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Synthesis, Halogenolysis, and Crystal Structure of Hypervalent Organobismuth Compounds (10-Bi-5)

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The stable 10-Bi-5 compounds (o-$C_6H_4C(CF_3)_2O$)$BiAr_2R$ (**3** (Ar, R): **3a,** p-$CH_3C_6H_4$, p-$CH_3C_6H_4$; **3b,** p-$CF_3C_6H_4$, p-$CF_3C_6H_4$; **3c,** p-FC_6H_4, p-FC_6H_4; **3d,** p-$CH_3C_6H_4$, p-$CF_3C_6H_4$; **3e,** p-$CF_3C_6H_4$, p-$CH_3C_6H_4$; **3f,** p-$CH_3C_6H_4$, PhC≡C; **3g,** p-$CH_3C_6H_4$, Me) were synthesized. The X-ray structures of **3a,f,g** showed distorted-trigonal-bipyramidal geometries, and the electronegative apical PhC≡C ligand of **3f** made the apical Bi–O bond (2.243(3) Å) shorter than the Bi–O bond of **3a,g** (2.323(4) Å in **3a** and 2.328(7) Å in **3g**). Halogenolysis of **3** with sulfuryl chloride or pyridinium bromide perbromide gave the five-coordinate bismuth compounds (o-$C_6H_4C(CF_3)_2O$)$BiAr^1Ar^2X$ (**6** (Ar^1, Ar^2, X): **6a,** p-$CH_3C_6H_4$, p-$CH_3C_6H_4$, Cl; **6b,** p-$CF_3C_6H_4$, p-$CF_3C_6H_4$, Cl; **6c,** p-FC_6H_4, p-FC_6H_4, Cl; **6d,** p-$CH_3C_6H_4$, p-$CH_3C_6H_4$, Br; **6e,** p-$CH_3C_6H_4$, p-$CF_3C_6H_4$, Cl; **6f,** p-$CH_3C_6H_4$, p-$CF_3C_6H_4$, Br) in good to quantitative yield with apical covalent Bi–halogen bonds which were clearly shown by the X-ray analysis of **6a,b,d,e.** The reactivity order of **3** for the halogenolysis was as follows: PhC≡C—Bi > Me—Bi > p-$CH_3C_6H_4$—Bi > p-$CF_3C_6H_4$—Bi. Direct halogenolysis of the bismuth–carbon bond was suggested. The variable-temperature ^{19}F NMR of unsymmetrically substituted **6e,f** did not show coalescence of the CF_3 groups up to 170 °C in a dilute solution of toluene-d_8, and the energies of inversion at the bismuth atom should be higher than 21 kcal mol^{-1} at 170 °C.

Introduction

Recently Barton et al. reported a series of phenylations utilizing pentavalent Bi–aryl compounds including $Bi(C_6H_5)_5$, indicating the uniqueness of the weak bonding of hypervalent bismuth compounds.[1] However, systematic studies for the preparation, structure, and reactivity of 10-Bi-5 type hypervalent organobismuth compounds have not been carried out mostly because of the instability of those compounds.[2] Especially, the number of hypervalent organobismuth compounds structurally determined by X-ray analysis has been relatively few,[3] and to our knowledge the energy barrier of pseudorotation, which is an indication of flexibility characteristic for five-coordinate species,[4] has not been determined yet. Recently we reported the preparation and some reactions of stable 10-Bi-5 compounds[5a] by use of a five-membered ligand, the so-called Martin ligand[6] (**1**), and also by use of transannular interaction.[5b] Here we report the preparation of several stable 10-Bi-5 compounds (**3** and **6**), seven of which were structurally determined by X-ray analysis to show the characteristic shortening of the apical Bi–O bond by increasing the electronegativity of the other apical group. The energy barrier of pseudorotation of **6e,f,** bearing five different substituents on the bismuth atom, was estimated.

Results and Discussion

Preparation of Trisubstituted λ^5-Bismuthanes 3a–c. 1,1,1-Trisubstituted 3,3-bis(trifluoromethyl)-3H-2,1-benzoxabismoles **3a–c** were prepared by the method outlined in Scheme I. The reaction of triarylbismuth dichloride (**2a–c**) with the dilithiated reagent of bis(trifluoromethyl)benzyl alcohol (**1**)[6] gave **3a–c** in good yield (53–61%). The best yields of **3a–c** were obtained in THF at −78 °C for 4–8 h. Major byproducts of the reaction were cyclic Bi(III) (**4**) and Ar_3Bi (**5**), and these products increased remarkably under the conditions of higher temperatures and longer reaction times. The use of $(p\text{-}CH_3C_6H_4)_3BiBr_2$ instead of $(p\text{-}CH_3C_6H_4)_3BiCl_2$ only slightly increased the yield of **3a** to 61%. Compounds **3** are stable to heat (<200 °C) and to atmospheric moisture. They could be purified by flash column chromatography (SiO_2) to give colorless crystals. Related compounds bearing different substituents on the bismuth atom were also isolated from the reaction of lithium reagents with λ^5-halogenobismuthanes (**6**) or from the protonolysis of a 12-Bi-6 ate complex (**7a**) (vide infra).

Reaction of 3a–c with Electrophiles. Compounds **3** were more reactive to electrophilic reagents than the corresponding antimony compounds **8**;[7] thus, **3a** reacted

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(1) Abramovitch, R. A.; Barton, D. H. R.; Finte, J.-P. *Tetrahedron* **1988,** *44,* 3039. Barton, D. H. R.; Blazejewski, J.-C.; Charpiot, B.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1981,** 503. Barton, D. H. R.; Bhathagar, N. Y.; Blazejewski, J.-C.; Charpiot, B.; Finet, J.-P.; Lester, D. J.; Motherwell, W. B.; Papoula, M. T. B.; Stanforth, S. P. *J. Chem. Soc., Perkin Trans. 1* **1985,** 2657.

(2) Hellwinkel, D. *Top. Curr. Chem.* **1983,** *109,* 1. Freedman, L. D.; Doak, G. O. *Chem. Rev.* **1982,** *82,* 15. Finet, J.-P. *Chem. Rev.* **1989,** *89,* 1487. Poller, R. C. *Compr. Org. Chem.* **1979,** *3,* 1111. Wardell, J. L. *Compr. Organomet. Chem.* **1982,** *2,* 681. *Gmelin Handbuch der Anorganischen Chemie*; Wieber, M., Ed.; Springer-Verlag: Berlin, 1977; Vol. 47, *Bismuth-Organische Verbindungen.*

(3) Schmuck, A.; Leopold, D.; Wallenhauer, S.; Seppelt, K. *Chem. Ber.* **1990,** *123,* 761. Schmuck, A.; Leopold, D.; Seppelt, K. *Chem. Ber.* **1989,** *122,* 803. Schmuck, A.; Pyykko, P.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 213. Barton, D. H. R.; Charpiot, B.; Dau, E. T. H.; Motherwell, W. B.; Pascard, C.; Pichon, C. *Helv. Chim. Acta* **1984,** *67,* 586.

(4) Martin, J. C. *Science (Washington, D.C.)* **1983,** *221,* 509. Holmes, R. R. *Pentacoordinated Phosphorus: Structure and Spectroscopy*; ACS Monograph 175; American Chemical Society: Washington, DC, 1980. Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Wiley: New York, 1976; p 82.

(5) (a) Akiba, K.; Ohdoi, K.; Yamamoto, Y. *Tetrahedron Lett.* **1988,** *29,* 3817. (b) Ohkata, K.; Takemoto, S.; Ohnishi, M.; Akiba, K. *Tetrahedron Lett.* **1989,** *30,* 4841.

(6) Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981,** *46,* 7049.

