

Chiral Chlorobismuthines Stabilized by the Intramolecular Coordination of an *N,N*-Dimethylamino Group: X-Ray Structure Analysis, Asymmetric Induction at the Bismuth Centre, and Dynamic Behaviour in Solution

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Chiral chlorobismuthines **3** stabilized by intramolecular coordination of an *N,N*-dimethylamino group have been synthesized by the selective fluorodearylation of the bismuthines **1** with boron trifluoride–diethyl ether, followed by halogen exchange of the resulting fluorobismuthines **2** with brine. An X-ray crystallographic structure analysis of **3b** revealed that the bismuth centre has a distorted pseudotrigonal bipyramidal structure through the formation of a hypervalent 3-centre 4-electron bond with the chlorine and nitrogen atoms at apical positions. ¹H NMR spectra of compounds **3** in CDCl₃ at room temperature reflected their fixed conformation in the solid state. Chiral chlorobismuthines **7a** and **7b** were obtained in a similar manner starting from optically pure (*R*)-*N,N*-dimethyl-1-phenylethylamine as a mixture of two diastereoisomers (77:23 and 78:22, respectively), the isomeric ratios of which were not influenced by the equatorial aryl groups present. Variable-temperature dynamic ¹H NMR spectra of the diastereoisomeric mixture of **7a** provided important information about its behaviour in solution; in [²H₈]toluene dynamic but reversible dissociation of intramolecular Bi–N coordination was observed only at elevated temperatures, while in [²H₆]-DMSO it occurred quite easily below room temperature, leading to the inversion of configuration at the chiral bismuth centre.

Bismuthines bearing three different ligands have a chiral bismuth centre and are of considerable interest as a potential chiral source for the inductive generation of optical activity. Although several chiral bismuthines have been reported previously,¹ none of them has been proved to have a pair of enantiomers. Recently, we have established a new general method for the synthesis of chiral triaryl bismuthines² and halogenobismuthines³ based on the intramolecular coordination of a sulfonyl group, and some of the former compounds were successfully resolved into a pair of enantiomers by HPLC using optical columns.² As a further extension of this work, we now report the synthesis, X-ray structure and ¹H NMR studies of some chiral chlorobismuthines stabilized by the intramolecular coordination of an *N,N*-dimethylamino group.⁴ In the present study, the introduction of 2-[(*R*)-1-(*N,N*-dimethylamino)ethyl]phenyl group† onto the chiral bismuth centre as an additional chiral source led to a mixture of two diastereoisomers of **7**, which demonstrated not only the generation of optical activity at the bismuth centre, but also revealed the suppression of the configurational inversion at a bismuth atom through intramolecular coordination by an *N,N*-dimethylamino group.

Results and Discussion

Starting from chlorodiaryl bismuthines and lithiated *N,N*-dimethylbenzylamine,⁶ chiral chlorobismuthines **3a–e** were synthesized through the fluorodearylation of **1** with boron trifluoride–diethyl ether and subsequent halogen exchange of **2** with brine as shown in Scheme 1. An ¹H NMR spectrum of compound **3c** exhibited the major structural features of this type of compound. Unlike *N,N*-dimethylbenzylamine, the NMe₂ and CH₂ groups of **3c** were both observed diastereo-

topically. The signals of the former group coalesced at 70 °C in [²H₈]toluene,‡ and this was also the case with other chlorobismuthines, except for compound **3e** where the coalescence temperature (*T*_C) was much elevated (90 °C).§ In contrast, ¹H NMR measurement in [²H₆]-DMSO resulted in a complete coalescence of the NMe₂ peaks even at room temperature. A large downfield shift of one of the aromatic proton signals was also observed.³ These observations are indicative of a distorted pseudotrigonal bipyramidal structure for **3** brought about the intramolecular coordination of a side-chain nitrogen atom. Replacement of a chlorine atom by bromine did not affect the coalescence temperature (compound **4**; *T*_C 65 °C). Chlorobismuthine **5** was also synthesized from *N,N*-dimethyl-1-naphthylamine in a similar manner.|| With this compound, the ¹H signals of the NMe₂ group did not coalesce even at 110 °C in [²H₈]toluene.¶

In order to confirm the structure of the chlorobismuthines **3**, an X-ray structure analysis was carried out for **3b** (Fig. 1).** As expected, the bismuth centre was shown to have a distorted pseudotrigonal bipyramidal configuration similar to that of

† It is possible to explain the coalescence of the NMe₂ group by two processes. One is the dissociation of the intramolecular Bi–N coordination bond followed by vertex inversion at the nitrogen atom and subsequent restoration of the Bi–N bond after rotation about the CH₂–N bond of 180°. The other is inversion of the configuration at the chiral bismuth centre without prior Bi–N dissociation. As detailed in the text, the former process provides the most reasonable explanation of the observations. Recently, the occurrence of the latter process (edge inversion) was reported for 1-(2'-*N,N*-dimethylaminomethyl)-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxabismole.^{4b}

