Hypervalent Bond Formation in Halogeno(2-acylphenyl)bismuthanes

Toshihiro Murafuji,* Takanori Mutoh, Kohichi Satoh, and Kazumi Tsunenari

Department of Chemistry, Faculty of Science, Yamaguchi University, Yoshida, Yamaguchi 753, Japan

Nagao Azuma

Department of Chemistry, Faculty of General Education, Ehime University, Matsuyama 790, Japan

Hitomi Suzuki*

Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-01, Japan

Received March 28, 1995[⊗]

Hypervalent bond formation has been found to occur at bismuth as the hypervalent center. The transformation of (2-acetylphenyl)bis(4-methylphenyl)bismuthane (**2b**) to (2-acetylphenyl)bromo(4-methylphenyl)bismuthane (**3b**) brings about a noticeable change in the electronic nature of the carbonyl function in the 2-acetylphenyl group, which is sensitively reflected in the IR, ^{1}H, and ^{13}C NMR spectra of compound **3b**. These spectral changes may be rationalized in terms of the formation of a hypervalent O–Bi–Br bond through intramolecular coordination of the carbonyl oxygen atom to the bismuth center. X-ray crystallography of **3b** has confirmed this interpretation.

Introduction

Hypervalent bond formation through intramolecular donor–acceptor interaction is a topic of growing interest in the chemistry of main group elements. Although many examples have hitherto been reported of the synthesis and characterization of such hypervalent compounds, most are concerned with those derived from silicon,[1] tin,[2] sulfur,[3] phosphorus,[4] and tellurium.[5,6] Heavy members of the group 15 family have not yet received much attention.[7] Recently, we reported the synthesis of some chiral chlorobismuthanes stabilized by the intramolecular coordination of sulfonyl and dimethylamino groups and confirmed the occurrence of the hypervalent O–Bi–Cl and N–Bi–Cl bonds, respectively, in these compounds by X-ray crystallography.[8–10] In order to illustrate further the potential ability of heteroatom functions to form such a hypervalent bond, we have constructed a simple molecular model system bearing the bismuth atom as a hypervalent center. With this model system, one can readily visualize the formation of a hypervalent bond on the basis of infrared and ^{1}H and ^{13}C NMR spectra.

Results and Discussion

When an organic functional group coordinates to a heteroatom center to form a hypervalent bond, there arises some electronic change within the group which should be sensitively reflected in its IR, ^{1}H, and ^{13}C

⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1995.

(1) (a) Frolov, Yu. L.; Voronkov, M. G.; Gavrilova, G. A.; Chipanina, N. N.; Gubanova, L. I.; D'yakov, V. M. *J. Organomet. Chem.* **1983**, *244*, 107. (b) Kupce, E.; Liepins, E.; Lukevics, E. *J. Organomet. Chem.* **1983**, *248*, 131. (c) Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; de Saxce, A.; Young, J. C. *J. Organomet. Chem.* **1990**, *395*, 1. (d) Corey, J. Y.; Rath, N. P.; John, C. S.; Corey, E. R. *J. Organomet. Chem.* **1990**, *399*, 221. (e) Gavrilova, G. A.; Chipanina, N. N.; Frolov, Yu. L.; Gubanova, L. I.; Voronkov, M. G. *J. Organomet. Chem.* **1991**, *418*, 291.

(2) (a) Kuivila, H. G.; Dixon, J. E.; Maxfield, P. L.; Scarpa, N. M.; Topka, T. M.; Tsai, K.-H.; Wursthorn, K. R. *J. Organomet. Chem.* **1975**, *86*, 89. (b) Weichmann, H.; Mugge, C.; Grand, A.; Robert, J. B. *J. Organomet. Chem.* **1982**, *238*, 343. (c) Jastrzebski, J. T. B. H.; Knaap, C. T.; van Koten, G. *J. Organomet. Chem.* **1983**, *255*, 287. (d) Jastrzebski, J. T. B. H.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1991**, *413*, 43. (e) Swami, K.; Nebout, B.; Farah, D.; Krishnamurti, R.; Kuivila, H. G. *Organometallics* **1986**, *5*, 2370. (f) Ochiai,M.; Iwaki, S.; Takaoka, Y.; Nagao, Y. *Organometallics* **1989**, *8*, 1751. (g) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontenagel, W. M. G. F.; Spek, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 5021. (h) Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Shiro, M.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4606.

(3) (a) Akiba, K.-y.; Takee, K.; Ohkata, K. *J. Am. Chem. Soc.* **1983**, *105*, 6965. (b) Iwasaki, F.; Akiba, K.-y.; Ohkata, K. *J. Am. Chem. Soc.* **1983**, *105*, 445. (c) Akiba, K.-y.; Takee, K.; Shimizu, Y.; Ohkata, K. *J. Am. Chem. Soc.* **1986**, *108*, 6320. (d) Ohkata, K.; Ohnishi, M.; Yoshinaga, K.; Akiba, K.-y.; Rongione, J. C.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 9270.

(4) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483 and references cited herein

(5) (a) Sadekov, I. D.; Maksimenko, A. A.; Minkin, V. I. *Khim. Geterotsikl. Soedin.* **1981**, *122*; *Chem. Abstr.* **1981**, *95*, 25027p. (b) Lohner, W.; Praefcke, K. *J. Organomet. Chem.* **1981**, *205*, 167. (c) Minkin, V. I.; Sadekov, I. D.; Maksimenko, A. A.; Kompan, O. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1991**, *402*, 331. (d) Abid, K. Y.; Al-Salim, N. I.; Greaves, M.; McWhinnie, W. R.; West, A. A.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1989**, 1697. (e) Maslakov, A. G.; McWhinnie, W. R.; Perry, M. C.; Shaikh, N.; McWhinnie, S. L. W.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1993**, 619.

(6) Piette, J. L.; Renson, M. *Bull. Soc. Chim. Belg.* **1970**, *79*, 367; *Chem. Abstr.* **1970**, *73*, 66200d.

(7) (a) Dräger, M.; Schmidt, B. M. *J. Organomet. Chem.* **1985**, *290*, 133. (b) Ohkata, K.; Ohnishi, M.; Akiba, K.-y. *Tetrahedron Lett.* **1988**, *29*, 5401. (c) Ohkata, K.; Takemoto, S.; Ohnishi, M.; Akiba, K.-y. *Tetrahedron Lett.* **1989**, *30*, 4841. (d) Chen, X.; Yamamoto, Y.; Akiba, K.-y.; Yoshida, S.; Yasui, M.; Iwasaki, F. *Tetrahedron Lett.* **1992**, *33*, 6653. (e) Yamamoto, Y.; Chen, X.; Akiba, K.-y. *J. Am. Chem. Soc.* **1992**, *114*, 7906. (f) Yamamoto, Y.; Ohdoi, K.; Chen, X.; Kitano, M.; Akiba, K.-y. *Organometallics* **1993**, *12*, 3297. (g) Brau, E.; Falke, R.; Ellner, A.; Beuter, M.; Kolb, U.; Dräger, M. *Polyhedron* **1994**, 365.