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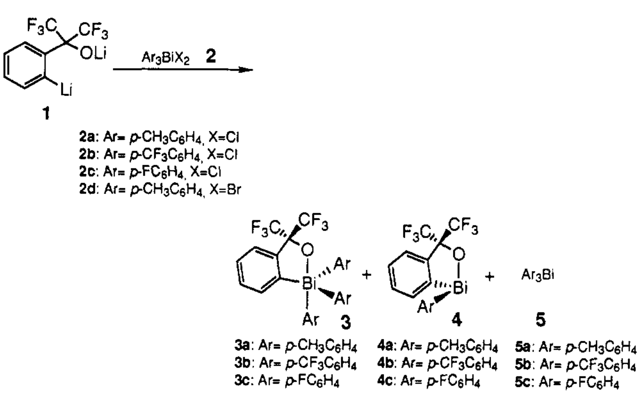
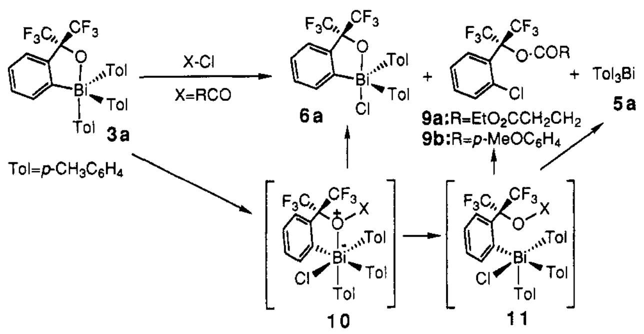
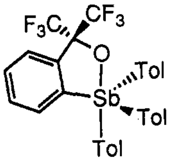
Scheme I



Scheme II



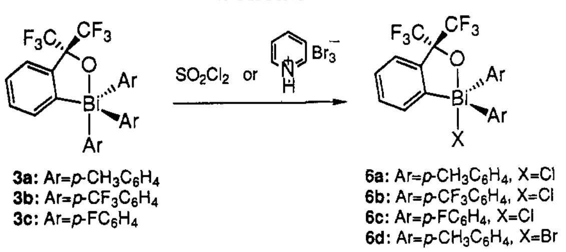
with acid chlorides such as ethyl succinyl chloride or *p*-methoxybenzoyl chloride in contrast to the inertness of **8a** with propionyl chloride. Ethyl succinyl chloride or *p*-methoxybenzoyl chloride reacted mainly on the oxygen of **3a** to give **9a** (84%) or **9b** (41%) and tri-*p*-tolylbismuth (**5a**) (61% with ethyl succinyl chloride, 38% with *p*-methoxybenzoyl chloride). In addition to **9a**, five-coordinated **6a** with an apical Bi–Cl bond was obtained. The probable mechanism for the reaction is illustrated in Scheme II. Thus, electrophiles reacted at the oxygen atom to form the 12-Bi-6 type intermediate **10**, and **10** collapsed to give **6a** by syn elimination and to **11** to afford **9a** and tri-*p*-tolylbismuth (**5a**) by reductive ligand coupling. The compound **6a** could be prepared from the reaction of **3a** with sulfuryl chloride in CH_2Cl_2 almost quantitatively (>95%) at room temperature, and the resulting *p*-chlorotoluene was isolated and quantitatively determined by GLC. Similarly, **6b–d** were obtained quantitatively from **3** with sulfuryl chloride or pyridinium bromide perbromide. Compounds **6a–d** were stable to atmospheric moisture and silica gel chromatography, could be recrystallized from benzene–ethanol to form colorless crystals, and gave correct elemental analyses.



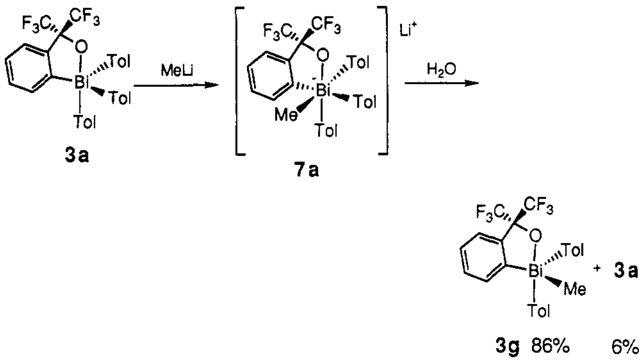
8a

Preparation of Other Substituted λ^5-Bismuthanes 3d–g. Methyl-substituted λ^5-bismuthane **3g** could be obtained by protonolysis of the six-coordinated bismuth ate complex **7a** (12-Bi-6) (Scheme IV) in a manner similar to that for the corresponding antimony ate complexes.[7] Thus, reaction of 1 equiv of methyllithium with **3a** was carried out at −78 °C and was quenched with aqueous NaCl. Compound **3g** was obtained in 86% yield in addition to a small amount (6%) of recovered **3a**. However, the method was not useful for the preparation of aryl-substituted compounds. Instead, substitution of λ^5-halogenobismuthanes **6a–d** with organolithium reagents was found to be a useful reaction for the preparation of pentavalent bismuth species. For example, compound **6a** with 1.1 equiv of (*p*-(trifluoromethyl)phenyl)lithium in THF at ambient temperature for 18 h afforded a 63% yield of **3d**. Similar reaction of **6b** with 1 equiv of (*p*-methylphenyl)lithium in THF for 50 min gave a mixture of **3d** (32%) and **3e** (16%). Reaction of **6a** with 1 equiv of (phenylethynyl)lithium afforded **3f** (10%). The structure of **3e** should be written so that R and Ar lie at equatorial positions and Ar is at an apical position.

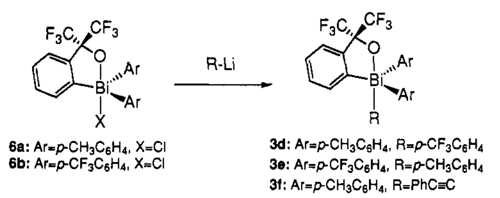
Scheme III



Scheme IV



Scheme V



Halogenolysis of Differently Substituted λ^5-Bismuthanes 3d–g. With λ^5-bismuthanes **3d–g** bearing different carbon substituents in hand, we investigated the selectivity of the Bi–C bonds in the halogenolysis. Chlorination of **3d–g** with sulfuryl chloride was carried out to prepare λ^5-bismuthanes with five different substituents. The results are shown in Scheme VI. From **3d** 81% of **6e** was isolated with elimination of *p*-chlorotoluene, in addition to 8% of **6a**. From **3e** 52% of **6b** was isolated in addition to 8% of **6e**. Thus, the elimination of *p*-chlorotoluene was preferred to the elimination of *p*-chloro(trifluoromethyl)benzene. Also, from **3f** only **6a** was obtained quantitatively. It is interesting to note that the reaction of **3g** gave **6a** as the main product (64%) and a small amount of the trivalent bismuth species (**12a**, which

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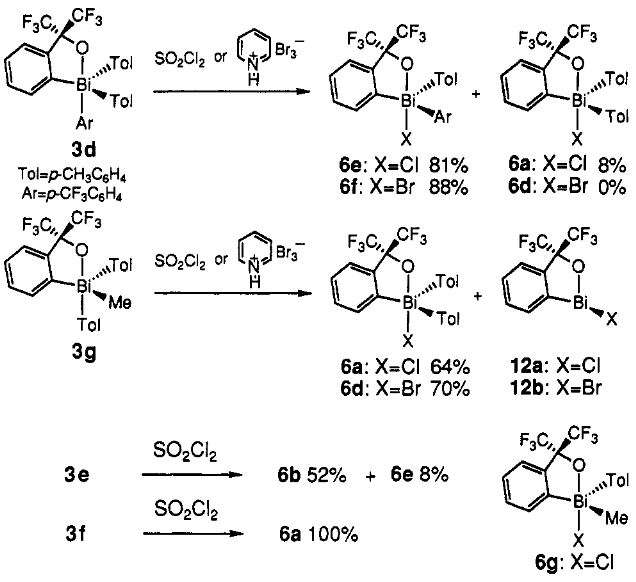
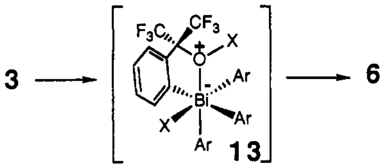
[7] Yamamoto, Y.; Fujikawa, H.; Fujishima, H.; Akiba, K. *J. Am. Chem. Soc.* **1989**, *111*, 2276. Akiba, K.; Fujikawa, H.; Sunaguchi, Y.; Yamamoto, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1245.

