The First X-ray Structure Determination of an Optically Pure Bismuthane

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(4-Chlorophenyl){(*S*)-2-[(*R*)-1-(dimethylamino)ethyl]ferrocenyl}iodobismuthane (**3b**), the first example of an optically pure bismuthane, was synthesized with exclusive stereoselectivity using Bi−N intramolecular coordination and the planar chirality of ferrocene. The variable-temperature ^{1}H NMR spectra measured in the range from −50 to +50 °C in $CDCl_3$ revealed that no epimerization takes place at the bismuth center. An X-ray crystallographic study demonstrated that the bismuth atom is diastereoselectively introduced into the substituted cyclopentadienyl ring and that the 4-chlorophenyl group occupies the exo position toward the iron atom. The absolute configuration around the bismuth atom was determined to be *R*. The longer intramolecular Bi−N distance of **3b** [2.71(1) Å] compared with those of chloro{2-[(*R*)-1-(dimethylamino)ethyl]phenyl}phenylbismuthane (**1a**,**b**) [2.55(2), 2.57(2) Å, respectively] indicates a weaker Bi−N coordination in the ferrocene system. The specific rotation of **3b**, $[\alpha]_D^{23}$ −546 (*c* 1.0, $CHCl_3$), is negatively much larger than that of bis(4-chlorophenyl){(*S*)-2-[(*R*)-1-(dimethylamino)ethyl]ferrocenyl}bismuthane (**5b**), $[\alpha]_D^{23}$ −330 (*c* 1.0, $CHCl_3$), which is considered to be the result of generation of the optically active center at bismuth.

Introduction

Construction of optically active heteroatom centers has attracted much interest in main group chemistry.[1] Although a number of compounds bearing such a center of the group 15 elements have been studied, the research has been limited to examples of phosphorus,[2] arsenic,[3] and antimony.[4] Bismuth occupies the last row of this group and is the heaviest stable element in nature; thus extension of such studies to compounds of bismuth is of interest. The paucity of such organobismuth compounds is most likely due to the lack of suitable methods for their preparation. Although we have succeeded in the synthesis of a diastereomeric mixture of chlorobismuthane **1** (**a**:**b** = 77:23 in $CDCl_3$) by asymmetric induction at a bismuth atom using the (*R*)-1-(dimethylamino)ethyl group as an auxiliary chiral ligand,[5] the optical resolution was unsuccessful due to cis/trans pairing crystals in ratio of 1:1.[6] In our preliminary communication,[7] we reported an efficient methodology for inducing exclusive stereocontrol over a chiral bismuth center by using Bi−N intramolecular coordination and the planar chirality of ferrocene. Thus, the relatively small C−Bi−C bond angle (~93°) enhances the repulsive interaction between the endo aromatic substituent and the ferrocene moiety, so that the exo isomer **2** is formed exclusively (Scheme 1).

The methodology is useful for the stereoselective synthesis of optically pure bismuthanes. We describe here the stereoselective synthesis, X-ray crystallographic study and behavior in solution of enantiomerically pure **3b**.

Results and Discussion

Compound **2** as prepared is a mixture of enantiomers because the bismuth is not introduced selectively into

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(1) (a) For boron: Shiner, C. S.; Garner, C. M.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 7167. (b) For silicon: Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964**, *86*, 3271. (c) For tin: Jastrzebski, J. T. B. H.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1991**, *413*, 43. (d) For selenium: Kamigata, N.; Nakamura, Y.; Kikuchi, K.; Ikemoto, I.; Shimizu, T.; Matsuyama, H. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1721. (e) For tellurium: Kamigata, N.; Matsuhisa, A.; Taka, H.; Shimizu, T. *J. Chem. Soc., Perkin Trans. 1* **1995**, 821.

(2) (a) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012. (b) Korpiun, O.; Lewis, R. A.; Chickos, J.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4842. (c) Horner, L.; Schedlbauer, F.; Beck, P. *Tetrahedron Lett.* **1964**, 1421.