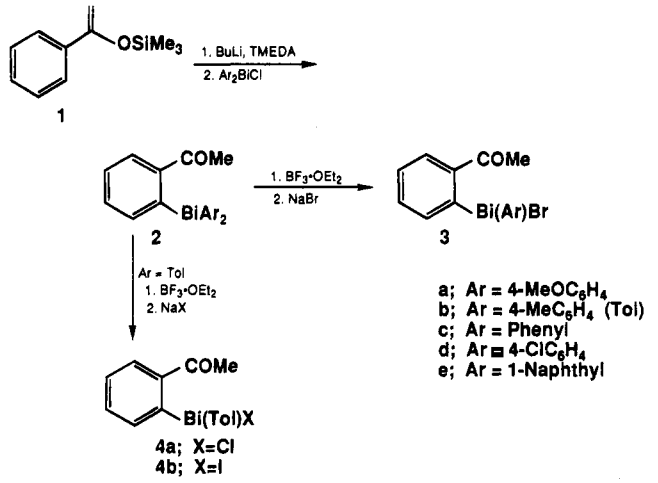
(8) Suzuki, H.; Murafuji, T.; Azuma, N. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1169.

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

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

0276-7333/95/2314-3848$09.00/0

Scheme 1



NMR spectra. On the basis of such an idea, we have designed a new type of triarylbismuthane, compounds **2** and **5** with an acetyl or a formyl group *ortho* to the bismuth atom center. With these compounds, information about the carbonyl function obtained from IR, ^1H, and ^{13}C NMR spectra is expected to provide evidence for the formation of a hypervalent bond.[11]

Synthesis. The directed *ortho*-lithiation of benzaldehyde and acetophenone is an attractive synthetic route to compounds **2** and **5**. However, due to the reactive nature of the carbonyl function and the high acidity of α-protons, both acetyl and formyl groups are not good directing substituents for *ortho*-lithiation. Piette and Renson reported the synthesis of butyl 2-formylphenyl telluride via the butyltellurenylation of 2-(diethoxymethyl)phenyllithium followed by deprotection.[6] However, this strategy is not applicable to the synthesis of compounds **2** and **5**, because the acid-catalyzed deprotection of acetal functionality after the introduction of bismuth atom leads to the concomitant cleavage of the bismuth–carbon bonds.

In order to overcome this difficulty, we chose the dilithiated compounds as starting materials (Schemes 1 and 2). They can be easily prepared from the reaction of trimethylsilyl enol ether of acetophenone and lithium α-amino alkoxide of benzaldehyde, respectively, with butyllithium.[12,13] A variety of diarylchlorobismuthanes reacted smoothly with the dilithiated derivatives to afford the required products in acceptable yield. These results demonstrate that the dilithiation method is useful for the introduction of the 2-acylphenyl group to a metal center, particularly in the case where the metal–carbon bond is acid-sensitive. Compounds **2** and **5** were converted to bromobismuthanes **3** and **6**, respectively, through fluorodearylation[8] with boron trifluoride–diethyl etherate and subsequent halogen exchange of the resulting fluorobismuthanes with sodium bromide. Chloro- and iodo-bismuthanes **4** and **7** were synthesized similarly via halogen exchange of the fluorobismuthanes with the respective alkali metal halides. In contrast to chlorobismuthane **4a**, chlorobismuthane **7a** was unstable and readily decomposed in solution to yield compound **8**.

Table 1. ^{13}C NMR Spectra (δ) of Compounds 2b and 3b

carbon	2b	3b	$\delta_{3b}-\delta_{2b}$
C(1)[a]	159.8	175.8	16.0
C(2)	141.5	143.1	1.6
C(3)	132.2	135.1	2.9
C(4)	127.5	128.3	0.8
C(5)	135.0	138.5	3.5
C(6)	140.3	140.7	0.4
C(7)	201.1	208.7	7.6
C(8)	27.2	27.4	0.2
C(9)[a]	158.5	174.2	15.7
C(10)	137.7	137.1	−0.6
C(11)	131.2	132.5	1.3
C(12)	136.8	138.2	1.4
C(15)	21.5	21.5	0.0

[a] *Ipso* carbon signals appear somewhat broadly.

Spectral Characterization. Spectral comparison of compound **2b** with **3b** clearly revealed an electronic change caused by the introduction of a bromine atom onto the bismuth atom. Compared with the parent bismuthane **2b** (1665 cm^{-1}), the IR spectrum of bromobismuthane **3b** showed a shift to lower frequency (40 cm^{-1}) of the carbonyl stretching vibration. The ^{13}C NMR spectra of these compounds were also informative (Table 1). The carbonyl carbon signal of compound **3b** was observed at downfield region (δ 208.7). In addition, C(3) and C(5) atoms of compound **3b** suffered deshielding compared to the C(4) and C(6) atoms in the same ring, indicating the occurrence of a resonance interaction with the carbonyl function through the intramolecular Bi–O interaction. It is clear that the inductive effect of the bromine atom is transmitted to the carbonyl carbon atom mainly through the intramolecular Bi–O interaction rather than through the Bi–C(1) bond. This also is indicated by the downfield shift of the carbonyl carbon signal with increasing electronegativity of the halogen atom on bismuth(Table 2; **4a** versus **4b**). The chemical shift of the carbonyl carbon signal was not influenced by the nature of aryl group. All these observations are consistent with the formation of a hypervalent bond through the intramolecular coordination of the carbonyl group to bismuth–halogen. The

Scheme 2

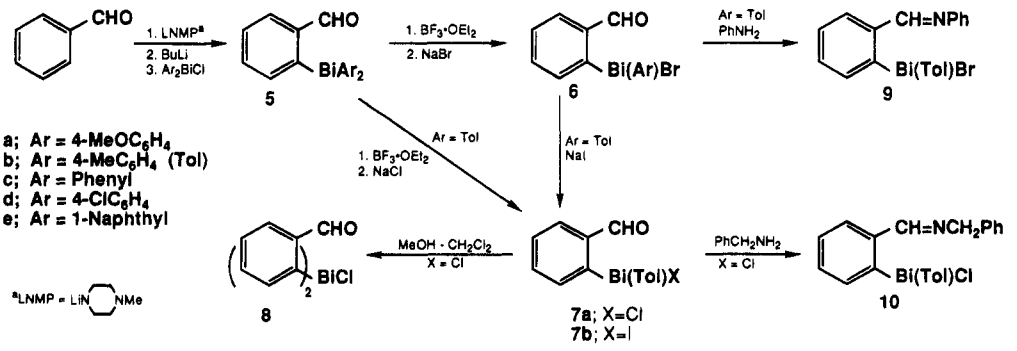


Table 2. Influence of Halogen Atoms and Aryl Groups on the Chemical Shifts (δ) of the Carbonyl Carbon Atoms

compound	chemical shift (δ)	compound	chemical shift (δ)
2b	201.1	**3a**	208.7
3b	208.7	**3c**	208.8
4a	209.2	**3d**	209.0
4b	207.5	**3e**	208.2

Table 3. Chemical Shifts (δ) of the Ring Carbon Atoms Attached to the Bismuth

	chemical shift (δ)	
compd	phenylene ring	tolyl ring
4a	185.3	177.9
3b	175.8	174.2
4b	172.1	166.8
2b	159.8	158.5

signals of the *ipso* carbon atoms attached to the bismuth atom could be observed clearly in several cases (Table 3). Only recently has the chemical shift of the *ipso* carbon atom been assigned for triphenylbismuthane itself.[14]

The case with the 2-formylphenyl system was similar. The formyl proton signal of **6e** showed a downfield shift (~0.4 ppm) relative to that of **5e** due to enhanced polarization of the carbonyl group by the formation of the hypervalent bond. Despite the anticipated activation of the carbonyl carbon atom, the reaction of compound **6b** with aniline to form imine **9** proceeded quite slowly as compared with benzaldehyde (checked in a competitive experiment). This may be understood in terms of steric hindrance to the approach of the amine to the C=O group in **6b**.