Scheme VI

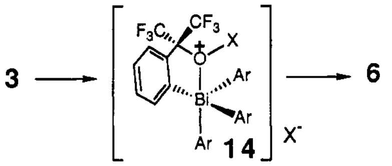


Scheme VII

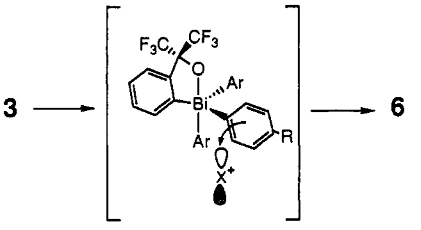
(i) initial complexation with the oxygen to form a 12-Bi-6 intermediate



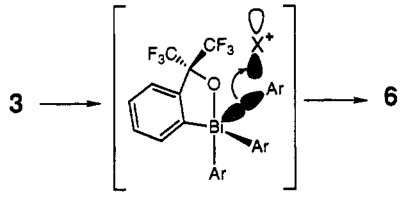
(ii) initial complexation with the oxygen to form a 10-Bi-5 intermediate



(iii) initial complexation with the π-electrons of substituted benzene

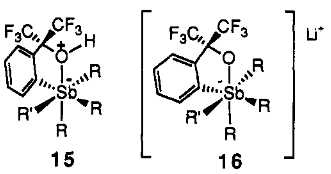


(iv) direct attack at the Bi-C bond



may be produced via **6g**. We could not isolate **6g**, but the results clearly showed that methyl chloride elimination to give **6a** was preferred to the elimination of *p*-chlorotoluene to give **6g**. Reactions of **3d** and **3g** with pyridinium bromide perbromide gave similar results with better selectivities. Thus, by the reaction of **3d** only **6f** could be isolated (88%) and **6d** was the only isolated product in the reaction of **3g** (70%). Thus, the preferred order of halogenolysis of the Bi–C(substituent) bond was concluded as follows: PhC≡C– > Me– > p-$CH_3C_6H_4$– > p-$CF_3C_6H_4$–.

The following mechanisms for the halogenolysis depicted in Scheme VII are possible: (i) initial complexation of the electrophiles with the oxygen atom to form the 12-Bi-6 betaine type intermediate **13** and consequent syn elimination to give **6** as in the reaction with acid chlorides (vide supra), (ii) initial complexation of the electrophiles with the oxygen atom to form the 10-Bi-5 oxonium type intermediate **14** and consequent syn elimination to give **6** followed by attack of X^-, (iii) initial complexation with the π electrons of substituted benzene, and (iv) direct attack at the Bi–carbon bonds without precomplexation of electrophiles. The 12-Bi-6 intermediate **13** was very similar to the proposed intermediate **15** for the protonolysis



15 **16**

of the corresponding 12-Sb-6 ate complexes **16**. The intermediacy of **15** was based on the detailed study of the protonolysis of **16** with a variety of substituents.[7] The Sb–C(tolyl) bond was much more reactive to protic acids than the Sb–C(methyl) bond, and the protonolysis of the corresponding 12-Bi-6 species **7a** provided a result similar to that for 12-Sb-6 as described in the previous section. Hence, the preferred Bi–C(methyl) bond cleavage in the halogenolysis cannot be expected from the 12-Bi-6 type intermediate mechanism i, and clearly it is not consistent with the initial π-complexation mechanism iii. Mechanism ii with 10-Bi-5 intermediate **14** seems not to be probable because the X-ray structural analyses of **3f** and **3g** showed the phenylethynyl group of **3f** was in an apical position and the methyl group of **3g** was in an equatorial position (vide infra). In spite of these site preferences, both groups were selectively halogenolyzed. If we can assume that the pseudorotation of the five-coordinated bismuth center of **14** is relatively free due to weakening of the Bi–O bond by halogenation, then the following possibility cannot be neglected.[8] In mechanism ii, the smallest group (ethynyl) is syn-halogenized first and, next, the most electron-rich one follows among equally sized groups. While we need more information to reach a conclusion on the mechanism, the direct electrophilic attack of halogen at the relatively more electron-rich bond without complexation, i.e., mechanism iv, is the preferred mechanism at present.

X-ray Crystal Structures of 2a, 3a,f,g, and 6a,b,d,e. Crystals of **2a**, **3a,f,g**, and **6a,b,d,e** suitable for X-ray analysis were obtained by recrystallization from acetonitrile for **3a,f,g** and from benzene–ethanol for **2a**, **6a,b,d,e**. The geometry about bismuth in these compounds was a distorted trigonal bipyramid (TBP) with the five-membered ring at the apical–equatorial sites of a TBP. The Bi–Cl or Bi–Br single bonds are slightly longer than the sum of the covalent radii between Bi and Cl atoms or Bi and Br atoms (2.51 Å for Bi–Cl or 2.66 Å for Bi–Br), suggesting that the Bi–X (X = halogen) bonds in these compounds are covalent. The calculated Bi–Cl bond length (2.51 Å) was also slightly shorter than the averaged Bi–Cl bond length (2.59 Å) of $(p\text{-}CH_3C_6H_4)_3BiCl_2$ (**2a**) and the reported averaged Bi–Cl bond length (2.57 Å) of Ph_3BiCl_2.[9] Such a slight lengthening of the apical Bi–Cl bond in these compounds and **6** may be due to three-center–four-electron bonding of the central bismuth atom. There were no short intermolecular contacts involving the bismuth and the halogen. Positions of substituents were

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(8) We thank a reviewer for the suggestion of this possibility.

(9) Brill, T. B.; Long, G. G. *Inorg. Chem.* **1970**, *9*, 1980.

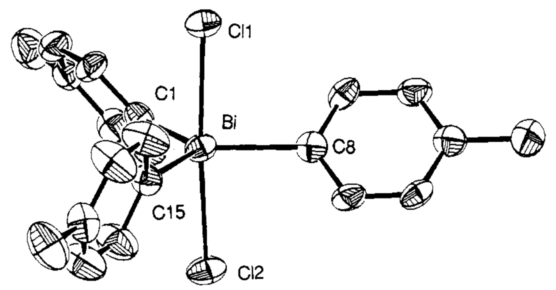

Figure 1. ORTEP diagram (30% probability ellipsoids) for **2a**.

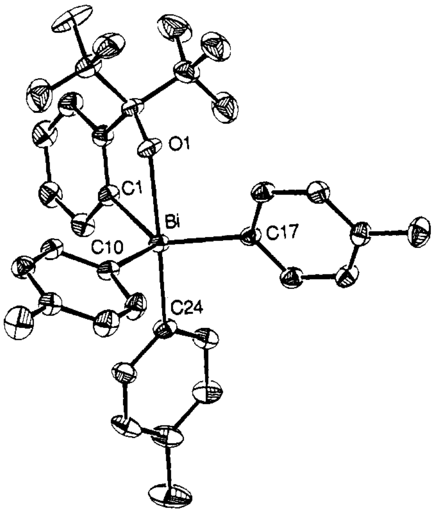

Figure 2. ORTEP diagram (30% probability ellipsoids) for **3a**.

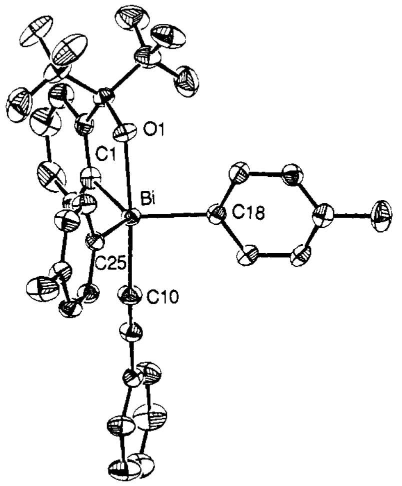

Figure 3. ORTEP diagram (30% probability ellipsoids) for **3f**.

