substituent is an ammonium or an amino group should not determine the direction of the bridge atom because the bridge atom of **2a**·HCl tend to face to *exo* while the bridge atom of **3a**·HCl face to *endo*. Thus, the direction of the bridge atom of HCl free **3a** would be *endo* similar to the structure of **3b**.

[12] This is the first preparation of these optically active bis *ortho*-substituted trichalcogena[3]ferrocenophanes, and the X-ray crystallographic structure of **5a** is demonstrated in the present study although a mixture of the *dl* and *meso*-**5a** has been prepared [9a].

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