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Hypervalent Tetracoordinate Organobismuth Compounds (10-Bi-4)

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ABSTRACT

A stable hypervalent 10-Bi-4 species, tetraethylammonium bis[α,α-bis(trifluoromethyl)benzenemethanolato(2-)-C^2*],Obismuthanate(1-), was prepared by the reaction of bismuth trichloride with 2 equiv of lithium 2-(2-lithiophenyl)-2-propoxide derivatives. The ate complex was inert toward MeI, instead, the corresponding nonfluorinated analogue, bis[α,α-bis(dimethyl)benzenemethanolato(2-)-*C^2*, O]bismuthanate(1-), was reactive enough toward MeI to give O-methylated product. Regioselective methylation at the nonfluorinated methanolate was observed in the reaction of unsymmetrically substituted ate complex, [α,α-bis(dimethyl)benzenemethanolato(2-)-*C^2*,O[ ]α,α-bis(trifluoromethyl) benzenemethanolato (2-)-*C^2*, O]bismuthanate(1-). Mechanism of isomerization of these ate complexes and related protonated compounds and the synthesis and stability of [α,α-bis(trifluoromethyl)-benzenemethanolato (2-) -*C^2*, O]diarylbismuthanate-(1-) were also described.*

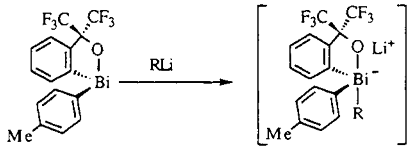
INTRODUCTION

Organobismuth(III) compounds containing electronegative atoms, such as halogen and oxygen, show Lewis acidic character [1]. Thus, from the corresponding tricoordinate bismuth halides or pseudohalides, tetracoordinate organobismuth compounds (10-Bi-4) have been prepared and several of the compounds have been characterized by X-ray crystallography [2–7]. However, reactions of these compounds have not been reported. Recently, we reported the formation and some reactions of stable bicyclic 10-Bi-4 ate complexes (**1**) which incorporated two molecules of five-membered ring ligands [8,9], the so-called Martin ligand [*o*-(1,1,1,3,3,3,-hexafluoropropyl-2-oxy)phenyl] [10]. Here, we report upon the stability of monocyclic ate complexes **3** bearing one Martin ligand and the reactions and isomerization at the central bismuth atom of **1** and related compounds.

RESULTS AND DISCUSSION

Synthesis and Stability of 10-Bi-4 Organobismuth Complexes (3) Bearing One Martin Ligand

Reactions of **4** [11] with lithium reagents were monitored by ^{19}F NMR spectroscopy at −50°C. Immediately after *p*-$CH_3C_6H_4Li$ was added to a solution of **4** in THF at −50°C, a pair of quartets (δ −75.7, −78.3, J = 8.7 Hz) for the nonequivalent CF_3 groups of **4** disappeared and only a singlet (δ −79.0) could be observed, indicating that a reaction had taken place very rapidly to form the ate complex **3a** (Equation 1). Complex **3** is thermally stable between 30 and −78°C.



(1)

4

3a: R=*p*-$CH_3C_6H_4$
3b: R=*n*-Bu

When *n*-BuLi (ca. 1 equiv) was added to a solution of **4** in THF, a pair of quartets (δ, −75.9, −76.6) was observed in place of the signals for **4**.

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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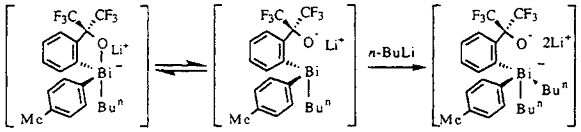
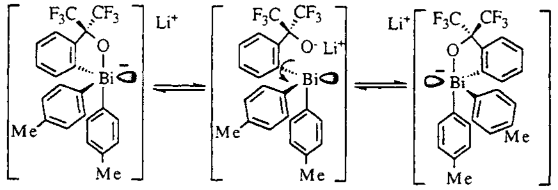
However, these peaks changed gradually to a broad singlet (δ, −76.0) as the temperature was raised to 25°C. Therefore, the ate complex **3b** was formed initially, but it decomposed thermally, giving hexafluorocumyl alcoholate as one of the products. When an excess amount of *n*-BuLi (ca. 3 equiv) was added, a very complicated spectrum was observed even at −50°C. The result indicates that the initially formed **3b** was in equilibrium with a ring-opened structure **5b**, and **5b** reacted with excess *n*-BuLi to form **6b** followed by its decomposition (Equation 2).