(3) Campbell, I. G. M.; Poller, R. C. *J. Chem. Soc.* **1956**, 1195.

(4) (a) Campbell, I. G. M.; Morrill, D. J. *J. Chem. Soc.* **1955**, 1662. (b) Campbell, I. G. M. *J. Chem. Soc.* **1952**, 4448. (c) Campbell, I. G. M. *J. Chem. Soc.* **1950**, 3109.

(5) Suzuki, H.; Murafuji, T.; Matano, Y.; Azuma, N. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2969.

(6) Murafuji, T.; Azuma, N.; Suzuki, H. *Organometallics* **1995**, *14*, 1542.

(7) Murafuji, T.; Mutoh, T.; Sugihara, Y. *J. Chem. Soc., Chem. Commun.* **1996**, 1693.

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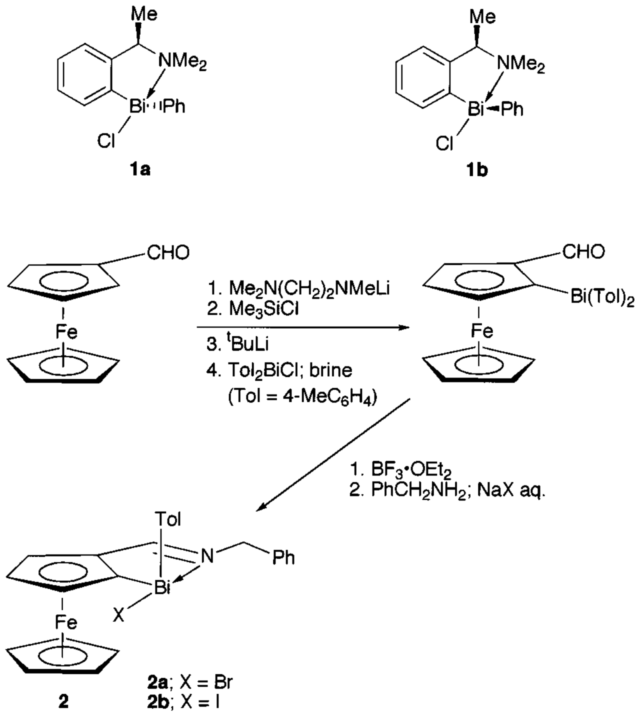
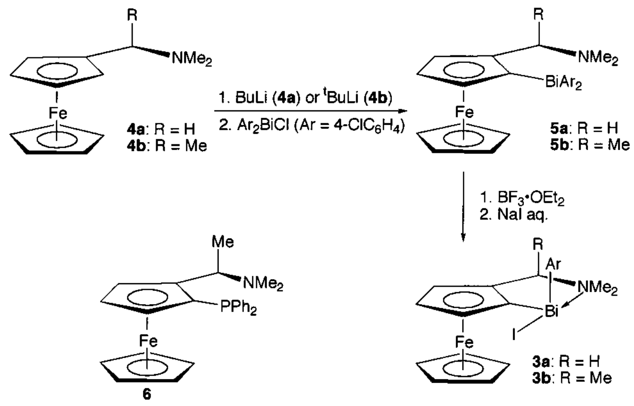
Scheme 1