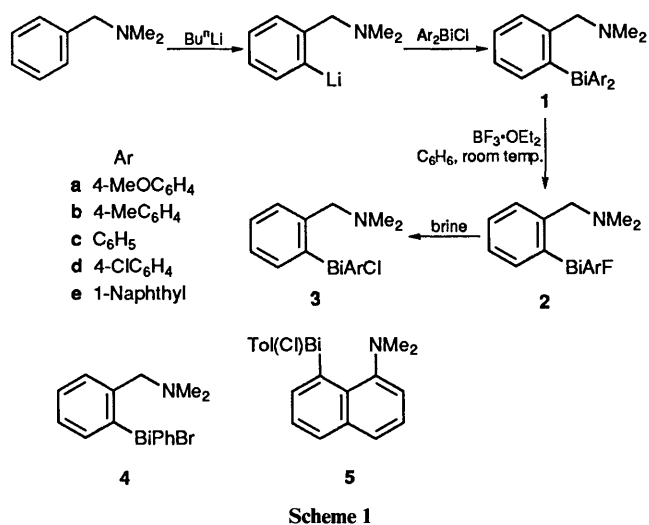
§ Coalescence temperatures for the chlorobismuthines **3a** and **3d** were observed at 66 and 65 °C, respectively, an indication of the importance of steric factors over electronic ones for the aryl groups present.

|| For *ortho*-lithiation of *N,N*-dimethyl-1-naphthylamine, see ref. 7.

¶ This may be attributed to the rigid geometry of **5**. A similar observation was reported for a chiral tin hydride.⁸

** Methanol molecules incorporated into crystal lattices are omitted for clarity.

† This functional group was previously employed for the synthesis of diastereoisomeric five-coordinated organosilicons^{5a,b} and organotin halides^{5c} with a chiral metal centre.



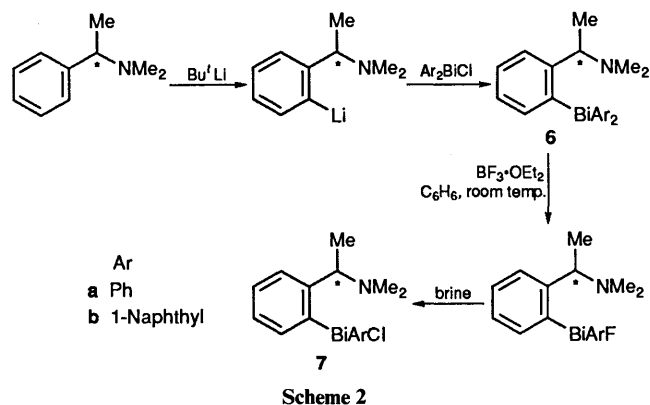
Scheme 1

Table 1 Selected bond lengths (Å) and angles (°) for compound **3b** with estimated standard deviations in parentheses

Bond length		Bond angle	
Bi–C(1)	2.246(6)	N–Bi–Cl	162.9(1)
Bi–C(10)	2.234(6)	C(1)–Bi–C(10)	93.7(2)
Bi–Cl	2.700(2)	C(1)–Bi–Cl	90.8(2)
Bi–N	2.525(6)	C(1)–Bi–N	72.5(2)
		C(10)–Bi–Cl	90.6(2)
		C(10)–Bi–N	86.5(2)
		Bi–N–C(7)	103.5(4)
		N–C(7)–C(2)	110.8(6)

the sulfonyl-stabilized chlorobismuthine,³ where the carbon atoms C(1) and C(10) occupy the equatorial plane with a C(1)–Bi–C(10) angle of 93.7(2)° (Table 1). The apical positions of the pseudotrigonal bipyramid are occupied by the nitrogen and chlorine atoms with an N–Bi–Cl angle of 162.9(1)°. The lone pair of electrons is considered to occupy the remaining equatorial position. The intramolecular Bi–N distance [2.525(6) Å] is longer than the sum of the covalent radii (2.14 Å), but much shorter than that of the van der Waals radii (3.66 Å), in accord with the operation of a strong interaction.^{9,10} The Bi–Cl bond length 2.700(2) Å is longer than those of chlorobis[2,4,6-tris(trifluoromethyl)phenyl]-bismuthine [2.463(3) Å]¹¹ and of a sulfonyl-stabilized chlorobismuthine [2.556(2) Å];³ this reflects the high Lewis basicity of the side-chain nitrogen atom. These observations are suggestive of the formation of a hypervalent 3-centre 4-electron bond over the N, Bi and Cl atoms. Owing to the staggered conformation of the substituent groups around the N–C(7) axis, one of the benzyl protons is located above the equatorial tolyl group, while the phenylene ring is tilted at a dihedral angle 17.70° against the plane formed by N, Cl and C(1) atoms. These findings provide a sound basis for understanding the diastereoselective formation of chiral chlorobismuthines. A bulky substituent introduced at the benzylic position is expected to prefer the equatorial position to lessen steric congestion, thus forcing another equatorial aryl group attached to the chiral bismuth centre into the position *trans* to it. We chose the optically pure 2-[(*R*)-1-(*N,N*-dimethylamino)ethyl]phenyl group* derived from commercial (+)-1-phenylethylamine as one of the aryl ligands and examined the transformation of compounds **6a** and **6b** into the diastereoisomeric chlorobismuthines **7a** and **7b** (Scheme 2).