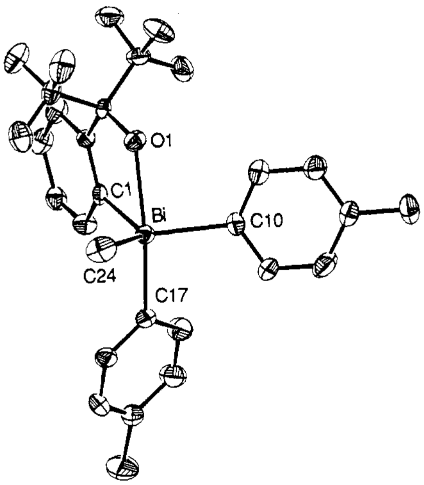

Figure 4. ORTEP diagram (30% probability ellipsoids) for **3g**.

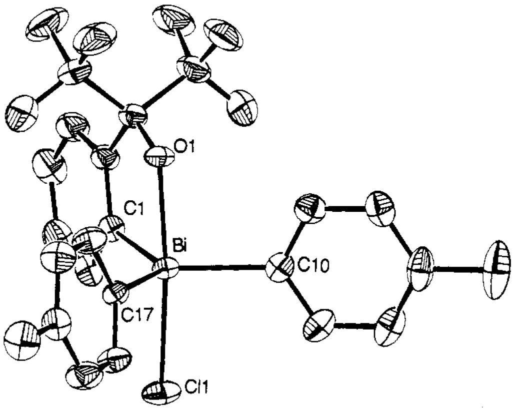

Figure 5. ORTEP diagram (30% probability ellipsoids) for **6a**.

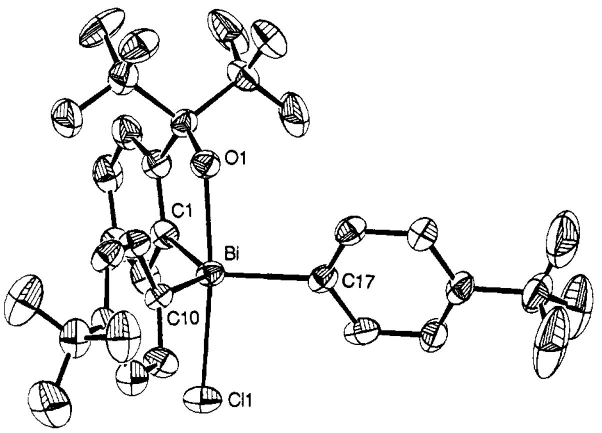

Figure 6. ORTEP diagram (30% probability ellipsoids) for **6b**.

consistent with electronegativities of substituents, that is, "apicophilicity".[10] Thus, halogens were in apical positions in λ^5-halogenobismuthanes, and the phenylethynyl group was also in an apical position and the methyl group was in an equatorial position. Figures 1–8 show the crystal structures of **2a**, **3a**,**f**,**g**, and **6a**,**b**,**d**,**e**, respectively. Selected bond lengths and bond angles for the structures of **2a**, **3a**,**f**,**g**, and **6a**,**b**,**d**,**e** are listed in Table I. It should be noted that the averaged apical Bi–O bond lengths of these compounds were affected only by the electronegativity of another apical group, in contrast to the insensitivity of the property of equatorial substituents. Although an increase in electron donation from the equatorial ligand to an apical three-center–four-electron bond was reported to lead to a longer apical bond length,[11] the apical Bi–O bond lengths of **6a**,**b**,**d**,**e** with an apical halogen and different equatorial substituted phenyl groups were very similar (2.179(6), 2.17(1), 2.184(8), 2.186(9) Å). In the ^{1}H NMR of **6a**,**e**,**b** the resonances at 8.73, 8.71, and 8.69 ppm, respectively, due to the proton ortho to the Bi atom in the

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(10) McDowell, R. S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5849. Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1686. Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54.

(11) Chopra, S. K.; Martin, J. C. *Heteroat. Chem.* **1991**, *2*, 1. Ross, M. R.; Martin, J. C. *Phosphorus Chemistry*; ACS Symposium Series 171; American Chemical Society: Washington, DC, 1980; p 429. Perrozzi, E. F.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1974**, *96*, 578, 6735.

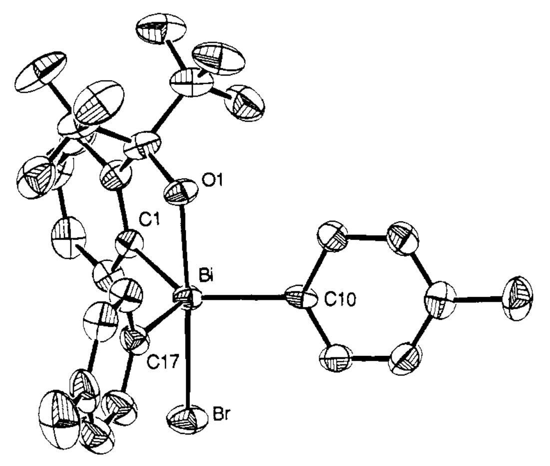


Figure 7. ORTEP diagram (30% probability ellipsoids) for **6d**.

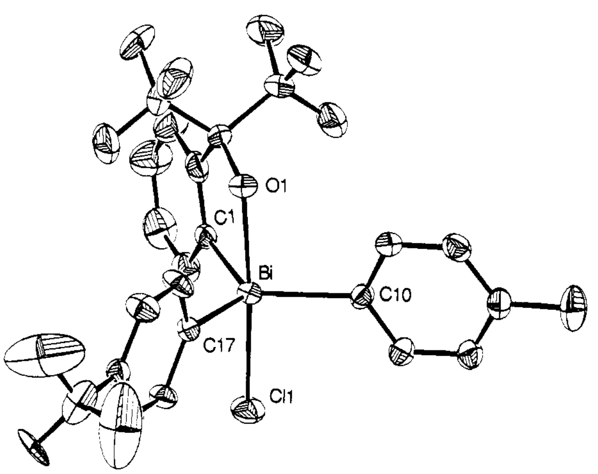
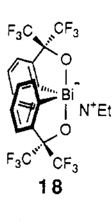
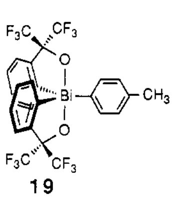


Figure 8. ORTEP diagram (30% probability ellipsoids) for **6e**.

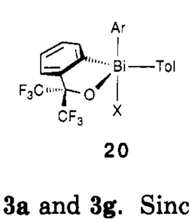
five-membered ring were considered to be affected by the polarization of the apical Bi–halogen bond.[12] Thus, the upfield shift of this proton with the increasing electron-withdrawing ability of the equatorial substituents indicates that the polarization of the apical Bi–Cl bond is decreased according to the decrease of electron density of the bismuth atom. Although the Bi–Cl bond lengths in the solid state seem to reflect this tendency, the difference of the lengths is too small to be discussed. In contrast, the apical Bi–O bond lengths of **6a,b,d,e** (2.17–2.185 Å) with an apical halogen are 0.06 Å shorter than that of **3f** with an apical phenylethynyl group (2.243(3) Å) and are 0.16 Å shorter than those of **3a** and **3g** with an apical tolyl group (2.323(4), 2.328(7) Å). Thus, the apical Bi–O bond length was found to increase as the electronegativity of the other apical group decreased. The averaged Bi–O bond length (2.29 Å) in the 10-Bi-4 anion **18**, which was recently reported by us,[13] was shorter than those of **3a** and **3g**. Since the Bi–O bond of **18** was lengthened by the anionic character of the compound **18** compared to the Bi–O bond length (2.17–2.18 Å) of **19**,[14] such short bond lengths of **18** and **19** were quite consistent with the above conclusion. The large difference in the lengths of the apical Bi–O bonds reflected the polarizable character of the apical three-center–four-electron hypervalent bond as shown in 10-S-4 sulfuranes and 10-P-5 phosphoranes.[15] The trend can be rationalized by considering the ionic "no-bond" resonance structures.[16] As the electronegativity of X increases compared to that of the other apical ligand, O, the contribution of resonance structure **17a** will increase relative to **17b** and the Bi–O bond length will decrease (Scheme VIII).