Scheme 2



one of the ortho positions in the substituted cyclopentadienyl ring.[7] If the coordinative imino group of **2** is replaced by the (*R*)-1-(dimethylamino)ethyl group, optically pure **3b** should form predominantly as a single diastereomer since bismuth can be introduced selectively into one of the ortho positions in the substituted cyclopentadienyl ring by using diastereoselective ortholithiation.[8] Initially, we examined the synthesis of iodobismuthane **3a** prior to **3b** to confirm the stereocontrol over a chiral bismuth center and the stability (Scheme 2).[9] As expected, **3a** was obtained in 30% overall yield as a single and stable diastereomer, where the 4-chlorophenyl group lies exo to the iron and a Bi−N intramolecular coordination bond forms. Thus, the proton signals of the unsubstituted cyclopentadienyl ring do not suffer from any upfield shift by the ring current of the 4-chlorophenyl group.[7] Furthermore, the one-proton signal of the substituted cyclopentadienyl ring is observed at a markedly downfield region (δ 4.85). Unlike **4a**, the proton signals of the CH_2 and Me_2N groups in **3a** appeared at ambient temperature as sharp AB doublets and a very broad singlet, respectively. At −50 °C in $CDCl_3$, the latter signal split into two sharp singlets, which coalesced at 20 °C. At this coalescence temperature, the proton signals of the Me_2N group in the benzene analogue of **3a**, that is, chloro(4-chlorophenyl){2-[(dimethylamino)methyl]phenyl}bismuthane, remained as two sharp singlets. These findings indicate that the nitrogen atom coordinates weakly with the bismuth atom in **3a** and that the dissociation−regeneration of the Bi−N bond together with concomitant vertex inversion at the nitrogen atom and rotation about the CH_2−N bond of 180° takes place at the coalescence temperature.

Optically pure iodobismuthane **3b** could be obtained in 35% overall yield as a single diastereomer by a method similar to that used for **3a** using diastereoselective ortholithiation.[8] The proton signals of the Me_2N group were observed at ambient temperature as two very broad singlets. The variable-temperature ^1H NMR spectra of **3b** measured in the range from −50 to +50 °C in $CDCl_3$ showed a trend similar to that observed in **3a**. Namely, the proton signals of the Me_2N group appeared at −50 °C as two sharp singlets. The coalescence temperature was 40 °C, which is higher than that of **3a**. Activation parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) for this process were estimated to be 13.5 kcal mol^{-1}, 17.5 kcal mol^{-1}, and 13.8 cal mol^{-1} deg^{-1} and 14.2 kcal mol^{-1}, 16.0 kcal mol^{-1}, and 5.7 cal mol^{-1} deg^{-1}, respectively, for **3a** and **3b**. It should be pointed out that the proton signals of the unsubstituted cyclopentadienyl ring showed essentially no shift even above the coalescence temperature. This indicates that the 4-chlorophenyl group is fixed toward the exo side and no epimerization takes place at the bismuth center.

A single-crystal X-ray crystallographic study revealed the stereochemistry at the chiral bismuth center of **3b** (Figure 1). Namely, the bismuth atom is diastereoselectively introduced into the substituted cyclopentadienyl ring, and furthermore, the 4-chlorophenyl group occupies an exo position toward the iron atom. The absolute configuration around the bismuth atom was determined to be *R* in accordance with the rule introduced by Martin in the case of optically active sulfuranes.[10] The bismuth center has a distorted pseudotrigonal bipyramidal configuration, where the carbon atoms C(1) and C(7) occupy an equatorial plane with a C(1)−Bi(1)−C(7) angle of 95.8(5)° (Table 2). The apical positions of the pseudotrigonal bipyramid are occupied by the nitrogen and iodine atoms with a N(1)−Bi(1)−I(1) angle of 161.4(2)°. The lone pair of electrons is considered to occupy the remaining equatorial position. The intramolecular Bi(1)−N(1) distance, 2.71(1) Å, is longer than the sum of the covalent radii (2.14 Å) but is much shorter than the sum of the van der Waals radii (3.66 Å).[5] In addition, the Bi(1)−I(1) bond length, 2.969(1) Å, is longer than the sum of the covalent radii (2.72 Å).[11] These observations support the formation of a Bi−N intramolecular coordination bond. The longer

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(8) For diastereoselective ortholithiation of **4b**, see: Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389.

(9) For ortholithiation of **4a**, see: Slocum, D. W.; Rockett, B. W.; Hauser, C. R. *J. Am. Chem. Soc.* **1965**, *87*, 1241.

(10) Martin, J. C.; Balthazor, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 152.