However, this attempt resulted only in a moderate diastereoselection (77:23 and 78:22, respectively)† irrespective of the aryl grouping present at the equatorial position; this suggested that a bulkier substituent was necessary at the benzylic position for the induction of higher diastereoselectivity. The ¹H NMR spectrum of a diastereoisomeric mixture of **7a** and **7b** reflected well the stereochemical difference between the two diastereoisomers. Relative to those of the major isomer, methyl and methine proton signals of the ethylidene group of the minor isomer were always observed a little upfield and downfield, respectively. This is in accord with the proposition that the minor isomer possesses a sterically unfavourable geometry in which the methyl and equatorial aryl groups are in a *cis* disposition, the former group being magnetically shielded by the ring current of the latter.



Scheme 2

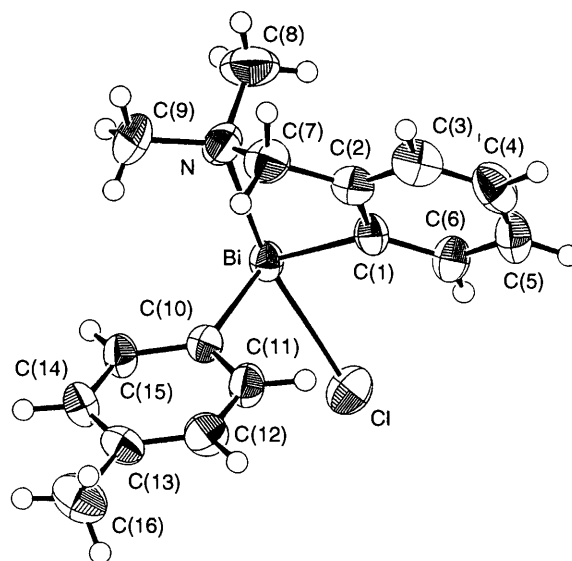


Fig. 1 An ORTEP drawing of chlorobismuthine **3b**

In order to study the dynamic behaviour at the coalescence temperature of chiral chlorobismuthines in solution, the variable-temperature dynamic ¹H NMR spectra were measured for the diastereoisomeric mixture of compound **7a**. The result showed that compound **7a** had very interesting behaviour in solution. The NMe₂ group of the major isomer coalesced at 60 °C in [²H₈]toluene, while the signals of the minor isomer remained *intact*. In contrast, the measurement in [²H₆]-DMSO showed complete coalescence of the signals at 30 °C for both

* For *ortho*-lithiation, see ref. 12.

† The diastereoisomeric ratios of **7a** and **7b** were determined from the integration of peak areas for the methyl and methine protons of the ethylidene group.

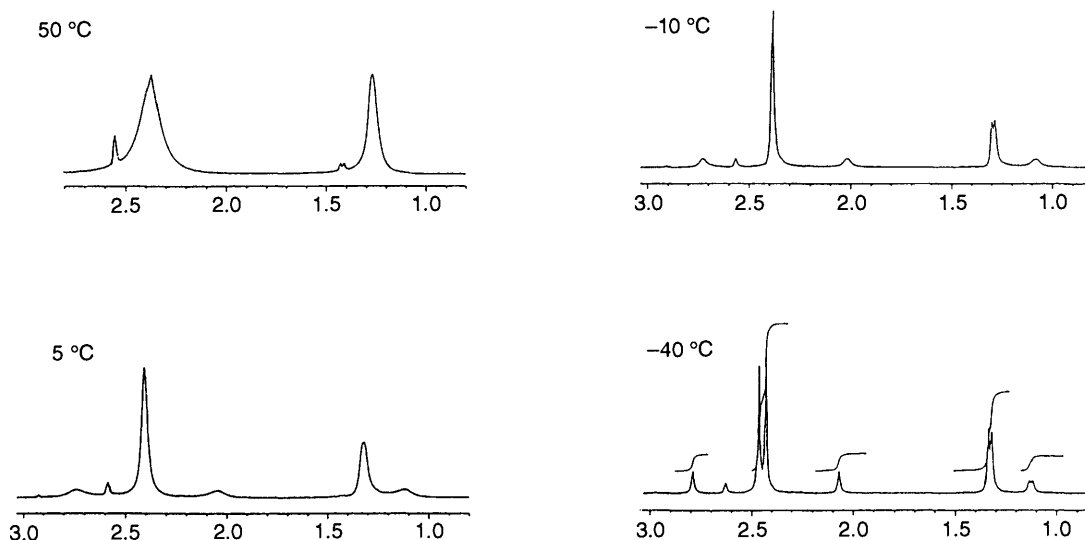


Fig. 2 Variable-temperature dynamic ^1H NMR spectra of a diastereoisomeric mixture of **7a** in CDCl_3 - $[\text{}^2\text{H}_6]$ -DMSO (4:1)