18



19



20

Pseudorotational Barrier of 6e,f. With λ^5-bismuthanes **6e,f** bearing five different substituents in hand, we could measure the pseudorotational barrier of λ^5-bismuthanes bearing a Martin ligand. As expected, the ^{19}F NMR of **6e,f** showed a pair of quartets (δ −75.10, −75.15 (J = 8 Hz) (split width ($\Delta\nu$) 20 Hz) in **6e** (*o*-dichlorobenzene); δ −76.40, −76.56 (J = 8 Hz) (split width ($\Delta\nu$) 61 Hz) in **6f** (toluene-d_8) for the CF_3 groups at room temperature, showing that these compounds possess stable configurations on this time scale. Coalescence of the two CF_3 groups could be observed at 150 °C (**6f**) and at 170 °C (**6e**), but coalescence was not observed up to 170 °C when the samples were diluted to $^1/_{10}$ concentration. Thus, the exchange observed is probably due to intermolecular halogen exchange. However, it can be concluded that the free energy of activation of the CF_3 exchange by an intramolecular inversion at the bismuth atom should be higher than 21 kcal mol^{-1}, which can be effected by a series of pseudorotations. The strain effected by the diequatorial placement of the five-membered ring **20**, which is required for the inversion, should be the reason for the high activation energy.

Experimental Section

Melting points were taken on a Yanagimoto micro melting point apparatus and were uncorrected. ^{1}H NMR (400-MHz) and ^{19}F NMR (376-MHz) spectra were recorded on a JEOL EX-400 spectrometer. ^{1}H NMR (90-MHz) and ^{19}F NMR (85-MHz) spectra were recorded on a Hitachi R-90H spectrometer. Chemical shifts are reported (δ scale) from internal tetramethylsilane for ^{1}H or from fluorotrichloromethane for ^{19}F. Flash column chromatography was carried out on Merck silica gel 9385. Thin-layer chromatography was performed with Merck silica gel GF-254 plates. All reactions were carried out under N_2 or Ar.

Solvents and Reagents. The preparation of lithium 1,1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propoxide (**1**) from *n*-BuLi, 10% *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), and the corresponding alcohol followed the published procedure.[6] Tris(*p*-methylphenyl)bismuth dichloride[16] and dibromide[15] were prepared by published procedures. Tris(*p*-fluorophenyl)bismuth dichloride (mp 134–136 °C) was prepared from the corresponding bismuthine[17] and sulfuryl chloride. Tris(*p*-(trifluoromethyl)-phenyl)bismuth dichloride (mp 140–143 °C) was prepared from bismuth trichloride and (*p*-(trifluoromethyl)phenyl)magnesium bromide, followed by reaction with excess sulfuryl chloride. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium-benzophenone.

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[12] Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4618. Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2711.

[13] Chen, X.; Yamamoto, Y.; Akiba, K.; Yoshida, S.; Yasui, M.; Iwasaki, F. *Tetrahedron Lett.* **1992**, *33*, 6653.

[14] Chen, X.; Kitano, M.; Ohdoi, K.; Yamamoto, Y.; Akiba, K., unpublished results.

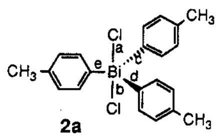
[15] Hayes, R. A.; Martin, J. C. In *Organic Sulphur Chemistry: Theoretical and Experimental Advances*; Csizmadia, E. G., Mangini, A., Bernardi, F., Eds.; Elsevier: Amsterdam, 1985; Chapter 8, pp 408–483.

[16] Livant, P.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 127.

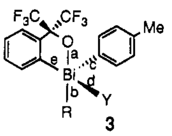
[17] Michaelis, A.; Marquardt, A. *Justus Liebigs Ann. Chem.* **1889**, *251*, 323.

[18] Gilman, H.; Yanblunky, H. L. *J. Am. Chem. Soc.* **1941**, *63*, 207.

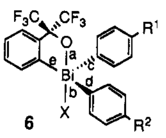
Table I. Selected Bond Lengths and Angles for 2a, 3a,f,g, and 6a,b,d,e



2a



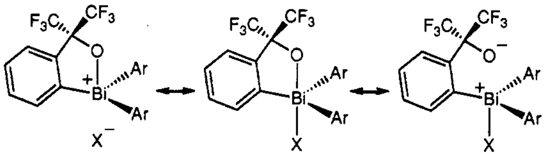
3



6

	2a	**3a**: R = p-$CH_3C_6H_4$; Y = p-$CH_3C_6H_4$	**3g**: R = p-$CH_3C_6H_4$; Y = CH_3	**3f**: R = $C{\equiv}CC_6H_4$; Y = p-$CH_3C_6H_4$	**6a**: X = Cl; R^1 = CH_3; R^2 = CH_3	**6d**: X = Br; R^1 = CH_3; R^2 = CH_3	**6b**: X = Cl; R^1 = CF_3; R^2 = CF_3	**6e**: X = Cl; R^1 = CH_3; R^2 = CF_3
				Bond Lengths (Å)				
a	2.590(4)	2.323(4)	2.328(7)	2.243(3)	2.179(6)	2.184(8)	2.17(1)	2.186(9)
b	2.595(4)	2.266(5)	2.25(1)	2.249(6)	2.562(3)	2.708(2)	2.558(4)	2.547(4)
c	2.23(2)	2.194(5)	2.21(1)	2.196(6)	2.201(8)	2.20(1)	2.22(1)	2.21(1)
d	2.22(1)	2.209(7)	2.21(1)	2.195(6)	2.191(8)	2.21(1)	2.19(1)	2.20(1)
e	2.19(1)	2.220(6)	2.19(1)	2.193(6)	2.196(8)	2.21(1)	2.20(1)	2.19(1)
				Bond Angles (deg)				
ab	176.0(1)	169.1(2)	168.2(3)	169.4(2)	170.0(2)	170.1(2)	170.7(2)	171.2(3)
cd	119.1(4)	103.8(2)	109.5(5)	108.2(2)	109.8(3)	109.0(4)	107.0(4)	110.7(5)
de	121.6(5)	115.5(2)	119.4(4)	126.8(2)	124.8(3)	122.6(4)	123.0(5)	124.4(5)
ec	119.2(4)	133.1(2)	124.0(4)	122.3(4)	124.2(3)	126.9(3)	129.1(5)	123.1(5)
ac	91.4(4)	87.4(2)	86.7(3)	89.8(2)	91.6(3)	90.0(3)	91.6(4)	90.5(4)
ad	90.0(4)	84.6(2)	84.2(4)	89.6(2)	91.5(2)	92.1(3)	92.9(4)	90.0(4)
ae	88.7(4)	73.1(2)	73.6(3)	75.9(2)	77.7(2)	77.5(3)	77.9(4)	77.5(4)
bc	92.1(4)	100.6(2)	99.4(4)	95.6(2)	94.4(2)	94.5(2)	92.7(3)	94.8(3)
bd	90.0(4)	100.4(2)	103.0(4)	108.2(2)	93.9(2)	94.8(3)	93.8(4)	94.6(4)
be	87.9(4)	96.6(2)	94.6(4)	93.6(2)	92.3(2)	92.8(3)	92.9(4)	93.7(4)

Scheme VIII



17a **17b**

Preparation of 3a–c. General Procedure. To a solution of 1 (30 mmol) in THF–n-hexane was added a solution of triarylbismuth dichloride (or dibromide) (2; 22 mmol) in 115 mL of THF at −78 °C with stirring under N_2. The mixture was stirred for 4.5–8 h at −78 °C and was quenched with aqueous NaCl. Extraction with ether (3 × 50 mL), drying ($MgSO_4$), and removal of the ether gave a mixture of **3–5**. Flash column chromatography (ethyl acetate–n-hexane) followed by recrystallization from ether–n-hexane gave colorless crystals of **3**.

3,3-Bis(trifluoromethyl)-1,1,1-tris(p-methylphenyl)-3H-2,1-benzoxabismole (3a): yield 55%; mp 206–209 °C; ^1H NMR ($CDCl_3$) 2.37 (s, 9 H), 7.28 (d, 6 H, J = 8 Hz), 7.64 (d, 6 H, J = 8 Hz), 7.37–7.55 (m, 3 H), 7.91–8.13 (m, 1 H); ^{19}F NMR ($CDCl_3$) −73.4 (s, 6 F). Anal. Calcd for $C_{30}H_{25}F_6OBi$: C, 49.73; H, 3.48. Found: C, 49.80; H, 3.46.