(11) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

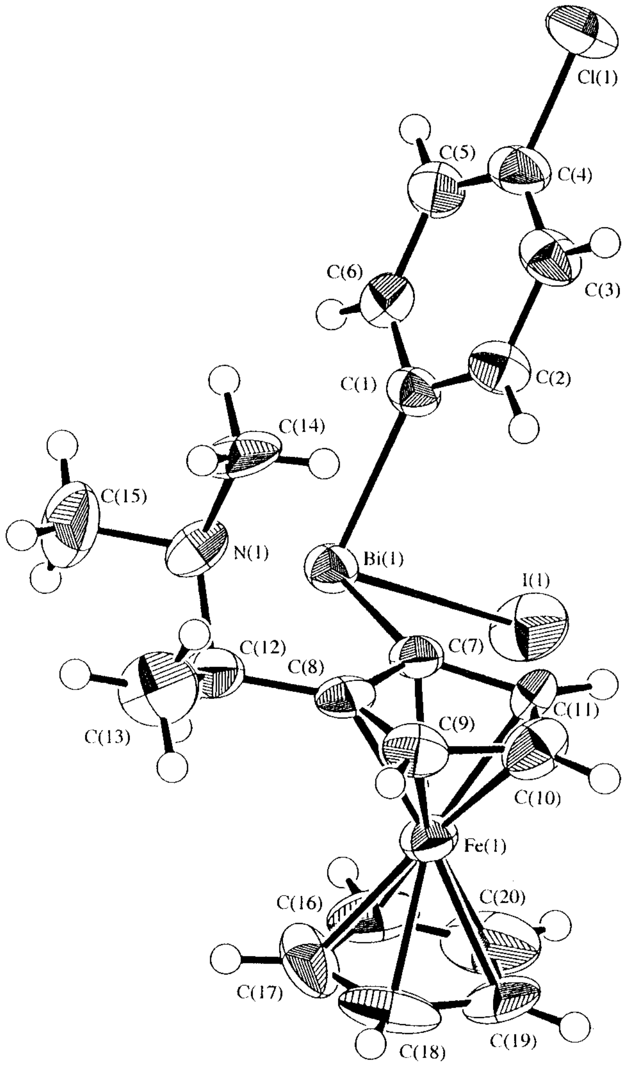

Figure 1. ORTEP drawing of a molecular structure of **3b**. – indicates 50% probability of ellipsoids.

Bi–N distance of **3b** compared with those of **1a**,**b** [2.55(2) and 2.57(2) Å, respectively][6] is ascribable to the large angles constituted by the vicinal substituents of the cyclopentadienyl ring, indicating a weaker Bi–N coordination in the ferrocene system. The intermolecular Bi(1)–I(1) distance of **3b**, 3.990(1) Å, which is within the sum of the van der Waals radii (4.24 Å),[11] suggests the interaction between these atoms.

Optically active **3b** has three different stereogenic centers within this molecule. The specific rotation $[\alpha]_D^{23}$ is -546 (*c* 1.0, $CHCl_3$), which is negatively much larger than those of **4b**, $[\alpha]_D^{24}$ +14.1 (*c* 1.6, EtOH),[12] and **5b**, $[\alpha]_D^{23}$ -330 (*c* 1.0, $CHCl_3$). The specific rotation of **5b** is comparable to that of compound **6**, the phosphorus homologue of **5b**, $[\alpha]_D^{25}$ -361 (*c* 0.6, $CHCl_3$).[12] If the molecular weights of **4b**, **5b**, and **3b** are taken into account, molecular rotations $[M]_D$ of these compounds are calculated at +36, -2270, and -3842, respectively. Such a large difference in the values between **3b** and **5b** is considered to arise from the generation of the stereogenic center at bismuth.

In conclusion, an optically pure bismuthane was synthesized for the first time with exclusive stereoselectivity by using Bi–N intramolecular coordination and the planar chirality of ferrocene. This strategy may serve as a guide for inducing stereocontrol over other heteroatom centers.