isomers. These observations indicated that in $[\text{}^2\text{H}_8]$ toluene the dissociation–restoration of the intramolecular Bi–N coordination took place at the coalescence temperature ($60\text{ }^\circ\text{C}$) without inversion of configuration at the chiral bismuth centre,* while in $[\text{}^2\text{H}_6]$ -DMSO complete inversion occurred at $30\text{ }^\circ\text{C}$ possibly by nucleophilic participation of the solvent. In order to show the dependence of the inversion on temperatures more clearly, a mixed solvent system of CDCl_3 and $[\text{}^2\text{H}_6]$ -DMSO (4:1) was employed to record the ^1H NMR spectra at low temperatures. As shown in Fig. 2, the signals corresponding to the minor isomer sharpened as the temperature was lowered. At $-40\text{ }^\circ\text{C}$ the NMe_2 groups of both isomers were observed diastereotopically, which reflected the operation of the intramolecular Bi–N coordination. When the temperature was raised to $-10\text{ }^\circ\text{C}$, the signals of the major isomer appeared homotopically while the signals of the minor one remained intact. Above this temperature, the signals of both isomers gradually began to coalesce, finally giving two broad signals at $50\text{ }^\circ\text{C}$. These observations were best accounted for by a sequence of two independent processes, *i.e.*, the reversible dissociation of the intramolecular Bi–N coordination (below $-10\text{ }^\circ\text{C}$) and the subsequent inversion of configuration at the chiral bismuth centre. Thus, the intramolecular Bi–N coordination was confirmed as suppressing the inversion of configuration at the chiral bismuth centre.†

No reports dealing with the synthesis of diastereoisomeric bismuthines with a chiral bismuth centre have hitherto appeared. The present results provide the first successful synthesis and characterization of such systems.

Experimental

General.—All reactions were carried out under argon unless otherwise noted. Hexane and diethyl ether were distilled under

argon from calcium hydride and sodium benzophenone ketyl, respectively, before use. Butyllithium was titrated against diphenylacetic acid. Thin layer chromatography was performed by using Merck precoated silica gel sheets 60F-254. Silica gel (Wakogel) of the size 200 mesh was used for column chromatography. Bismuth(III) chloride was purified by refluxing with thionyl chloride. ^1H NMR spectra were recorded in CDCl_3 on a Varian Gemini-200 (200 MHz) spectrometer with tetramethylsilane as an internal standard. Variable-temperature dynamic ^1H NMR spectra were recorded on a JEOL JMN-GX 400 (400 MHz) spectrometer. Coupling constants J are given in Hz. IR spectra were obtained on a SHIMADZU FTIR-8100 spectrophotometer. Mass spectra were determined on a SHIMADZU GCMS-QP2000A spectrometer at an ionization potential 70 eV. Elemental analyses were performed at Microanalytical Laboratory, Institute for Chemical Research, Kyoto University.

Chloro[2-(dimethylaminomethyl)phenyl](4-methoxyphenyl)-bismuthine 3a.—Chlorobis(4-methoxyphenyl)bismuthine (*ca.* 10 mmol) was generated by stirring tris(4-methoxyphenyl)-bismuthine (3.53 g, 6.66 mmol) and bismuth(III) chloride (1.05 g, 3.33 mmol) in diethyl ether (15 cm^3) for 1 h at room temperature. To a well stirred suspension of chlorobismuthine thus obtained was added dropwise at $-50\text{ }^\circ\text{C}$ a suspension of lithiated *N,N*-dimethylbenzylamine⁶ (*ca.* 10 mmol), generated from butyllithium (10 mmol) and *N,N*-dimethylbenzylamine (1.35 g, 10 mmol) in the same solvent (20 cm^3). The resulting mixture was stirred for 3 h, during which time the temperature was gradually raised to the ambient. After the addition of boron trifluoride–diethyl ether (*ca.* 15 mmol) at room temperature to the mixture it was quenched with brine (20 cm^3) and extracted with ethyl acetate ($50\text{ cm}^3 \times 4$). The combined extracts were evaporated under reduced pressure to leave a brown oily residue, which was purified by silica gel column chromatography, using hexane–ethyl acetate (3:1) as an eluent, to afford crude compound **3a**. Recrystallization of this from hexane– C_6H_6 (5:1) gave pure *product 3a* as crystals (1.46 g, 30%), m.p. 145 – $147\text{ }^\circ\text{C}$; δ_{H} 2.30 (3 H, s, Me), 2.53 (3 H, s, Me), 3.58 (1 H, d, J_{AB} 14.3), 3.78 (3 H, s, OMe), 3.89 (1 H, d, J_{AB} 14.3), 6.99 (2 H, d, J_{AB} 8.6, MeOArH), 7.42–7.65 (3 H, m, ArH), 7.98 (2 H, d, J_{AB} 8.6, MeOArH) and 8.89 (1 H, d, J 7.4, ArH); ν_{max} (KBr)/ cm^{-1} 1580, 1560, 1490, 1450, 1280, 1250, 1180, 1060, 1030, 850, 810, 790 and 760; m/z 450 (21%, M–Cl), 380 (31, $\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{BiCl}$), 378 (94, $\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{BiCl}$), 343 (36, $\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Bi}$), 209 (97, Bi) and 134 (94, $\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4$)