4a: yield 30%; mp >300 °C; ^1H NMR (acetone-d_6) 2.24 (s, 3 H), 7.29–8.14 (m, 8 H); ^{19}F NMR (acetone-d_6) −74.9 (q, 3 F, J = 8.6 Hz), −77.4 (q, 3 F, J = 8.6 Hz). Anal. Calcd for $C_{16}H_{11}F_6OBi$: C, 35.44; H, 2.04. Found: C, 35.39; H, 1.98.

3,3-Bis(trifluoromethyl)-1,1,1-tris(p-(trifluoromethyl)phenyl)-3H-2,1-benzoxabismole (3b): yield 53%; mp 199–201 °C; ^1H NMR ($CDCl_3$) 7.23–8.20 (m, 16 H); ^{19}F NMR ($CDCl_3$) −61.9 (s, 9 F), −73.4 (s, 6 F). Anal. Calcd for $C_{30}H_{16}F_{15}OBi$: C, 40.65; H, 1.82. Found: C, 40.88; H, 1.84.

4b: yield 41%; mp 223–225 °C (ether–n-hexane); ^1H NMR (acetone-d_6) 6.95–8.40 (m, 8 H); ^{19}F NMR (acetone-d_6) −63.6 (s, 3 F), −75.1 (q, 3 F, J = 8.6 Hz), −77.6 (q, 3 F, J = 8.6 Hz). Anal. Calcd for $C_{16}H_8F_9OBi$: C, 32.23; H, 1.35. Found: C, 32.25; H, 1.29.

5b: yield 5%; mp 147–149 °C (ether–n-hexane); ^1H NMR ($CDCl_3$) 7.65 (d, 6 H, J = 8.1 Hz), 7.83 (d, 6 H, J = 8.1 Hz). Anal. Calcd for $C_{21}H_{12}F_9Bi$: C, 39.15; H, 1.89. Found: C, 39.37; H, 1.88.

3,3-Bis(trifluoromethyl)-1,1,1-tris(p-fluorophenyl)-3H-2,1-benzoxabismole (3c): yield 61%; mp 161–163 °C; ^1H NMR ($CDCl_3$) 7.0–8.3 (m, 16 H); ^{19}F NMR ($CDCl_3$) −74.1 (s, 6 F), −108.5 (br s, 3 F). Anal. Calcd for $C_{27}H_{16}F_9OBi$: C, 44.04; H, 2.19. Found: C, 44.13; H, 2.13.

4c: yield 23%; mp 224–227 °C (ether–n-hexane); ^1H NMR (acetone-d_6) 7.0–8.2 (m, 8 H); ^{19}F NMR (acetone-d_6) −75.2 (q, 3 F, J = 8.6 Hz), −77.7 (q, 3 F, J = 8.6 Hz), −113.7 (br s, 1 F). Anal. Calcd for $C_{15}H_8F_7OBi$: C, 32.99; H, 1.48. Found: C, 33.17; H, 1.49.

Reaction of 3a with Ethyl Succinyl Chloride. To a solution of **3a** (0.314 g, 0.43 mmol) in 2 mL of benzene was added ethyl succinyl chloride (0.080 mL, 0.56 mmol) at room temperature. The reaction mixture was stirred for 8.5 h at 50 °C. The products were separated by TLC (ethyl acetate–n-hexane, 1:5). Compounds **9a** (0.148 g, 84%), **6a** (0.022 g, 8%), and **5a** (0.128 g, 61%) were obtained.

3,3-Bis(trifluoromethyl)-1-chloro-1,1-bis(p-methylphenyl)-3H-2,1-benzoxabismole (6a): mp 186–189 °C (benzene–ethanol); ^1H NMR ($CDCl_3$) 2.38 (s, 6 H), 7.43 (d, 4 H, J = 8 Hz), 7.60–8.05 (m, 3 H), 8.17 (d, 4 H, J = 8 Hz), 8.73 (d, 1 H, J = 7 Hz); ^{19}F NMR ($CDCl_3$) −74.1 (s, 6 F). Anal. Calcd for $C_{23}H_{18}F_6OClBi$: C, 41.30; H, 2.71. Found: C, 41.07; H, 2.70.

9a: ^1H NMR ($CDCl_3$) 1.24 (t, 3 H, J = 7.0 Hz), 2.50–3.10 (m, 4 H), 4.15 (q, 2 H, J = 7.0 Hz), 7.2–7.7 (m, 4 H).

Reaction of 3a with p-Methoxybenzoyl Chloride. To a solution of **3a** (0.317 g, 0.44 mmol) in 2 mL of benzene was added p-methoxybenzoyl chloride (0.075 mL, 0.54 mmol) at room temperature. The reaction mixture was stirred for 10 h under reflux. The products were separated by TLC (ethyl acetate–n-hexane, 1:5). Compounds **9b** (0.074 g, 41%), recovered **3a** (0.065 g, 21%), and **5a** (0.079 g, 38%) were obtained.

9b: ^1H NMR (acetone-d_6) 3.92 (s, 3 H), 7.13 (d, 2 H, J = 9.0 Hz), 7.72–7.77 (m, 4 H), 8.07 (d, 2 H, J = 9.0 Hz).

Reaction of 3 with Sulfuryl Chloride. General Procedure. To a solution of **3** (2 mmol) in 10 mL of CH_2Cl_2 was added 0.2 mL of sulfuryl chloride (2.5 mmol) at −78 °C with stirring. The solution was warmed to room temperature and stirred for 14 h at this temperature. The mixture was evaporated in vacuo, and the residue was recrystallized to give colorless crystals of **6**. **6a**: yield 95% from **3a**.

3,3-Bis(trifluoromethyl)-1-chloro-1,1-bis(p-(trifluoromethyl)phenyl)-3H-2,1-benzoxabismole (6b): yield 97% (from **3b**); mp 145–146 °C (ether–n-hexane); ^1H NMR ($CDCl_3$) 7.60–8.10 (m, 3 H), 7.90 (d, 4 H, J = 8.4 Hz), 8.51 (d, 4 H, J = 8.4 Hz), 8.69 (dd, 1 H, J = 7.6 Hz, 1.2 Hz); ^{19}F NMR ($CDCl_3$) −61.8 (s, 6 F), −73.3 (s, 6 F). Anal. Calcd for $C_{23}H_{12}F_{12}OClBi$: C, 35.56; H, 1.56. Found: C, 35.79; H, 1.57.