Table 1. Crystal and Structure Determination Data for 3b

formula	$C_{20}H_{22}BiClFeIN$
fw	703.59
temp, K	298
a, Å	11.147(5)
b, Å	20.402(4)
c, Å	9.417(2)
V, Å^3	2142(1)
crystal color and shape	red-brown and plate
crystal system	orthorhombic
space group	$P2_12_12_1$
Z	4
F(000)	1312
D_{calcd}, g cm^{-3}	2.182
crystal dimensions, mm	0.35 × 0.30 × 0.15
λ, Å (graphite-monochromated Mo Kα)	0.710 69
diffractometer	Rigaku AFC5R
μ, cm^{-1}	104.17
collection range	$2\theta_{max} = 55°$
scan type	$\omega-2\theta$
scan rate, deg min^{-1}	16.0
scan width, deg	$0.84 + 0.30 \tan\theta$
no. of unique reflections	2824
no. of observed data	2013 [$I > 3.00\sigma(I)$]
no. of variables	227
range of transmission factors	0.43–1.00
R^a	0.038
$R_w{}^a$	0.035
maximum peak in final Fourier map, e Å^{-3}	1.53
minimum peak in final Fourier map, e Å^{-3}	-1.55
goodness of fit	1.28

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$; $w = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3b, with Esd's in Parentheses

	Bond Lengths		
Bi(1)–N(1)	2.71(1)	Bi(1)–C(1)	2.24(1)
Bi(1)–C(7)	2.19(1)	Bi(1)–I(1)	2.969(1)
	Bond Angles		
N(1)–Bi(1)–I(1)	161.4(2)	C(1)–Bi(1)–C(7)	95.8(5)
C(1)–Bi(1)–I(1)	89.1(3)	C(7)–Bi(1)–I(1)	92.1(3)
N(1)–C(12)–C(8)	107(1)	Bi(1)–C(7)–C(8)	119(1)
Bi(1)–C(7)–C(11)	135(1)		

Experimental Section

General Comments. All reactions were carried out under argon. Diethyl ether and dichloromethane were distilled from calcium hydride under nitrogen before use. Bismuth(III) chloride was purified by refluxing with thionyl chloride. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Hitachi R-250H (250 MHz) and JEOL EX-400 (400 MHz) spectrometer, respectively, with tetramethylsilane as an internal standard. Variable-temperature ^1H NMR spectra were measured in $CDCl_3$ on a JEOL GSX-400 (400 MHz). IR spectra were obtained as KBr pellets on a Nicolet Impact 410 spectrophotometer. Optical rotations were taken with HORIBA SEPA-200.

***exo*-[2-(*N*-Benzylformimidoyl)ferrocenyl]bromo(4-methylphenyl)bismuthane (2a).** Chlorobis(4-methylphenyl)bismuthane (~3 mmol) was generated by stirring tris(4-methylphenyl)bismuthane (964 mg, 2 mmol) and bismuth(III) chloride (315 mg, 1 mmol) in diethyl ether (10 mL) for 1 h at room temperature. To a solution of lithiated *N*,*N*,*N*′-trimethylethylenediamine (~4 mmol) prepared from *N*,*N*,*N*′-trimethylethylenediamine (0.51 mL, 4 mmol) and *n*-butyllithium (4

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(12) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138.