Compounds **6** and **7a** are not so stable and slowly decompose on standing in air. Relative stability decreases in the order **6a,b** > **6c** > **6d,e** > **7a**. However, they can be stored without appreciable change under argon in a refrigerator. By treatment with benzylamine, compound **7a** could be isolated as a stable crystalline solid in the form of an imino-stabilized chlorobismuthane **10**. This may be taken as an example demonstrating the enhanced stability of the hypervalent N–Bi–Cl bond over the hypervalent O–Bi–Cl bond.

Molecular Structures. In order to confirm the formation of a hypervalent O–Bi–halogen bond, X-ray structure analysis was carried out for compound **3b** (Figure 1). As expected, the bismuth center was shown to have a distorted pseudotrigonal bipyramidal configuration similar to those of the sulfonyl- and dimethylamino-stabilized chlorobismuthanes,[8–10] where the carbon atoms C(1) and C(9) occupy the equatorial plane with a C(1)–Bi–C(9) angle of 95.1(4)° (Table 4). The apical positions of the pseudotrigonal bipyramid are occupied by the carbonyl oxygen and bromine atoms with an O–Bi–Br angle of 160.8(2)°. The lone pair of electrons is considered to occupy the remaining equatorial position. The intramolecular Bi–O distance (2.519(7) Å) is longer than the sum of the covalent radii (2.10 Å) but is much shorter than that of the van der Waals radii (3.72 Å), in accord with the operation of a strong interaction between the bismuth and oxygen atoms. The Bi–Br bond length, 2.746(1) Å, is longer than the sum of the covalent radii (2.60 Å). All these observations support the formation of a hypervalent three-center four-electron bond over the oxygen, bismuth, and bromine atoms in compound **3b**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound 3b with Estimated Standard Deviations in Parentheses

bond lengths		bond angles	
Bi–C(1)	2.26(1)	O–Bi–Br	160.8(2)
Bi–C(9)	2.24(1)	C(1)–Bi–C(9)	95.1(4)
Bi–Br	2.746(1)	C(1)–Bi–Br	90.9(3)
Bi–O	2.519(7)	C(9)–Bi–Br	93.0(3)
O–C(7)	1.24(1)	C(1)–Bi–O	70.8(3)
		C(9)–Bi–O	83.0(3)
		C(7)–O–Bi	113.3(7)

Experimental Section

General Comments. All reactions were carried out under nitrogen unless otherwise noted. Diethyl ether, hexane, and benzene were distilled from calcium hydride under nitrogen before use. Butyllithium was titrated against diphenylacetic acid. TLC was performed by using Merck precoated silica gel sheets 60F-254. Kieselgel 60 (Merck 9385) was used for column chromatography. Bismuth(III) chloride was purified by refluxing with thionyl chloride. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Hitachi R-250H (250 MHz) and Varian Gemini-200 (200 MHz) spectrometers with tetramethylsilane as an internal standard and are reported in δ. Coupling constants J are given in Hz. IR spectra were obtained as KBr pellets on a Shimadzu FTIR-8100 spectrophotometer. Elemental analyses were performed at Microanalytical Laboratory, Institute for Chemical Research, Kyoto University, Japan.

Preparation of (2-Acetylphenyl)diarylbismuthanes 2. Typical Procedure 1. Acetophenone trimethylsilyl enol ether **1** was prepared according to the reported procedure.[15] Chlorobis(4-methoxyphenyl)bismuthane (ca. 3 mmol) was generated by stirring tris(4-methoxyphenyl)bismuthane (1.06 g, 2 mmol) and bismuth(III) chloride (315 mg, 1 mmol) in diethyl ether (10 mL) for 1 h at room temperature. Lithiation of acetophenone trimethylsilyl enol ether was carried out by modifying the reported procedure:[12] To a stirred solution of TMEDA (1.36 mL, 9 mmol) in hexane (5 mL) was added dropwise at ice bath temperature butyllithium (9 mmol) followed by acetophenone trimethylsilyl enol ether **1** (576 mg, 3 mmol), and the mixture was stirred for 24 h at room temperature. To a suspension of the lithium compound thus obtained was added at room temperature an ethereal suspension of the above chlorobismuthane, and the resulting dark brown mixture was stirred for additional 15 min to complete the reaction. The mixture was quenched with brine (5 mL), benzene (10 mL) was added, and the insoluble polymeric substances were removed by filtration. The organic layer was separated and evaporated under reduced pressure to leave (2-acetylphenyl)bis(4-methoxyphenyl)bismuthane **2a** as a yellow oily residue. Attempted purification of this product by chromatography on silica gel using hexane–ethyl acetate (5:1) as the solvent led to extensive decomposition. Thus the oily residue was used without further purification for the synthesis of (2-acetylphenyl)bromo(4-methoxyphenyl)bismuthane, **3a**.

Typical Procedure 2. To a suspension of the lithium compound (ca. 3 mmol) derived from silyl enol ether **1** was added at room temperature a suspension of chlorobismuthane

(11) The intramolecular Bi–O interaction has previously been suggested for chlorobis[2-(isopropoxycarbonyl)ethyl]bismuthane: Nakamura, E., Shimada, J.; Kuwajima, I. *Organometallics* **1985**, *4*, 641.

(12) Klein, J.; Medlik-Balan, A. *J. Org. Chem.* **1976**, *41*, 3307.

(13) (a) Comins, D. L.; Brown, J. D.; Mantlo, N. B. *Tetrahedron Lett.* **1982**, *23*, 3979. (b) Comins, D. L.; Brown, J. D. *Tetrahedron Lett.* **1983**, *24*, 5465. (c) Comins, D. L.; Brown, J. D. *J. Org. Chem.* **1984**, *49*, 1078.

(14) Ali, M.; McWhinnie, W. R.; West, A. A. *J. Chem. Soc., Dalton Trans.* **1990**, 899.

(15) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(ca. 3 mmol), prepared by stirring tris(4-methylphenyl)bismuthane (964 mg, 2 mmol) and bismuth(III) chloride (315 mg, 1 mmol) in diethyl ether (10 mL), and the resulting mixture was stirred for 15 min. Similar work up as described above gave (2-acetylphenyl)bis(4-methylphenyl)bismuthane, **2b**, as a yellow oil, which was purified by chromatography on silica gel using hexane–ethyl acetate (5:1) as the eluent and recrystallized from MeOH–CH_2Cl_2 (5:1). Crystals: yield, 23%; mp 114–116 °C. ^{1}H NMR: 2.30 (6 H, s, Me), 2.61 (3 H, s, Me), 7.17 (4 H, d, J_{AB} = 7.9, MeAr*H*), 7.37–7.50 (2 H, m, MeCOAr*H*), 7.57 (4 H, d, J_{AB} = 7.9, MeAr*H*), 7.94 (1 H, d, J = 7.3, MeCOAr*H*), 8.13 (1 H, d, J = 7.3, MeCOAr*H*). ^{13}C NMR: 21.5, 27.2, 127.5, 131.2, 132.2, 135.0, 136.8, 137.7, 140.3, 141.5, 158.5, 159.8, 201.1. IR: 1665, 1260, 790, 765, 600, 480 cm^{-1}. Anal. Calcd for $C_{22}H_{21}BiO$: C, 51.8; H, 4.1. Found: C, 51.7; H, 4.0.