* Free energies of activation ($\Delta G^\ddagger_{T_c}$) for this process at coalescence temperatures (T_c) were estimated to be 16.4, 16.7 and 16.5 kcal mol $^{-1}$, respectively, for chlorobismuthines **3a**, **3c** and **3d**.

† Triorganyltin halides are known to undergo a facile inversion of configuration at the tin atom *via* an $\text{S}_{\text{N}}2$ type mechanism. In order to block this pathway, the intramolecular coordination has manifested itself as a very effective methodology. Our results clearly demonstrate the contribution of the intramolecular Bi–N coordination to the stabilization of the chiral bismuth centre. For chiral tin halides, see ref. 13.

(Found: C, 39.3; H, 4.0; N, 3.0. $C_{16}H_{19}BiClNO$ requires C, 39.6; H, 3.9; N, 2.9%).

Chloro[2-(dimethylaminomethyl)phenyl](4-methylphenyl)bismuthine 3b.—To a well stirred suspension of chlorobismuthine (ca. 10 mmol) generated from tris(4-methylphenyl)bismuthine (3.21 g, 6.66 mmol) and bismuth(III) chloride (1.05 g, 3.33 mmol) in diethyl ether (15 cm³) was added dropwise at $-50^{\circ}C$ a suspension of lithiated *N,N*-dimethylbenzylamine (ca. 10 mmol) in the same solvent (20 cm³). The resulting mixture was stirred for 3 h, during which time the temperature was gradually raised to the ambient. After the addition of boron trifluoride-diethyl ether (ca. 15 mmol) at room temperature to the mixture it was quenched with brine (20 cm³). A similar manipulation as described for **3a** followed by recrystallization from hexane- CH_2Cl_2 (5:1) afforded **compound 3b** as crystals (1.97 g, 42%), m.p. 145–147 $^{\circ}C$; δ_H 2.28 (6 H, s, Me), 2.54 (3 H, s, Me), 3.60 (1 H, d, J_{AB} 14.5), 3.89 (1 H, d, J_{AB} 14.5), 7.32 (2 H, d, J_{AB} 7.9, MeArH), 7.43–7.65 (3 H, m, ArH), 7.98 (2 H, d, J_{AB} 7.9, MeArH) and 8.90 (1 H, d, J 7.3, ArH); $\nu_{max}(KBr)/cm^{-1}$ 1460, 1430, 1030, 1000, 800, 750 and 440 (Found: C, 40.9; H, 4.1; N, 2.9. $C_{16}H_{19}BiClN$ requires C, 40.9; H, 4.1; N, 3.0%). Recrystallization of **3b** from methanol gave a well-crystallized solid of 1:1 solvated composition.

Chloro[2-(dimethylaminomethyl)phenyl]phenylbismuthine 3c.—To a well stirred suspension of chlorobismuthine (ca. 10 mmol) generated from triphenylbismuthine (2.93 g, 6.66 mmol) and bismuth(III) chloride (1.05 g, 3.33 mmol) in diethyl ether (15 cm³) was added dropwise at $-50^{\circ}C$ a suspension of lithiated *N,N*-dimethylbenzylamine (ca. 10 mmol) in the same solvent (20 cm³) and the resulting mixture was stirred for 3 h, during which time the temperature was gradually raised to the ambient. After the addition of boron trifluoride-diethyl ether (ca. 15 mmol) at room temperature to the mixture it was quenched with brine (20 cm³). A similar manipulation as described above followed by recrystallization from hexane- C_6H_6 (5:1) afforded **compound 3c** as crystals (2.14 g, 47%), m.p. 145–147 $^{\circ}C$; δ_H 2.28 (3 H, s, Me), 2.54 (3 H, s, Me), 3.57 (1 H, d, J_{AB} 13.9), 3.89 (1 H, d, J_{AB} 13.9), 7.29–7.67 (6 H, m, ArH), 8.10 (2 H, d, J 8.0, ArH) and 8.89 (1 H, d, J 7.4, ArH); $\nu_{max}(KBr)/cm^{-1}$ 1450, 1430, 1420, 1000, 840, 760, 740, 700, 450 and 440 (Found: C, 39.7; H, 3.7; N, 3.1. $C_{15}H_{17}BiClN$ requires C, 39.5; H, 3.8; N, 3.1%).