Table II. Crystal Data for 2a, 3a,f,g, and 6a,b,d,e

	2a	**3a**	**3f**	**3g**
formula	$C_{21}H_{21}Cl_2Bi$	$C_{30}H_{25}F_6OBi$	$C_{31}H_{23}F_6OBi$	$C_{24}H_{21}F_6OBi$
mol wt	553.28	724.50	734.50	648.40
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
cryst dimens, mm	0.40 × 0.35 × 0.25	0.80 × 0.45 × 0.20	0.30 × 0.15 × 0.15	0.80 × 0.70 × 0.60
a, Å	15.406(3)	10.546(1)	13.826(4)	29.026(5)
b, Å	19.741(3)	11.411(2)	19.802(6)	8.362(2)
c, Å	15.384(3)	12.764(2)	10.425(3)	9.568(2)
α, deg	90	91.08(1)	90	90
β, deg	117.37(1)	111.89(1)	103.97(2)	93.62(1)
γ, deg	90	98.90(1)	90	90
V, Å^3	4155(1)	1403.2(4)	2770(1)	2317.6(7)
Z	8	2	4	4
D_{calc}, g cm^{-3}	1.77	1.96	1.76	1.86
abs coeff, cm^{-1}	83.31	61.18	61.64	73.59
$F(000)$	2040	700	1416	1240
radiation; λ, Å	Mo Kα; 0.710 73	Mo Kα; 0.710 73	Mo Kα; 0.710 73	Mo Kα; 0.710 73
temp, °C	23 ± 1	23 ± 1	23 ± 1	23 ± 1
2θ(max), deg	50	55	55	55
scan rate, deg/min	6.0	16.0	12.0	12.0
linear decay, %	30		8	8
data collected	$+h,-k,\pm l$	$+h,\pm k,+l$	$\pm h,-k,\pm l$	$\pm h,-k,\pm l$
total data collcd; unique, obsd	4900; 3667, 2436 ($I > 3\sigma(I)$)	7052; 6449, 5831 ($I > 3\sigma(I)$)	5416; 4880, 3721 ($I > 3\sigma(I)$)	6090; 5327, 3510 ($I > 3\sigma(I)$)
R(int)	0.18	0.02	0.03	0.07
no. of params refined	223	349	358	295
R, R_w, S	0.057, 0.065, 1.15	0.039, 0.036, 2.14	0.039, 0.036, 1.17	0.049, 0.074, 0.70
max shift in final cycle	0.06	0.17	0.14	0.13
final diff map max, e Å^{-3}	1.20	2.53	0.79	2.36
	6a	**6b**	**6d**	**6e**
formula	$C_{23}H_{18}F_6ClOBi$	$C_{23}H_{12}F_{12}ClOBi$	$C_{23}H_{18}F_6BrOBi$	$C_{23}H_{15}F_9ClOBi$
mol wt	668.80	776.80	713.27	722.80
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2/a$
cryst dimens, mm	0.90 × 0.90 × 0.80	0.80 × 0.60 × 0.40	0.66 × 0.55 × 0.42	1.00 × 0.70 × 0.35
a, Å	9.292(3)	25.375(7)	9.557(2)	22.704(6)
b, Å	10.573(3)	12.092(3)	10.426(2)	9.210(2)
c, Å	11.996(3)	16.834(4)	12.054(3)	11.562(4)
α, deg	99.26(2)	90	100.17(2)	90
β, deg	92.73(2)	110.15(2)	92.51(2)	98.14(2)
γ, deg	92.32(3)	90	97.33(2)	90
V, Å^3	1151.0(7)	4849(2)	1169.9(4)	2393(1)
Z	2	8	2	4
D_{calc}, g cm^{-3}	1.93	2.13	2.02	2.01
abs coeff, cm^{-1}	75.19	71.79	89.67	72.52
$F(000)$	636	2928	672	1368
radiation; λ, Å	Mo Kα; 0.710 73	Mo Kα; 0.710 73	Mo Kα; 0.710 73	Mo Kα; 0.710 73
temp, °C	23 ± 1	23 ± 1	23 ± 1	23 ± 1
2θ(max), deg	55	55	55	55
scan rate, deg/min	16.0	12.0	12.0	12.0
linear decay, %		5	20	3
data collected	$+h,\pm k,\pm l$	$\pm h,+k,+l$	$\pm h,\pm k,\pm l$	$h,+k,\pm l$
total data collcd; unique, obsd	5692; 5278, 4598 ($I > 3\sigma(I)$)	6133; 5579, 3870 ($I > 3\sigma(I)$)	5822; 5383, 4490 ($I > 3\sigma(I)$)	6050; 5480, 4045 ($I > 3\sigma(I)$)
R(int)	0.04	0.11	0.05	0.05
no of params refined	295	376	295	322
R, R_w, S	0.049, 0.057, 1.17	0.059, 0.103, 0.83	0.064, 0.082, 1.35	0.076, 0.091, 1.51
max shift in final cycle	0.05	1.42	0.11	0.07
final diff map max, e Å^{-3}	3.36	1.76	5.86	5.06

3,3-Bis(trifluoromethyl)-1-chloro-1,1-bis(*p*-fluorophenyl)-3*H*-2,1-benzoxabismole (6c): yield 88% (from **2c**); mp 125–127 °C (ethanol); ^{1}H NMR ($CDCl_3$) 7.10–8.70 (m, 12 H); ^{19}F NMR ($CDCl_3$) −106.5 (br s, 2 F), −74.6 (s, 6 F). Anal. Calcd for $C_{21}H_{12}F_8OClBi$: C, 37.27; H, 1.79. Found: C, 37.28; H, 1.66.

3,3-Bis(trifluoromethyl)-1-bromo-1,1-bis(*p*-methylphenyl)-3*H*-2,1-benzoxabismole (6d). To a solution of **3a** (3.44 g, 4.75 mmol) in 10 mL of CH_2Cl_2 was added a solution of pyridinium bromide perbromide (2.00 g, 6.25 mmol) in 10 mL of CH_2Cl_2 at 0 °C with stirring. The solution was warmed to room temperature and stirred for 2 h at this temperature. The mixture was quenched with saturated NaCl solution, and the products were extracted with ether. After drying over $MgSO_4$, the solvent was removed in vacuo. The residue was recrystallized from ether to give colorless crystals of **6d**. **6d**: yield 2.78 g (82%); mp 182–185 °C; ^{1}H NMR ($CDCl_3$) 2.38 (s, 6 H), 7.40 (d, 4 H, J = 8 Hz), 7.5–8.0 (m, 3 H), 8.20 (d, 4 H, J = 8 Hz), 8.77 (d, 1 H, J = 8 Hz); ^{19}F NMR ($CDCl_3$) −75.2 (s, 6 F). Anal. Calcd for $C_{23}H_{18}F_6OBrBi$: C, 38.73; H, 2.54. Found: C, 38.83; H, 2.49.

Reaction of 3a with MeLi. To a solution of **3a** (1.012 g, 1.40 mmol) in 10 mL of THF was added 1 mL of methyllithium (1.43 M ether solution) at −78 °C with stirring under N_2. The reaction mixture was quenched with water, after being stirred for 1.5 h at −78 °C, to give **3a** (0.058 g, 6%) and **3g** (0.783 g, 86%), which were separated by flash column chromatography (ethyl acetate–*n*-hexane, 1:4).

3,3-Bis(trifluoromethyl)-1-methyl-1,1-bis(*p*-methylphenyl)-3*H*-2,1-benzoxabismole (3g): mp 161–164 °C (ether–*n*-hexane); ^{1}H NMR ($CDCl_3$) 2.39 (s, 6 H), 2.63 (s, 3 H), 7.30 (d, 4 H, J = 8 Hz), 7.30–7.60 (m, 3 H), 7.58 (d, 4 H, J = 8 Hz), 7.70–8.20 (m, 1 H); ^{19}F NMR ($CDCl_3$) −73.4 (s, 6 F). Anal. Calcd for $C_{24}H_{21}F_6OBi$: C, 44.46; H, 3.26. Found: C, 44.28; H, 3.14.

3,3-Bis(trifluoromethyl)-1-(*p*-(trifluoromethyl)phenyl)-1,1-bis(*p*-methylphenyl)-3*H*-2,1-benzoxabismole (3d). (*p*-(Trifluoromethyl)phenyl)lithium, prepared from reaction of *p*-bromobenzotrifluoride (0.43 mL, 3.07 mmol) with *n*-BuLi (2.05 mL, 3.18 mmol) in THF (8 mL) at −78 °C, was added to a solution of **6a** (1.85 g, 2.77 mmol) in 12 mL of THF at −78 °C. The solution was warmed to room temperature and stirred for 17.5 h at this temperature. The mixture was quenched with saturated NaCl solution, and the products were extracted with ether. After drying over $MgSO_4$, the solvent was removed in vacuo. The residue was recrystallized from ether-*n*-hexane to give colorless crystals of **3d**. **3d**: yield 1.37 g (63%); mp 182–185 °C; ^1H NMR ($CDCl_3$) 2.39 (s, 6 H), 7.10–8.20 (m, 16 H); ^{19}F NMR ($CDCl_3$) −62.1 (s, 3 F), −73.3 (s, 6 F). Anal. Calcd for $C_{30}H_{22}F_9OBi$: C, 46.29; H, 2.85. Found: C, 46.39; H, 2.75.