(2-Acetylphenyl)diphenylbismuthane, 2c. Crystals: yield, 23%; mp 96–98 °C (MeOH–CH_2Cl_2 (5:1)). ^{1}H NMR: 2.63 (3 H, s, Me), 7.26–7.50 (8 H, m, ArH), 7.69 (4 H, d, J = 6.1, C_6H_5), 7.92 (1 H, d, J = 7.3, MeCOAr*H*), 8.16 (1 H, d, J = 7.3, MeCOAr*H*). ^{13}C NMR 27.2, 127.3, 127.6, 130.3, 132.3, 135.2, 137.7, 140.4, 141.5, 201.2; *ipso* carbon signals were too weak to be assigned. IR 1660, 1260, 760, 725, 700, 600 cm^{-1}. Anal. Calcd for $C_{20}H_{17}BiO$: C, 49.8; H, 3.5. Found: C, 49.6; H, 3.5.

(2-Acetylphenyl)bis(4-chlorophenyl)bismuthane, 2d. Crystals: yield, 38%; mp 129–131 °C (MeOH–CH_2Cl_2 (5:1)). ^{1}H NMR: 2.63 (3 H, s, Me), 7.30 (4 H, d, J_{AB} = 7.9, ClArH), 7.40–7.60 (2 H, m, MeCOAr*H*), 7.57 (4 H, d, J_{AB} = 7.9, ClArH), 7.84 (1 H, d, J = 6.7, MeCOAr*H*), 8.18 (1 H, d, J = 6.7, MeCOAr*H*). ^{13}C NMR: 27.2, 128.0, 130.6, 132.6, 133.7, 135.5, 139.0, 140.2, 141.3, 201.4; *ipso* carbon signals were too weak to be assigned. IR: 1660, 1260, 1090, 1000, 800, 765, 710 cm^{-1}. Anal. Calcd for $C_{20}H_{15}BiCl_2O$: C, 43.6; H, 2.7. Found: C, 43.4; H, 2.7.

Typical Procedure 3. Chlorobis(1-naphthyl)bismuthane (ca. 3 mmol) was generated by stirring tris(1-naphthyl)bismuthane (1.18 g, 2 mmol) and bismuth(III) chloride (315 mg, 1 mmol) in CH_2Cl_2 (10 mL) for 2 h at 45 °C and employed as an ethereal suspension after removal of CH_2Cl_2 under reduced pressure. To a suspension of the lithium compound (ca. 3 mmol) derived from silyl enol ether **1** was added at room temperature a suspension of the above chlorobismuthane (ca. 3 mmol) in diethyl ether (10 mL), and the resulting mixture was stirred for 15 min. After the addition of brine (5 mL), the mixture was diluted with benzene (10 mL) and the insoluble substance was removed by filtration. The organic layer was separated and evaporated under reduced pressure to leave crude (2-acetylphenyl)bis(1-naphthyl)bismuthane, **2e**, as a yellow oil, which was purified by chromatography on silica gel followed by recrystallization from MeOH–CH_2Cl_2 (5:1). Crystals: yield, 14%; mp 235–237 °C (decomp). ^{1}H NMR: 2.64 (3 H, s, Me), 7.23–7.32 (4 H, m, ArH), 7.43–7.50 (5 H, m, ArH), 7.78–7.93 (7 H, m, ArH), 8.12–8.21 (2 H, m, ArH). ^{13}C NMR: 27.1, 125.5, 125.8, 127.8, 127.9, 128.9, 129.0, 130.9, 132.4, 134.7, 135.3, 138.0, 139.1, 141.5, 157.7, 163.0, 200.9; one carbon peak could not be assigned due to weak signal response. IR: 1660, 1260, 785, 770 cm^{-1}. Anal. Calcd for $C_{28}H_{21}BiO$: C, 57.7; H, 3.6. Found: C, 58.1; H, 3.6.

Preparation of (2-Acetylphenyl)arylbromobismuthanes 3. Typical Procedure. To a stirred mixture of crude compound **2a** (ca. 1 mmol) and benzene (3 mL) was added dropwise at ice bath temperature boron trifluoride–diethyl etherate (ca. 3 mmol), and after 5 min the reaction was quenched by the addition of saturated aqueous NaBr (3 mL). The organic layer was extracted with ethyl acetate (5 mL × 2), and the combined extracts were evaporated under reduced pressure to leave an oily residue, which was crystallized from MeOH–CH_2Cl_2 (5:1) to afford (2-acetylphenyl)bromo(4-methoxyphenyl)bismuthane, **3a**, as crystals: yield, 12%; mp 153–155 °C. ^{1}H NMR: 2.69 (3 H, s, Me), 3.73 (3 H, s, OMe), 6.98 (2 H, d, J_{AB} = 8.5, MeOAr*H*), 7.66 (1 H, dt, J = 7.9 and 1.2, MeCOAr*H*), 7.97 (1 H, dt, J = 7.3 and 1.2, MeCOAr*H*), 8.05 (2 H, d, J_{AB} = 8.5, MeOAr*H*), 8.25 (1 H, d, J = 7.9, MeCOAr*H*), 9.21 (1 H, d, J = 7.3, MeCOAr*H*). ^{13}C NMR: 27.4, 55.1, 117.5, 128.4, 135.1, 138.5, 138.7, 140.7, 143.1, 159.4, 169.0, 180.7, 208.7. IR: 1630, 1580, 1490, 1290, 1250, 1180, 810, 765 cm^{-1}. Anal. Calcd for $C_{15}H_{14}BiBrO_2$: C, 35.0; H, 2.7. Found: C, 34.7; H, 2.8.

(2-Acetylphenyl)bromo(4-methylphenyl)bismuthane, 3b. Crystals: yield, 83%; mp 174–176 °C (decomp) (MeOH–CH_2Cl_2 (5:1)). ^{1}H NMR: 2.25 (3 H, s, Me), 2.69 (3 H, s, Me), 7.31 (2 H, d, J_{AB} = 7.9, MeAr*H*), 7.66 (1 H, t, J = 7.3, MeCOAr*H*), 7.97 (1 H, t, J = 7.3, MeCOAr*H*), 8.05 (2 H, d, J_{AB} = 7.9, MeAr*H*), 8.24 (1 H, d, J = 7.3, MeCOAr*H*), 9.21 (1 H, d, J = 7.9, MeCOAr*H*). ^{13}C NMR: 21.5, 27.4, 128.3, 132.5, 135.1, 137.1, 138.2, 138.5, 140.7, 143.1, 174.2, 175.8, 208.7. IR: 1625, 1550, 1300, 1280, 800, 765, 615, 480 cm^{-1}. Anal. Calcd for $C_{15}H_{14}BiBrO$: C, 36.1; H, 2.8. Found: C, 36.2; H, 2.8.