Chloro(4-chlorophenyl)[2-(dimethylaminomethyl)phenyl]bismuthine 3d.—To a well stirred suspension of chlorobismuthine (ca. 10 mmol) generated from tris(4-chlorophenyl)bismuthine (3.62 g, 6.66 mmol) and bismuth(III) chloride (1.05 g, 3.33 mmol) in diethyl ether (15 cm³) was added dropwise at $-50^{\circ}C$ a suspension of lithiated *N,N*-dimethylbenzylamine (ca. 10 mmol) in the same solvent (20 cm³). The resulting mixture was stirred for 3 h, during which time the temperature was gradually raised to the ambient. After the addition of boron trifluoride-diethyl ether (ca. 15 mmol) at room temperature to the mixture it was quenched with brine (20 cm³). A similar manipulation as described above followed by recrystallization from hexane- C_6H_6 (5:1) afforded **compound 3d** as crystals (2.93 g, 60%), m.p. 174–176 $^{\circ}C$ (decomp.); δ_H 2.32 (3 H, s, Me), 2.54 (3 H, s, Me), 3.57 (1 H, d, J_{AB} 14.0), 3.94 (1 H, d, J_{AB} 14.0), 7.42–7.67 (5 H, m, ArH), 8.00 (2 H, d, J_{AB} 8.2, ClArH) and 8.88 (1 H, d, J 7.3, ArH); $\nu_{max}(KBr)/cm^{-1}$ 1560, 1470, 1460, 1440, 1380, 1080, 1050, 1010, 840, 810, 750, 710, 490 and 440 (Found: C, 36.9; H, 3.3; N, 2.9. $C_{15}H_{16}BiCl_2N$ requires C, 36.75; H, 3.3; N, 2.9%).

Chloro[2-(dimethylaminomethyl)phenyl](1-naphthyl)bismuthine 3e.—Chlorobis(1-naphthyl)bismuthine (ca. 10 mmol) was generated by stirring tris(1-naphthyl)bismuthine (3.93 g,

6.66 mmol) and bismuth(III) chloride (1.05 g, 3.33 mmol) in CH_2Cl_2 (15 cm³) for 2 h at $45^{\circ}C$ and employed as an ethereal suspension after removal of CH_2Cl_2 under reduced pressure. To a well stirred suspension of chlorobismuthine in diethyl ether (15 cm³) was added dropwise at $-50^{\circ}C$ a suspension of lithiated *N,N*-dimethylbenzylamine (ca. 10 mmol) in the same solvent (20 cm³) and the resulting mixture was stirred for 3 h, during which time the temperature was gradually raised to the ambient. After the addition of boron trifluoride-diethyl ether (ca. 15 mmol) at room temperature, the mixture was quenched with brine (20 cm³). Work-up as described above followed by recrystallization from hexane- CH_2Cl_2 (5:1) afforded **compound 3e** as crystals (2.02 g, 40%), m.p. 200–203 $^{\circ}C$ (decomp.); δ_H 2.04 (3 H, s, Me), 2.55 (3 H, s, Me), 3.56 (1 H, d, J_{AB} 13.7), 3.88 (1 H, d, J_{AB} 13.7), 7.44–7.70 (6 H, m, ArH), 7.88–7.98 (2 H, m, ArH), 8.30 (1 H, d, J 8.1, ArH), 8.60 (1 H, d, J 6.9, ArH) and 8.90 (1 H, d, J 7.0, ArH); $\nu_{max}(KBr)/cm^{-1}$ 1500, 1460, 1440, 1250, 1010, 840, 800, 770, 750, 510 and 440 (Found: C, 44.9; H, 3.8; N, 2.7. $C_{19}H_{19}BiClN$ requires C, 45.1; H, 3.8; N, 2.8%).

Bromo[2-(dimethylaminomethyl)phenyl]phenylbismuthine 4.—To a well stirred solution of **compound 3c** (455 mg, 1 mmol) in benzene (5 cm³) was added saturated aqueous NaBr (3 cm³) and the resulting mixture was stirred for 1 h. The organic layer was extracted with ethyl acetate (10 cm³ \times 2) and the combined extracts were evaporated under reduced pressure to leave an oily residue, which was crystallized from hexane- CH_2Cl_2 (5:1) to afford **compound 4** as crystals (499 mg, 100%), m.p. 163–165 $^{\circ}C$; δ_H 2.30 (3 H, s, Me), 2.55 (3 H, s, Me), 3.58 (1 H, d, J_{AB} 13.9), 3.89 (1 H, d, J_{AB} 13.9), 7.30–7.64 (6 H, m, ArH), 8.11 (2 H, d, J 7.9) and 9.03 (1 H, d, J 7.3, ArH); $\nu_{max}(KBr)/cm^{-1}$ 1450, 1010, 1000, 840, 770, 730, 700 and 440; m/z 343 (30%, M – BrC₆H₅), 209 (92, Bi) and 134 (100, Me₂NCH₂C₆H₄).