3,3-Bis(trifluoromethyl)-1,1-bis(*p*-(trifluoromethyl)phenyl)-1-(*p*-methylphenyl)-3*H*-2,1-benzoxabismole (3e). To a solution of **6b** (1.19 g, 1.54 mmol) in 3 mL of ether was added 1.21 mL of (*p*-methylphenyl)lithium (1.54 mmol, 1.27 M ether solution) at −78 °C with stirring. The solution was stirred for 50 min at this temperature, and the mixture was quenched with saturated NH_4Cl solution. The products were extracted with ether. After drying over $MgSO_4$, the solvent was removed in vacuo. The residue was chromatographed (ethyl acetate–*n*-hexane, 1:20) to give colorless crystals of **3e**. **3e**: yield 0.19 g (16%); mp 164–166 °C (ether–*n*-hexane); ^1H NMR ($CDCl_3$) 2.40 (s, 3 H), 7.10–8.20 (m, 16 H); ^{19}F NMR ($CDCl_3$) −61.7 (s, 6 F), −72.8 (s, 6 F). Anal. Calcd for $C_{30}H_{19}F_{12}OBi$: C, 43.28; H, 2.30. Found: C, 43.48; H, 2.26.

Compound **3d** was also obtained in 32% yield (0.41 g, 0.49 mmol).

3,3-Bis(trifluoromethyl)-1-(phenylethynyl)-1,1-bis(*p*-methylphenyl)-3*H*-2,1-benzoxabismole (3f). To a solution of **6a** (1.18 g, 1.76 mmol) in 4.5 mL of THF was added 1.1 equiv of (phenylethynyl)lithium, prepared from phenylacetylene (0.25 mL, 2.28 mmol) and *n*-BuLi (1.25 mL, 1.94 mmol, 1.55 M *n*-hexane solution), at −78 °C with stirring. The solution was stirred for 15 min at this temperature. The mixture was quenched with saturated NaCl solution, and the products were extracted with ether. After drying over $MgSO_4$, the solvent was removed in vacuo. The residue was chromatographed (ethyl acetate–*n*-hexane, 1:10) to give colorless crystals of **3f**. **3f**: yield 0.13 g (10%); mp 178–181 °C (ether–*n*-hexane); ^1H NMR ($CDCl_3$) 2.35 (s, 6 H), 7.2–7.5 (m, 3 H), 7.35 (d, 4 H, J = 8.1 Hz), 7.5–8.1 (m, 5 H), 8.37 (d, 4 H, J = 8.1 Hz), 8.6–8.8 (m, 1 H); ^{19}F NMR ($CDCl_3$) −72.5 (s, 6 F). Anal. Calcd for $C_{31}H_{23}F_6OBi$: C, 50.69; H, 3.16. Found: C, 50.93; H, 3.13.

3,3-Bis(trifluoromethyl)-1-chloro-1-(*p*-(trifluoromethyl)phenyl)-1-(*p*-methylphenyl)-3*H*-2,1-benzoxabismole (6e). To a solution of **3d** (0.061 g, 0.08 mmol) in 0.5 mL of $CDCl_3$ was added 0.05 mL of sulfuryl chloride (0.6 mmol) at room temperature. The solution was kept for 50 min at this temperature. The solvent was removed in vacuo, and the residue was subjected to TLC (ethyl acetate–*n*-hexane, 1:5) to give **6e**. **6e**: yield 0.041 g (81%); mp 141–142 °C (benzene–ethanol); ^1H NMR ($CDCl_3$) 2.38 (s, 3 H), 7.46 (d, 2 H, J = 8.4 Hz), 7.50–8.00 (m, 5 H), 8.19 (d, 2 H, J = 8.4 Hz), 8.50 (d, 2 H, J = 8.6 Hz), 8.71 (dd, 1 H, J = 7.6, 1.4 Hz); ^{19}F NMR ($CDCl_3$) −62.9 (s, 3 F), −74.4 (s, 6 F); ^{19}F NMR (376 MHz, *o*-dichlorobenzene) −63.60 (s, 3 F), −75.10 (q, 3 F, J = 8 Hz), −75.15 (q, 3 F, J = 8 Hz). Anal. Calcd for $C_{23}H_{15}F_9ClOBi$: C, 38.22; H, 2.09. Found: C, 38.51; H, 2.12.

Compound **6a** was also obtained in 8% yield (0.004 10 g, 0.085 mmol).

3,3-Bis(trifluoromethyl)-1-bromo-1-(*p*-(trifluoromethyl)phenyl)-1-(*p*-methylphenyl)-3*H*-2,1-benzoxabismole (6f). To a solution of **3d** (0.076 g, 0.09 mmol) in 0.7 mL of $CDCl_3$ was added pyridinium bromide perbromide (0.07 g, 0.2 mmol) at room temperature. The solution was kept for 1.5 h at this temperature. The mixture was quenched with saturated NaCl solution, and the products were extracted with ether. After drying over $MgSO_4$, the solvent was removed in vacuo. The residue was subjected to TLC (ethyl acetate–*n*-hexane, 1:5) to give **6f**. **6f**: yield 0.066 g (88%); mp 134–136 °C (ether–*n*-hexane); ^1H NMR ($CDCl_3$) 2.38 (s, 3H), 7.44 (d, 2 H, J = 7.8 Hz), 7.50–8.00 (m, 5 H), 8.23 (d, 2 H, J = 7.8 Hz), 8.53 (d, 2 H, J = 8.1 Hz), 8.75 (dd, 1 H, J = 7.7, 1.3 Hz); ^{19}F NMR ($CDCl_3$) −61.5 (s, 3 F), −73.1 (s, 6 F); ^{19}F NMR (376 MHz, toluene-d_8) −65.04 (s, 3 F), −76.40 (q, 3 F, J = 8 Hz), −76.56 (q, 3 F, J = 8 Hz). Anal. Calcd for $C_{23}H_{18}F_9OBrBi$: C, 36.01; H, 1.97. Found: C, 36.29; H, 1.96.

Reaction of 3f with Sulfuryl Chloride. To a solution of **3f** (0.052 g, 0.071 mmol) in 0.65 mL of $CDCl_3$ was added 0.03 mL of sulfuryl chloride (0.37 mmol) at room temperature. The solution was kept for 6.5 h at this temperature. The mixture was quenched with saturated NaCl solution, and the products were extracted with ether. After drying over $MgSO_4$, the solvent was removed to give only **6a**.

Dynamic NMR Measurement of 6e,f. ^{19}F NMR (376-MHz) spectra of **6e,f** were measured on a JEOL EX-400 spectrometer, and temperatures were calibrated using the chemical shift difference of ethylene glycol.

X-ray Structure Determination of 2a, 3a,f,g, and 6a,b,d,e. Crystal data and numerical details of the structure determinations are given in Table II. Crystals suitable for X-ray structure determination were mounted on a Mac Science MXC3 diffractometer and irradiated with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) for data collection. Lattice parameters were determined by least-squares fitting of 24–33 reflections with $29° < 2\theta < 35°$, $31° < 2\theta < 35°$, $31° < 2\theta < 35°$, $31° < 2\theta < 35°$, $31° < 2\theta < 35°$, $31° < 2\theta < 35°$, $32° < 2\theta < 35°$, and $31° < 2\theta < 41°$ for **2a**, **3a,f,g**, and **6a,b,d,e**, respectively. Data were collected with the ω-scan mode. All data were corrected for absorption[19] and extinction;[20] in addition data for **2a**, **3f,g**, and **6b,d,e** were corrected for the observed linear decay of the reference reflections. The structures were solved by a direct method with the program Monte Carlo-Multan.[21] Refinement on F was carried out by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms in **3a** and **6b** could be found on a difference Fourier map; these coordinates were included in the refinement with isotropic thermal parameters. The hydrogen atoms in **2a**, **3f,g**, and **6a,d,e** were included in the refinement on calculated positions (C–H = 1.0 Å) riding on their carrier atoms with isotropic thermal parameters. All the computations were carried out on a Titan-750 computer.

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Supplementary Material Available: Tables of positional and thermal parameters and complete interatomic distances and angles and additional ORTEP drawings for **2a**, **3a,f,g**, and **6a,b,d,e** (103 pages). Ordering information is given on any current masthead page.

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(19) Furusaki, A. *Acta Crystallogr.* **1979**, *A35*, 220.

(20) Katayama, C. *Acta Crystallogr.* **1986**, *A42*, 19.

(21) Coppens, P.; Hamilton, W. C. *Acta Crystallogr.* **1970**, *A26*, 71.