(2-Acetylphenyl)bromophenylbismuthane, 3c. Crystals: yield, 87%; mp 146–148 °C (MeOH–CH_2Cl_2 (5:1)). ^{1}H NMR: 2.69 (3 H, s, Me), 7.25 (1 H, t, J = 7.3, C_6H_5), 7.50 (2 H, t, J = 7.3, C_6H_5), 7.67 (1 H, t, J = 7.3, MeCOAr*H*), 7.98 (1 H, t, J = 7.3, MeCOAr*H*), 8.17 (2 H, d, J = 7.0, C_6H_5), 8.25 (1 H, d, J = 7.3, MeCOAr*H*), 9.21 (1 H, d, J = 7.3, MeCOAr*H*). ^{13}C NMR: 27.4, 128.2, 128.4, 131.7, 135.1, 137.1, 138.6, 140.7, 143.1, 177.3, 180.8, 208.8. IR: 1620, 1280, 770, 730 cm^{-1}. Anal. Calcd for $C_{14}H_{12}BiBrO$: C, 34.7; H, 2.5. Found: C, 34.8; H, 2.4.

(2-Acetylphenyl)bromo(4-chlorophenyl)bismuthane, 3d. Crystals: yield, 86%; mp 157–159 °C (decomp) (MeOH–CH_2Cl_2 (5:1)). ^{1}H NMR: 2.69 (3 H, s, Me), 7.40 (2 H, d, J_{AB} = 7.9, ClAr*H*), 7.68 (1 H, t, J = 7.3, MeCOAr*H*), 7.99 (1 H, t, J = 7.3, MeCOAr*H*), 8.09 (2 H, d, J_{AB} = 7.9, ClAr*H*), 8.25 (1 H, d, J = 7.9, MeCOAr*H*), 9.19 (1 H, d, J = 7.9, MeCOAr*H*). ^{13}C NMR: 27.4, 128.6, 131.7, 134.3, 135.2, 138.6, 138.7, 140.6, 143.1, 174.9, 180.4, 209.0. IR: 1630, 1280, 1085, 1005, 800, 765 cm^{-1}. Anal. Calcd for $C_{14}H_{11}BiBrClO$: C, 32.4; H, 2.1. Found: C, 32.7; H, 2.1.

(2-Acetylphenyl)bromo(1-naphthyl)bismuthane, 3e. Crystals: yield, 82%; mp 225–227 °C (decomp) (MeOH–CH_2Cl_2 (5:1)). ^{1}H NMR: 2.58 (3 H, s, Me), 7.43–7.53 (2 H, m, Ar*H*), 7.61–7.75 (2 H, m, Ar*H*), 7.85 (1 H, d, J = 8.6, Ar*H*), 7.95 (1 H, d, J = 8.5, Ar*H*), 8.05 (1 H, t, J = 7.9, Ar*H*), 8.24 (1 H, d, J = 7.9, Ar*H*), 8.48–8.55 (2 H, m, Ar*H*), 9.26 (1 H, d, J = 7.3, MeCOAr*H*). ^{13}C NMR: 27.2, 125.8, 126.2, 128.6, 128.7, 129.3, 129.7, 130.0, 135.1, 135.5, 138.4, 138.5, 141.0, 143.3, 179.1, 179.8, 208.2; one carbon signal was too weak to be assigned. IR: 1615, 1280, 790, 770 cm^{-1}. Anal. Calcd for $C_{18}H_{14}BiBrO$: C, 40.4; H, 2.6. Found: C, 40.1; H, 2.7.

(2-Acetylphenyl)chloro(4-methylphenyl)bismuthane, 4a. To a stirred solution of compound **2b** (255 mg, 0.5 mmol) in benzene (3 mL) was added dropwise at ice bath temperature boron trifluoride–diethyl etherate (ca. 2 mmol). After 5 min, the mixture was quenched with brine (3 mL) and the organic layer was extracted with ethyl acetate (5 mL × 2). The combined extracts were evaporated under reduced pressure to leave an oily residue, which was crystallized from MeOH–CH_2Cl_2 (5:1) to afford **4a** as crystals: yield 90%; mp 175–177 °C. ^{1}H NMR: 2.24 (3 H, s, Me), 2.68 (3 H, s, Me), 7.33 (2 H, d, J_{AB} = 7.9, MeAr*H*), 7.63 (1 H, t, J = 7.3, MeCOAr*H*), 8.00 (1 H, t, J = 7.3, MeCOAr*H*), 8.03 (2 H, d, J_{AB} = 7.9, MeAr*H*), 8.25 (1 H, d, J = 7.3, MeCOAr*H*), 9.06 (1 H, d, J = 7.3, MeCOAr*H*). ^{13}C NMR: 21.5, 27.4, 128.2, 132.4, 135.2, 136.4 (× 2), 138.1, 138.3, 143.1, 177.9, 185.3, 209.2. IR: 1625, 1550, 1280, 800, 765, 615, 480 cm^{-1}. Anal. Calcd for $C_{15}H_{14}BiClO$: C, 39.6; H, 3.1. Found: C, 39.6; H, 3.1.

(2-Acetylphenyl)iodo(4-methylphenyl)bismuthane, 4b. To a stirred solution of compound **3b** (249 mg, 0.5 mmol) in benzene (3 mL) was added dropwise saturated aqueous NaI (3 mL). After 15 min, the organic layer was extracted with ethyl acetate (5 mL × 2). The combined extracts were evaporated under reduced pressure to leave an oily residue,

which was crystallized from MeOH–CH_2Cl_2 (5:1) to afford **4b** as crystals: yield 89%; mp 148–150 °C. ^{1}H NMR: 2.25 (3 H, s, Me), 2.68 (3 H, s, Me), 7.25 (2 H, d, J_{AB} = 7.9, MeAr*H*), 7.70 (1 H, dt, J = 7.6 and 1.3, MeCOAr*H*), 7.87 (1 H, dt, J = 7.4 and 1.3, MeCOAr*H*), 8.07 (2 H, d, J_{AB} = 7.9, MeAr*H*), 8.23 (1 H, dd, J = 7.7 and 1.1, MeCOAr*H*), 9.42 (1 H, dd, J = 7.7 and 1.1, MeCOAr*H*). ^{13}C NMR: 21.6, 27.1, 128.5, 132.4, 134.5, 138.0, 138.2, 139.0, 143.1, 145.6, 166.7, 172.1, 207.5. IR: 1625, 1285, 800, 770, 480 cm^{-1}. Anal. Calcd for $C_{15}H_{14}BiIO$: C, 33.0; H, 2.6. Found: C, 33.0; H, 2.6.