Chloro[8-(dimethylamino)-1-naphthyl](4-methylphenyl)bismuthine 5.—To a well stirred suspension of chlorobismuthine (ca. 10 mmol) generated from tris(4-methylphenyl)bismuthine (3.21 g, 6.66 mmol) and bismuth(III) chloride (1.05 g, 3.33 mmol) in diethyl ether (15 cm³) was added dropwise at $-50^{\circ}C$ a suspension of 8-lithio-*N,N*-dimethyl-1-naphthylamine⁷ generated from butyllithium (10 mmol) and *N,N*-dimethyl-1-naphthylamine (1.71 g, 10 mmol) in the same solvent (20 cm³). The resulting mixture was stirred for 3 h, during which time the temperature was gradually raised to the ambient. After the addition of boron trifluoride-diethyl ether (ca. 15 mmol) at room temperature to the mixture it was quenched with brine (20 cm³) and extracted with ethyl acetate (50 cm³ \times 4). The combined extracts were evaporated under reduced pressure to leave a brown oily residue, which was crystallized from hexane- CH_2Cl_2 (5:1) to afford **compound 5** as crystals (2.02 g, 40%), m.p. 193–195 $^{\circ}C$; δ_H 2.20 (3 H, s, Me), 2.68 (3 H, s, NMe), 3.02 (3 H, s, NMe), 7.18 (2 H, d, J_{AB} 7.9, MeArH), 7.33 (1 H, d, J 7.6, ArH), 7.46 (1 H, t, J 7.7, ArH), 7.73 (2 H, d, J_{AB} 7.9, MeArH), 7.88 (1 H, d, J 8.0, ArH), 7.99 (1 H, t, J 8.1, ArH), 8.08 (1 H, d, J 6.9, ArH) and 9.24 (1 H, d, J 6.6, ArH); $\nu_{max}(KBr)/cm^{-1}$ 1560, 1490, 1450, 1360, 1210, 1030, 1010, 930, 850, 820, 800, 780, 610 and 480; m/z 470 (18%, M – Cl), 416 (33, M – MeC₆H₄), 414 (100 M – MeC₆H₄), 209 (43, Bi) and 170 (23, M – MeC₆H₄BiCl).

Chloro[2-(R)-(1-dimethylaminoethyl)phenyl]phenylbismuthine 7a.—To a well stirred suspension of chlorobismuthine (ca. 10 mmol) generated from triphenylbismuthine (2.93 g, 6.66 mmol) and bismuth(III) chloride (1.05 g, 3.33 mmol) in diethyl ether (15 cm³) was added dropwise at $-50^{\circ}C$ a suspension of lithiated (+)-*N,N*-dimethyl- α -phenylethylamine¹² (ca. 10 mmol) generated from butyllithium (10 mmol) and (+)-*N,N*-dimethyl-1-phenylethylamine (1.49 g, 10 mmol)

in hexane (20 cm³) and the resulting mixture was stirred for 3 h, during which time the temperature was gradually raised to the ambient. After the addition of boron trifluoride–diethyl ether (*ca.* 15 mmol) at room temperature to the mixture it was quenched with brine (20 cm³). A similar manipulation as described for **3a** followed by recrystallization from hexane–CH₂Cl₂ (5:1) afforded a diastereoisomeric mixture of **7a** as crystals (2.25 g, 48%), m.p. 136–138 °C; *major isomer*: δ_{H} 1.31 (3 H, d, *J* 6.7, CHMe), 2.36 (3 H, s, NMe), 2.39 (3 H, s, NMe), 3.57 (1 H, q, *J* 6.7, CHMe), 7.29–7.36 (1 H, m, ArH), 7.47–7.54 (4 H, m, ArH), 7.65–7.72 (1 H, m, ArH), 8.08 (2 H, d, *J* 7.4, ArH) and 8.94 (1 H, d, *J* 7.3, ArH); *minor isomer*: δ_{H} 1.09 (3 H, d, *J* 7.0, CHMe), 2.03 (3 H, s, NMe), 2.70 (3 H, s, NMe), 3.89 (1 H, q, *J* 7.0, CHMe), 7.29–7.36 (1 H, m, ArH), 7.47–7.54 (4 H, m, ArH), 7.65–7.72 (1 H, m, ArH), 8.15 (2 H, d, *J* 7.6, ArH) and 8.94 (1 H, d, *J* 7.3, ArH); *m/z* 434 (22%, M – Cl), 394 (34, M – C₆H₅), 392 (100, M – C₆H₅), 209 (81, Bi) and 148 (63, Me₂NCHMeC₆H₄) (Found: C, 40.7; H, 4.1; N, 3.0. C₁₆H₁₉BiClN requires C, 40.9; H, 4.1; N, 3.0%).