mmol) in diethyl ether (10 mL) was added at ice bath temperature formylferrocene (428 mg, 2 mmol) followed after 15 min by chlorotrimethylsilane (0.25 mL, 2 mmol), and the mixture was stirred for 1 h at room temperature. Then, *tert*-butyllithium (4 mmol) was added dropwise at −78 °C and the temperature was maintained for 30 min. To the lithium compound thus obtained was added at this temperature a suspension of the above chlorobismuthane, and the resulting mixture was stirred for 15 min, during which time the temperature was raised to 0 °C. After addition of brine (5 mL), the mixture was diluted with ethyl acetate (10 mL) and the insoluble polymeric substances were filtered off. The organic layer was separated and evaporated under reduced pressure to leave a brown oil, which was purified by chromatography on deactivated silica gel (10% water) using benzene as eluent to afford crude (2-formylferrocenyl)bis(4-methylphenyl)bismuthane. To a solution of this bismuthane (204 mg, 0.3 mmol) in C_6H_6 (5 mL) was added dropwise at ice bath temperature boron trifluoride−diethyl etherate until the bismuthane was consumed (checked by TLC). After addition of benzylamine (107 mg, 1 mmol), the reaction was quenched by saturated aqueous NaBr (3 mL) and the organic layer was evaporated under reduced pressure to afford crude **2a**. Recrystallization from C_6H_6−hexane (5:1) gave pure product as reddish orange crystals: yield, 20%; mp 190−192 °C (dec); ^{1}H NMR δ 2.26 (3H, s, Me), 4.25 (5H, s, C_5H_5), 4.44 (1H, d, J_{AB} = 14.0 Hz, CH_2), 4.54 (1H, d, J_{AB} = 14.0 Hz, CH_2), 4.67 (1H, m, C_5H_3), 4.76 (1H, m, C_5H_3), 5.19 (1H, m, C_5H_3), 7.15−7.38 (7H, m, ArH), 7.99 (2H, d, J_{AB} = 7.3 Hz, MeAr*H*), 8.70 (1H, s, CHN); IR (cm^{-1}) 1610 (C=N). Anal. Calcd for $C_{25}H_{23}BiBrFeN$: C, 44.0; H, 3.4; N, 2.05. Found: C, 43.6: H, 3.65; N, 2.1.

***exo*-[2-(*N*-Benzylformimidoyl)ferrocenyl]iodo(4-methylphenyl)bismuthane (2b).** To a solution of (2-formylferrocenyl)bis(4-methylphenyl)bismuthane (204 mg, 0.3 mmol) in C_6H_6 (5 mL) was added dropwise at ice bath temperature boron trifluoride−diethyl etherate until the bismuthane was consumed (checked by TLC). After an addition of benzylamine (107 mg, 1 mmol), the reaction was quenched by saturated aqueous NaI (3 mL) and the organic layer was evaporated under reduced pressure to afford crude **2b**. Recrystallization from C_6H_6−hexane (5:1) gave pure product as reddish orange crystals: yield, 16%; mp 212−214 °C; ^{1}H NMR δ 2.27 (3H, s, Me), 4.25 (5H, s, C_5H_5), 4.43 (1H, d, J_{AB} = 14.0 Hz, CH_2), 4.53 (1H, d, J_{AB} = 14.0 Hz, CH_2), 4.66 (1H, m, C_5H_3), 4.71 (1H, m, C_5H_3), 5.27 (1H, m, C_5H_3), 7.16−7.22 (4H, m, ArH), 7.35−7.37 (3H, m, ArH), 8.00 (2H, d, J_{AB} = 7.9 Hz, MeAr*H*), 8.63 (1H, s, CHN); IR (cm^{-1}) 1610 (C=N). Anal. Calcd for $C_{25}H_{23}BiFeIN$: C, 41.2; H, 3.2; N, 1.9. Found: C, 40.8: H, 3.15; N, 1.95.