(2-Formylphenyl)bis(1-naphthyl)bismuthane, 5e. *Ortho*-lithiated lithium α-amino alkoxide was generated according to the reported procedure[13] by adding lithium *N*-methylpiperazide (ca. 3 mmol) to benzaldehyde (3 mmol) in benzene (5 mL) and subsequently heating the solution with excess of butyllithium (9 mmol) at reflux for 12 h. To a suspension of the dilithiated compound (ca. 3 mmol) thus obtained in benzene (5 mL) was added dropwise at ice bath temperature a suspension of chlorobis(1-naphthyl)bismuthane (ca. 3 mmol) in diethyl ether (10 mL), and the resulting mixture was stirred for 15 min. This chlorobismuthane (ca. 3 mmol) was generated by stirring tris(1-naphthyl)bismuthane (1.18 g, 2 mmol) and bismuth(III) chloride (315 mg, 1 mmol) in CH_2Cl_2 (10 mL) for 2 h at 45 °C and employed as an ethereal suspension after removal of CH_2Cl_2 under reduced pressure. After the addition of brine (5 mL), the mixture was diluted with benzene (10 mL) and the insoluble polymeric substances were filtered off. The organic layer was separated and evaporated under reduced pressure to leave a yellow oil, which was purified by chromatography on silica gel using hexane–ethyl acetate (5:1) as the eluent to afford crude compound **5e**. Recrystallization from MeOH–CH_2Cl_2 (5:1) gave pure product as crystals: yield, 17%; mp 170–172 °C. ^{1}H NMR: 7.24–8.15 (18 H, m, Ar*H*), 10.18 (1 H, s, CHO). ^{13}C NMR: 125.6, 125.9, 128.1, 128.2, 128.9, 129.2, 130.7, 134.7, 136.3, 137.2, 138.1, 139.0, 141.1, 141.5, 156.7, 161.0, 195.0. IR: 1665, 1560, 1500, 1200, 790, 785, 770, 760 cm^{-1}. Anal. Calcd for $C_{27}H_{19}BiO$: C, 57.0; H, 3.4. Found: C, 56.6; H, 3.3.

Preparation of Arylbromo(2-formylphenyl)bismuthanes 6. Typical Procedure. Chlorobis(4-methoxyphenyl)-bismuthane (ca. 3 mmol) was generated by stirring tris(4-methoxyphenyl)bismuthane (1.06 g, 2 mmol) and bismuth(III) chloride (315 mg, 1 mmol) in diethyl ether (10 mL) for 1 h at room temperature. To a suspension of the *ortho*-lithiated lithium α-amino alkoxide (ca. 3 mmol) generated from benzaldehyde in benzene (5 mL) was added dropwise at ice bath temperature a suspension of the above chlorobismuthane (ca. 3 mmol), and the resulting mixture was stirred for 15 min. After the addition of brine (5 mL), the mixture was worked up in a manner as described in the preparation of **5e** to give a yellow oil containing compound **5a**, which was treated with boron trifluoride–diethyl etherate (ca. 3 mmol) in benzene (5 mL) at ice bath temperature. The reaction mixture was immediately quenched with saturated aqueous NaBr (3 mL). The organic layer was extracted with ethyl acetate (5 mL × 2), and the combined extracts were evaporated under reduced pressure to leave an oily residue, which was purified by chromatography on silica gel using hexane–ethyl acetate (5:1) as the eluent to afford crude bromo(2-formylphenyl)(4-methoxyphenyl)bismuthane **6a** as a yellow oil. Recrystallization from MeOH–CH_2Cl_2 (5:1) gave pure product as crystals: yield, 16%; mp 125–127 °C. ^{1}H NMR: 3.73 (3 H, s, OMe), 6.99 (2 H, d, J_{AB} = 8.6, MeOAr*H*), 7.76 (1 H, t, J = 7.3, HCOAr*H*), 7.96 (1 H, t, J = 7.3, HCOAr*H*), 8.07 (2 H, d, J_{AB} = 8.6, MeOAr*H*), 8.22 (1 H, d, J = 7.3, HCOAr*H*), 9.15 (1 H, d, J = 7.3, HCOAr*H*), 10.67 (1 H, s, CHO). ^{13}C NMR: 55.1, 117.6, 128.7, 137.9, 138.9, 139.3, 141.1, 143.9, 159.6, 200.5; *ipso* carbon atoms were too weak to be observed. IR: 1640, 1575, 1490, 1285, 1245, 1210, 1180 cm^{-1}. Anal. Calcd for $C_{14}H_{12}BiBrO_2$: C, 33.5; H, 2.4. Found: C, 33.5; H, 2.4.

Bromo(2-formylphenyl)(4-methylphenyl)bismuthane, 6b. Crystals: yield, 24%; mp 139–141 °C (MeOH–CH_2Cl_2 (5:1)). ^{1}H NMR: 2.25 (3 H, s, Me), 7.32 (2 H, d, J_{AB} = 7.3, MeAr*H*), 7.75 (1 H, t, J = 7.3, HCOAr*H*), 7.95 (1 H, t, J = 7.3, HCOAr*H*), 8.07 (2 H, d, J_{AB} = 7.3, MeAr*H*), 8.22 (1 H, d, J = 7.9, HCOAr*H*), 9.15 (1 H, d, J = 7.3, HCOAr*H*), 10.68 (1 H, s, CHO). ^{13}C NMR: 21.6, 128.7, 132.6, 137.3, 137.9, 138.4, 139.3, 141.1, 143.9, 174.3, 180.7, 200.6. IR: 1640, 1550, 1210, 800, 760, 475 cm^{-1}. Anal. Calcd for $C_{14}H_{12}BiBrO$: C, 34.7; H, 2.5. Found: C, 34.8; H, 2.5.

Bromo(2-formylphenyl)phenylbismuthane, 6c. Crystals:[16] yield, 20%; mp 138–140 °C (MeOH–CH_2Cl_2 (5:1)). ^{1}H NMR: 7.26–8.21 (8 H, m, ArH), 9.17 (1 H, d, J = 8.0, HCOAr*H*), 10.69 (1 H, s, CHO). ^{13}C NMR: 128.3, 128.7, 131.8, 137.3, 137.9, 139.3, 141.0, 143.9, 177.1, 180.7, 200.6. IR: 1630, 1570, 1550, 1210, 850, 765, 735, 680, 665 cm^{-1}.

Bromo(4-chlorophenyl)(2-formylphenyl)bismuthane, 6d. Crystals:[16] yield, 27%; mp 155–157 °C (MeOH–CH_2Cl_2 (5:1)). ^{1}H NMR: 7.42 (2 H, d, J_{AB} = 7.3, ClAr*H*), 7.77 (1 H, t, J = 7.3, HCOAr*H*), 7.98 (1 H, t, J = 7.3, HCOAr*H*), 8.12 (2 H, d, J_{AB} = 7.3, ClAr*H*), 8.24 (1 H, d, J = 7.3, HCOAr*H*), 9.14 (1 H, d, J = 7.3, HCOAr*H*), 10.68 (1 H, s, CHO). ^{13}C NMR: 128.9, 131.8, 134.5, 138.0, 138.8, 139.5, 141.0, 143.8, 200.7; *ipso* carbon signals could not be assigned. IR: 1630, 1570, 1550, 1215, 1080, 1000, 855, 800, 760, 715, 665, 480 cm^{-1}.