Chloro[2-(R)-(1-dimethylaminoethyl)phenyl](1-naphthyl)bismuthine 7b.—Chlorobis(1-naphthyl)bismuthine (*ca.* 10 mmol) was generated by stirring tris(1-naphthyl)bismuthine (3.93 g, 6.66 mmol) and bismuth(III) chloride (1.05 g, 3.33 mmol) in CH₂Cl₂ (15 cm³) for 2 h at 45 °C and, after removal of CH₂Cl₂ under reduced pressure, used as an ethereal suspension. To a well stirred suspension of chlorobismuthine was added dropwise at –50 °C a suspension of lithiated (+)-*N,N*-dimethyl-1-phenylethylamine (*ca.* 10 mmol) in hexane (20 cm³) and the resulting mixture was stirred for 3 h, during which time the temperature was gradually raised to the ambient. After the addition of boron trifluoride–diethyl ether (*ca.* 15 mmol) at room temperature, the mixture was quenched with brine (20 cm³). A similar manipulation as described for **3a** followed by recrystallization from hexane–CH₂Cl₂ (5:1) afforded a diastereoisomeric mixture of **7b** as crystals (2.34 g, 45%), m.p. 180–184 °C; *major isomer*: δ_{H} 1.26 (3 H, d, *J* 6.7, CHMe), 2.12 (3 H, s, NMe), 2.37 (3 H, s, NMe), 3.62 (1 H, q, *J* 6.7, CHMe), 7.43–7.96 (8 H, m, ArH), 8.30 (1 H, d, *J* 8.1, ArH), 8.57 (1 H, d, *J* 6.8, ArH) and 8.92 (1 H, d, *J* 7.3, ArH); *minor isomer*: δ_{H} 1.01 (3 H, d, *J* 6.9, CHMe), 1.84 (3 H, s, NMe), 2.67 (3 H, s, NMe), 3.84 (1 H, q, *J* 6.9, CHMe), 7.43–7.96 (8 H, m, ArH), 8.30 (1 H, d, *J* 8.1, ArH), 8.70 (1 H, d, *J* 6.8, ArH) and 8.92 (1 H, d, *J* 7.3, ArH); *m/z* 484 (22%, M – Cl), 394 (33) M – C₁₀H₇), 392 (99, M – C₁₀H₇), 357 (68, Me₂NCHMeC₆H₄Bi), 209 (100, Bi) and 148 (84, Me₂NCHMeC₆H₄) (Found: C, 46.1; H, 4.0; N, 2.9. C₂₀H₂₁BiClN requires C, 46.2; H, 4.1; N, 2.7%).

X-Ray Crystallography of Compound 3b.—A crystal of dimensions 0.500 × 0.400 × 0.380 mm grown from methanol at ambient temperature was used for X-ray crystallography.

Crystal data. C₁₇H₂₃BiClNO, *M* = 501.81. Triclinic, space group = P $\bar{1}$, *a* = 10.318(2), *b* = 10.564(2), *c* = 10.197(2) Å, α = 108.08(2), β = 118.68(1), γ = 71.35(1)°, *V* = 907.4(7) Å³, *Z* = 2, *D_c* = 1.883 g cm⁻³. Colourless block; μ (Mo-K α , λ = 0.710 69 Å) = 98.34 cm⁻¹. Intensity data were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo-K α radiation and a 12KW rotating anode generator using the ω -2 θ scan technique to a maximum 2 θ value of 55.0°. Scans of (0.94 + 0.30 tan θ)° were made at a speed of 16.0 deg min⁻¹ (in omega). Of the 4398 reflections which were collected, 4168 were unique (*R_{int}* = 0.039). Data were corrected for Lorentz, polarization and absorption effects. Empirical correction for the absorption was made based on azimuthal or Ψ scans¹⁴ (transmission factors: 0.79–1.00). The correction for the secondary extinction was also made at the final stage of the refinement (coefficient: 6.14 × 10⁻⁶). The structure was solved by the Patterson method.¹⁵ The non-hydrogen atoms were

refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3401 observed reflections [*I* > 3.00 σ (*I*)] and 191 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.034 and *R_w* = 0.035. The residual electron densities in the final difference Fourier map ranged from –1.61 to 1.48 e⁻/Å³. The weighting scheme, *w* = 1/ σ^2 (*F_o*), was employed. Neutral atom scattering factors were taken from Cromer and Waber.¹⁶ Anomalous dispersion effects were included in *F_c*;¹⁷ the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.¹⁸ All calculations were performed on a VAX station 3200 computer using the TEXSAN¹⁹ crystallographic software package from the Molecular Structure Corporation. The ORTEP²⁰ program was used to obtain the drawing Fig. 1. Selected bond lengths and bond angles are given in Table 1. Full details of crystal data, fractional atomic coordinates, bond lengths, bond angles, hydrogen coordinates, structure factors and thermal parameters of compound **3b** have been deposited at the Cambridge Crystallographic Data Centre.

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