Bis(4-chlorophenyl){2-[(dimethylamino)methyl]ferrocenyl}bismuthane (5a). Chlorobis(4-chlorophenyl)bismuthane (∼2 mmol) was generated by stirring tris(4-chlorophenyl)bismuthane (723 mg, 1.33 mmol) and bismuth(III) chloride (211 mg, 0.7 mmol) in diethyl ether (10 mL) for 2 h at room temperature. To a suspension of ortholithiated [(*N*,*N*-dimethylamino)methyl]ferrocene[9] (∼2 mmol) generated from [(*N*,*N*-dimethylamino)methyl]ferrocene (0.4 mL, 2 mmol) and *n*-butyllithium (4 mmol) in diethyl ether (5 mL) was added dropwise at ice bath temperature a suspension of the above chlorobismuthane, and the resulting mixture was stirred for 15 min. After the addition of brine (5 mL), the mixture was diluted with ethyl acetate (10 mL) and the insoluble polymeric substances were filtered. The organic layer was separated and evaporated under reduced pressure to leave a brown oil, which was purified by chromatography on silica gel using hexanes−ethyl acetate (5:1) as the eluent to afford crude **5a**. Recrystallization from hexane−ethyl acetate (10:1) gave pure product as orange crystals: yield, 36%; mp 135−137 °C; ^{1}H NMR δ 1.92 (6H, s, Me_2N), 2.94 (1H, d, J_{AB} = 12.8 Hz, CH_2N), 3.66 (1H, d, J_{AB} = 12.8 Hz, CH_2N), 3.85 (1H, m, C_5H_3), 4.02 (5H, s, C_5H_5), 4.24 (2H, m, C_5H_3), 7.26 (2H, d, J_{AB} = 7.9 Hz, ArH), 7.34 (2H, d, J_{AB} = 7.9 Hz, ArH), 7.65 (2H, d, J_{AB} = 7.9 Hz, ArH), 7.73 (2H, d, J_{AB} = 7.9 Hz, ArH); IR (cm^{-1}) 1470, 1087, 1007, 803. Anal. Calcd for $C_{25}H_{24}BiCl_2FeN$: C, 44.5; H, 3.6; N, 2.1. Found: C, 44.3: H, 3.65; N, 2.0.

***exo*-(4-Chlorophenyl){2-[(dimethylamino)methyl]ferrocenyl}iodobismuthane (3a).** To a solution of **5a** (348 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise at ice bath temperature boron trifluoride−diethyl etherate until **5a** was consumed (checked by TLC). The reaction was quenched by the addition of saturated aqueous NaI (3 mL) and the organic layer was evaporated under reduced pressure to afford crude **3a**. Recrystallization from ethyl acetate gave pure product as orange crystals: yield, 83%; mp 153−157 °C (dec); ^{1}H NMR δ 2.30 (6H, br s, Me_2N), 3.14 (1H, d, J_{AB} = 14 Hz, CH_2N), 3.76 (1H, d, J_{AB} = 14 Hz, CH_2N), 4.26 (5H, s, C_5H_5), 4.29 (1H, m, C_5H_3), 4.48 (1H, m, C_5H_3), 4.85 (1H, m, C_5H_3), 7.38 (2H, d, J_{AB} = 7.9 Hz, ArH), 8.10 (2H, d, J_{AB} = 7.9 Hz, ArH); IR (cm^{-1}) 1470, 1004, 830, 812. Anal. Calcd for $C_{19}H_{20}BiClFeIN$: C, 33.1; H, 2.9; N, 2.0. Found: C, 32.9: H, 2.9; N, 2.0.

Bis(4-chlorophenyl){(*S*)-2-[(*R*)-1-(dimethylamino)ethyl]ferrocenyl}bismuthane (5b). Diastereoselective ortholithiation of (*R*)-(+)-*N*,*N*-dimethyl-1-ferrocenylethylamine (**4b**) was carried out by modifying the reported procedure.[8] To a solution of **4b** (0.51 mL, 2 mmol) in diethyl ether (10 mL) was added at ice bath temperature *tert*-butyllithium (2.1 mmol), and the mixture was stirred at room temperature for 2 h. To a suspension of the lithium compound thus obtained was added at ice bath temperature an ethereal suspension of chlorobis(4-chlorophenyl)bismuthane (∼2 mmol), and the resulting mixture was stirred for 15 min. Similar workup as described for **5a** followed by purification by chromatography on silica gel using hexane−ethyl acetate (5:1) as the eluent afforded crude **5b**. Recrystallization from hexane−ethyl acetate (10:1) gave pure product as orange crystals: yield, 42%; mp 115−116 °C; ^{1}H NMR δ 1.14 (3H, d, *J* = 6.7 Hz, Me), 1.79 (6H, s, Me_2N), 3.89 (1H, m, C_5H_3), 4.01 (5H, s, C_5H_5), 4.05 (1H, q, *J* = 6.7 Hz, MeC*H*), 4.26 (2H, m, C_5H_3), 7.26 (2H, d, J_{AB} = 7.9 Hz, ArH), 7.33 (2H, d, J_{AB} = 8.5 Hz, ArH), 7.64 (2H, d, J_{AB} = 7.9 Hz, ArH), 7.73 (2H, d, J_{AB} = 8.5 Hz, ArH); IR (cm^{-1}) 1471, 1087, 1007, 803. $[\alpha]_D^{23}$ −330 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{26}H_{26}BiCl_2FeN$: C, 45.4; H, 3.8; N, 2.0. Found: C, 45.4: H, 4.0; N, 1.9.