Bromo(2-formylphenyl)(1-naphthyl)bismuthane, 6e. Chlorobis(1-naphthyl)bismuthane (ca. 3 mmol) was generated by stirring tris(1-naphthyl)bismuthane (1.18 g, 2 mmol) and bismuth(III) chloride (315 mg, 1 mmol) in CH_2Cl_2 (10 mL) for 2 h at 45 °C and was employed as an ethereal suspension after removal of CH_2Cl_2 under reduced pressure. To a stirred suspension of the *ortho*-lithiated lithium α-amino alkoxide (ca. 3 mmol) generated from benzaldehyde in benzene (5 mL) was added dropwise at ice bath temperature a suspension of the above chlorobismuthane (ca. 3 mmol) in diethyl ether (10 mL), and the reaction mixture was stirred for additional 15 min. Similar work-up as described for **6a** afforded compound **6e**: crystals,[16] yield, 14%; mp 193–195 °C (decomp) (MeOH–CH_2Cl_2 (5:1)). ^{1}H NMR: 7.44–7.53 (2 H, m, ArH), 7.66 (1 H, t, J = 6.7, ArH), 7.79 (1 H, t, J = 7.3 ArH), 7.86 (1 H, d, J = 7.9, ArH), 7.96 (1 H, d, J = 8.5, ArH), 8.03 (1 H, t, J = 7.9, ArH), 8.19 (1 H, d, J = 7.3, ArH), 8.49 (1 H, d, J = 8.5, ArH), 8.60 (1 H, d, J = 6.7, ArH), 9.21 (1 H, d, J = 7.3, HCOAr*H*), 10.56 (1 H, s, CHO). Due to extensive decomposition of **6e** during the measurement of ^{13}C NMR, only one signal, at δ_C 200.1, was assigned as the carbonyl carbon. IR: 1635, 1550, 1250, 1210, 845, 790, 770 cm^{-1}.

(2-Formylphenyl)iodo(4-methylphenyl)bismuthane, 7b. To a solution of compound **6b** (242 mg, 0.5 mmol) in benzene (3 mL) was added saturated aqueous NaI (3 mL), and the resulting mixture was stirred for 15 min. The organic layer was extracted with ethyl acetate (5 mL × 2), and the combined extracts were evaporated under reduced pressure to leave an oily residue, which was crystallized from MeOH–CH_2Cl_2 (5:1) to afford **7b** as crystals: yield, 88%; mp 141–143 °C. ^{1}H NMR: 2.25 (3 H, s, Me), 7.27 (2 H, d, J_{AB} = 7.3, MeAr*H*), 7.76–7.91 (2 H, m, HCOAr*H*), 8.09 (2 H, d, J_{AB} = 7.3, MeAr*H*), 8.18 (1 H, J = 7.3, HCOAr*H*), 9.36 (1 H, d, J = 7.7, HCOAr*H*), 10.51 (1 H, s, CHO). ^{13}C NMR: 21.6, 128.7, 132.5, 137.6, 138.3, 138.5, 139.7, 143.7, 146.2, 199.5; *ipso* carbon signals were too weak to be assigned. IR: 1635, 1575, 1555, 1210, 950, 795, 750, 660, 480 cm^{-1}. Anal. Calcd for $C_{14}H_{12}BiIO$: C, 31.6; H, 2.3. Found: C, 31.6; H, 2.3.

Chlorobis(2-formylphenyl)bismuthane, 8. To a suspension of the *ortho*-lithiated lithium α-amino alkoxide (ca. 3 mmol) derived from benzaldehyde in benzene (5 mL) was added dropwise at ice bath temperature a suspension of chlorobismuthane (ca. 3 mmol), generated from tris(4-methylphenyl)bismuthane (964 mg, 2 mmol) and bismuth(III) chloride (315 mg, 1 mmol) in diethyl ether (10 mL), and the

(16) This compound decomposed while waiting for elemental analysis.

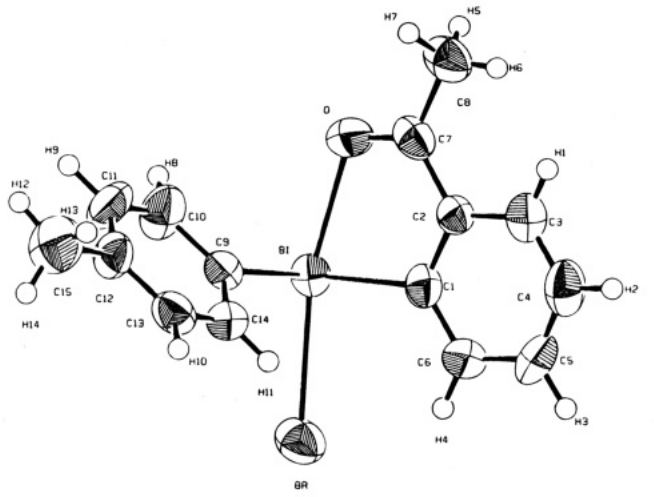


Figure 1.

Table 5. Positional Parameters and Isotropic Thermal Parameters (Å²) for 3b[a]

atom	*x*	*y*	*z*	*B*(eq)[b]
Bi	0.09598(5)	0.48044(3)	0.67273(3)	3.68(2)
Br	0.0101(1)	0.2652(1)	0.71497(8)	5.50(6)
O	0.2310(9)	0.6417(6)	0.6000(5)	4.7(4)
C(1)	0.190(1)	0.420(1)	0.5459(6)	3.8(5)
C(2)	0.264(1)	0.4995(8)	0.4958(6)	3.5(5)
C(3)	0.325(1)	0.467(1)	0.4159(7)	4.6(5)
C(4)	0.310(1)	0.316(1)	0.3861(7)	5.4(7)
C(5)	0.231(1)	0.281(1)	0.4329(8)	4.8(6)
C(6)	0.175(1)	0.310(1)	0.5138(7)	4.4(5)
C(7)	0.278(1)	0.617(1)	0.5275(7)	4.2(5)
C(8)	0.347(1)	0.707(1)	0.4749(7)	5.3(6)
C(9)	0.337(1)	0.4691(9)	0.7527(6)	3.5(4)
C(10)	0.391(2)	0.558(1)	0.8068(8)	6.4(7)
C(11)	0.536(2)	0.557(1)	0.8544(8)	6.4(7)
C(12)	0.647(1)	0.467(1)	0.8518(7)	4.5(5)
C(13)	0.593(1)	0.379(1)	0.7976(7)	4.5(6)
C(14)	0.446(1)	0.3788(9)	0.7493(7)	4.1(5)
C(15)	0.810(2)	0.469(1)	0.902(1)	7.4(8)
H(1)	0.3781	0.5215	0.3824	5.5
H(2)	0.3534	0.3401	0.3324	6.5
H(3)	0.2148	0.2072	0.4102	5.7
H(4)	0.1264	0.2542	0.5476	5.2
H(5)	0.2677	0.7643	0.4625	6.3
H(6)	0.3783	0.6770	0.4209	6.3
H(7)	0.4401	0.7387	0.5075	6.3
H(8)	0.3229	0.6219	0.8104	7.6
H(9)	0.5662	0.6194	0.8912	7.7
H(10)	0.6614	0.3153	0.7937	5.3
H(11)	0.4160	0.3162	0.7124	5.0
H(12)	0.8222	0.5369	0.9350	8.9
H(13)	0.8922	0.4649	0.8619	8.9
H(14)	0.8204	0.4066	0.9413	8.9

[a] Numerals in parentheses are estimated standard deviations. [b] $B(\text{eq}) = 1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos a)B_{23}]$.

resulting mixture was stirred for 15 min. After the addition of brine (5 mL) and then benzene (10 mL), the insoluble polymeric substances were removed by filtration. The organic layer was separated and evaporated under reduced pressure to leave a yellow oily residue, which was purified by chromatography on silica gel using hexane−ethyl acetate (5:1) as the eluent to afford (2-formylphenyl)bis(4-methylphenyl)bismuthane, **5b**. A solution of **5b** in benzene (3 mL) was treated with boron trifluoride diethyl etherate (ca. 3 mmol) at ice bath temperature, and the resulting mixture was immediately quenched with brine (3 mL). The organic layer was separated and evaporated under reduced pressure to leave impure chloro(2-formylphenyl)(4-methylphenyl)bismuthane **7a** as a yellow oily residue. Attempted recrystallization of this product from MeOH−CH_2Cl_2 (5:1), however, resulted in the decomposition to compound **8**: crystals, yield, 12%; mp 208−210 °C (decomp). ^{1}H NMR: 7.65 (2 H, t, J = 7.3, C_6H_4), 7.86 (2 H, t, J = 7.3, C_6H_4), 8.12 (2 H, d, J = 7.3, C_6H_4), 8.81 (2 H, d, J = 7.9, C_6H_4), 10.53 (2 H, s, CHO). IR: 1630, 1555, 1220, 1200, 855, 840, 755, 665 cm^{-1}. Anal. Calcd for $C_{14}H_{10}BiClO_2$: C, 37.0; H, 2.2. Found: C, 37.4; H, 2.4.