***exo*-(4-Chlorophenyl){(*S*)-2-[(*R*)-1-(dimethylamino)ethyl]ferrocenyl}iodobismuthane (3b).** To a solution of **5b** (344 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise at ice bath temperature boron trifluoride−diethyl etherate until **5b** was consumed (checked by TLC). The reaction was quenched by the addition of saturated aqueous NaI (3 mL), and the organic layer was evaporated under reduced pressure to afford crude **3b**. Recrystallization from ethyl acetate gave pure product as orange crystals: yield, 83%; mp 176−179 °C (dec); ^{1}H NMR δ 1.13 (3H, d, *J* = 6.7 Hz, Me), 1.55 (3H, br s, NMe), 2.55 (3H, br s, NMe), 4.23 (1H, q, *J* = 6.7 Hz, MeC*H*), 4.24 (5H, s, C_5H_5), 4.32 (1H, m, C_5H_3), 4.45 (1H, m, C_5H_3), 4.82 (1H, m, C_5H_3), 7.38 (2H, d, J_{AB} = 7.9 Hz, ArH), 8.10 (2H, d, J_{AB} = 7.9 Hz, ArH); ^{13}C NMR δ 8.2, 37.4(br), 44.3(br), 62.9, 69.9, 70.2, 72.0, 79.8, 99.7, 103.4, 131.0, 134.4, 139.2, 164.1; IR (cm^{-1}) 1090, 1008, 801. $[\alpha]_D^{23}$ −546 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{20}H_{22}BiClFeIN$: C, 34.1; H, 3.15; N, 2.0. Found: C, 34.1: H, 3.15; N, 2.0.

X-ray Crystallography. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator. The data were collected at 298 K using the $\omega-2\theta$ scan technique to a maximum 2θ value of 55.0°. Scans of $(0.84 + 0.30 \tan \theta)°$ were made at a speed of 16.0 deg min^{-1} (in ω). A total of 2824 unique reflections were collected. The intensities of three representative reflections measured after every 150 reflections declined by 0.29%. A linear correction factor was applied to the data to account for this phenomenon. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.43 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient 1.02×10^{-7}). The structure was solved by the Patterson method.[13] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement against $|F|$ was based on 2013 observed reflections [$I > 3.00\sigma(I)$] and 227 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.038$ and $R_w = 0.035$. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.53 and -1.55 e/Å^3, respectively. Neutral-atom scattering factors were taken from Cromer and Waber.[14] Anomalous dispersion effects were included in F_{calcd};[15] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[16] All calculations were performed using the TEXSAN[17] crystallographic software package of Molecular Structure Corp.

The chirality has been examined by the test of the R factor ratio.[18] The R_w factor for the structure refinement without anomalous dispersion effect was 0.052 for 227 variables and 2013 observations. Inclusion of the anomalous dispersion gave the R_w factors of 0.0656 and 0.0937 for the present and its enantiomeric structure, respectively, which yielded the R factor ratio of 1.43. The corresponding significance point is $R_{b,\ N,\ \alpha} = R_{1,\ 1786,\ 0.005} = 1.002$, so that the enantiomeric structure can be rejected with the probability higher than 99.5%.[19]

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Supporting Information Available: Full details of crystal data, fractional atomic coordinates, bond lengths, bond angles, hydrogen coordinates, and thermal parameters for **3b** and a unit cell diagram (33 pages). Ordering information is given on any current masthead page.

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