Bromo(4-methylphenyl)[2-(*N*-phenylformimidoyl)phenyl]bismuthane, 9. A stirred mixture of compound **6b** (484 mg, 1 mmol) and aniline (ca. 1.5 mmol) in benzene (3 mL) was heated at reflux for 4 h. The reaction mixture was evaporated to leave an oily residue, which was crystallized from MeOH to afford compound **9**: crystals, yield, 82%; mp 218−220 °C. ^{1}H NMR: 2.22 (3 H, s, Me), 7.13 (2 H, d, J = 6.7, C_6H_5), 7.22 (2 H, d, J_{AB} = 7.9, MeC_6H_4), 7.34−7.45 (3 H, m, C_6H_5), 7.70 (1 H, t, J = 7.3, C_6H_4CHN), 7.79 (1 H, t, J = 7.3, C_6H_4CHN), 8.00 (2 H, d, J_{AB} = 7.9, MeC_6H_4), 8.06 (1 H, d, J = 7.3, C_6H_4-CHN), 9.22 (1 H, d, J = 7.3, C_6H_4CHN), 9.24 (1 H, s, CHN). IR: 1615, 1590, 1575, 1550, 1490, 1190, 920, 890, 795, 760, 710, 690, 545, 480, 425 cm^{-1}. Anal. Calcd for $C_{20}H_{17}BiBrN$: C, 42.9; H, 3.1; N, 2.5. Found: C, 42.8; H, 3.0; N,2.4.

Chloro(4-methylphenyl)[2-(*N*-benzylformimidoyl)phenyl]bismuthane, 10. Benzylamine (ca. 1.5 mmol) was added dropwise to a stirred mixture of crude chloro(2-formylphenyl)-(4-methylphenyl)bismuthane **7a** (ca. 1 mmol) and benzene (3 mL) at room temperature, and after 5 min the reaction was quenched by the addition of brine (1 mL). The organic layer was extracted with ethyl acetate (5 mL × 2), and the combined extracts were evaporated under reduced pressure to leave an oily residue, which was crystallized from MeOH−CH_2Cl_2 (5:1) to afford compound **10**: crystals, yield, 69%; mp 210−212 °C. ^{1}H NMR: 2.25 (3 H, s, Me), 4.64 (1 H, d, J_{AB} = 14.0, CH_2-Ph), 4.73 (1 H, d, J_{AB} = 14.0, CH_2Ph), 7.14−7.41 (7 H, m, ArH), 7.62 (1 H, dt, J = 6.1 and 1.2, C_6H_4CHN), 7.76 (1 H, dt, J = 6.0 and 1.6, C_6H_4CHN), 7.85 (2 H, d, J_{AB} = 7.9, MeC_6H_4), 7.94 (1 H, dd, J = 6.1 and 1.2, C_6H_4CHN), 8.99 (1 H, d, J = 7.3, C_6H_4CHN), 9.22 (1 H, s, CHN). IR: 1625, 1440, 1035, 800, 770, 755, 700, 480 cm^{-1}. Anal. Calcd for $C_{21}H_{19}BiClN$: C, 47.6; H, 3.6. Found: C, 47.3; H, 3.6.

X-ray Crystallography of Compound 3b. A crystal of dimension 0.430 × 0.180 × 0.180 mm^3 grown from MeOH−CH_2Cl_2 (5:1) at ambient temperature was used for X-ray crystallography.

Crystal Data. $C_{15}H_{14}BiBrO$: M = 499.16, monoclinic, space group $P2_1/c$, a = 8.241(2) Å, b = 11.885(3) Å, c = 15.179(2) Å, β = 95.04(1)°, V = 1480.9(5) Å^3, Z = 4, D_{calcd} = 2.239 g cm^{-3}. Colorless prisms; μ(Mo Kα, λ = 0.710 69 Å) = 145.29 cm^{-1}. Intensity data were collected on a Rigaku AFC5R diffractometer with graphite−monochromated Mo Kα radiation and a 12 KW rotating anode generator using the $\omega-2\theta$ scan technique to a maximum 2θ-value of 55.0°. Scans of (0.68 + 0.30 tan θ)° were made at a speed of 16.0 deg min^{-1} (in ω). Of the 3816 reflections that were collected, 3579 were unique (R_{int} = 0.082). Data were corrected for Lorentz, polarization, and absorption effects. Empirical correction for the absorption was made based on azimuthal or Ψ scans[17] (transmission factors: 0.56−1.00). The correction for secondary extinction was applied (coefficient: 4.997 × 10^{-7}). The structure was solved by the Patterson method.[18] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1950 observed reflections ($I > 3.00\,\sigma(I)$) and 164 variable parameters and converged with unweighted and weighted agreement factors of R = 0.036 and R_w = 0.034. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.97

(17) North, A. C.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A*, **1968**, *24*, 351.
(18) Structure solution method: Calbrese, J. C. PHASE: Patterson Heavy Atom Solution Extractor. Ph.D. Thesis, University of Wisconsin−Madison, Madison, WI, 1972.
(19) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV. Table 2.2A.
(20) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

and -1.00 e/Å^3, respectively. The weighting scheme, $w = 1/\sigma^2(F_o)$, was employed. Neutral atom scattering factors were taken from Cromer and Waber.[19] Anomalous dispersion effects were included in F_{calcd};[20] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[21] All calculations were performed on a VAX station 3200 computer using the TEXSAN[22] crystallographic software package from the Molecular Structure Corporation. The ORTEP-II program[23] was used to obtain the drawing in Figure 1. Selected bond lengths, bond angles, and atomic coordinates are given in Tables 4 and 5.

Acknowledgment. The present work was supported by Grants-in-Aid for Scientific Research (Nos. 05236101 and 06740550) from the Ministry of Education, Science and Culture of Japan. T.M. thanks Mr. T. Ikegami (Kyoto University) for the measurement of ^{13}C NMR spectra.

Supporting Information Available: For **3b**, full details of crystal data, fractional atomic coordinates, bond lengths, bond angles, hydrogen coordinates, thermal parameters, and unit cell and PLUTO diagrams (19 pages). Ordering information is given on any current masthead page.

OM9502289

(21) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press; Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(22) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1985.

(23) Johnson, C. K.; ORTEP-II. Report ORNL-5138; National Technical Information Service, U.S. Department of Commerce: Springfield, VA, 1976.