3 b 5 b 6 b (2)

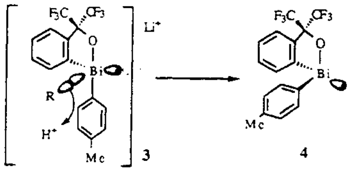
The ^{19}F NMR spectrum of **3a** should show a pair of quartets if it is configurationally stable. The fact that **3a** showed only a singlet can be explained by the occurrence of a fast exchange between **3a**, **3a′**, and **3a″** (Equation 3).



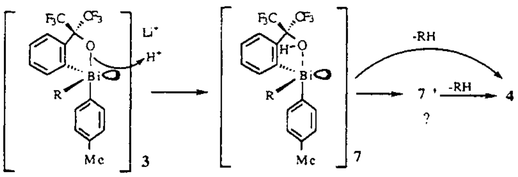
3 a 3 a ′ 3 a ″ (3)

These ate complexes **3** were quite unstable to atmospheric moisture and decomposed immediately in the presence of water to give **4** plus R-H. There are four possible mechanisms of the protonolysis: (i) direct attack at the Bi–R bond by a proton, with cleavage of the Bi–C bond, (ii) formation of ring-opened alcohol **7** by bismuth–oxygen bond cleavage followed by elimination of RH, (iii) direct attack on the bismuth atom by a proton, followed by ligand coupling from Bi, (iv) formation of *p*-tolyllithium by Bi–C bond dissociation, followed by reaction of the *p*-tolyllithium with a proton (Scheme 1). Pathway (iv) should not be operative because the ate complex **3a** did not react with electrophiles such as MeI, PhCOCl, and $C_6H_4CH_2Br$ (vide infra). Although we could not observe **7** even after treating a solution of **3** with water at −50°C, we prefer mechanism (ii) at present because of the following: (a) in the reaction of **8**, which has a methyl group in place of one of the CF_3 groups, with water, unstable **9** could be observed as the initial product giving **10** upon standing [12] (Equation 4); (b) in the reaction of hexacoordinate bismuth anions bearing two Martin ligands, protonation took place at the oxygen atom to give an isolable pentacoordinate alcohol, followed by fast cyclization with elimination of hydrocarbon [13,14]; (c) the central bismuth atom in **3** was not nucleophilic enough to react with methyl iodide (vide infra), while the corresponding antimony ate complexes did react with methyl iodide at the central antimony atom to give a pentacoordinate λ^5-stibane [15,16]; and (d) 1,1,1-tris(*p*-methylphenyl)-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxabismole reacted with acyl chlorides at the oxygen [17,18].

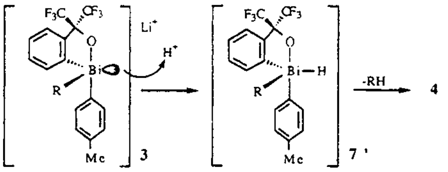
(i) direct attack of the bismuth–carbon bond toward a proton



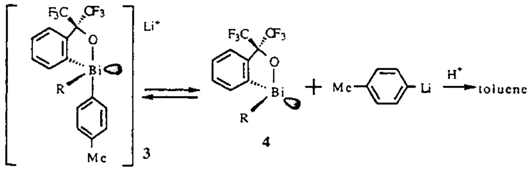
(ii) attack of the oxygen atom toward a proton followed by bismuth–oxygen bond cleavage



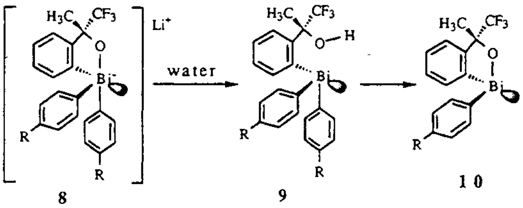
(iii) direct attack on the bismuth atom by a proton



(iv) Bi–C dissociation followed by protonolysis

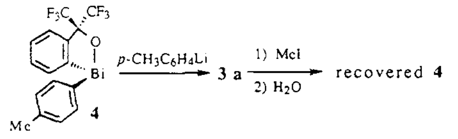


SCHEME 1

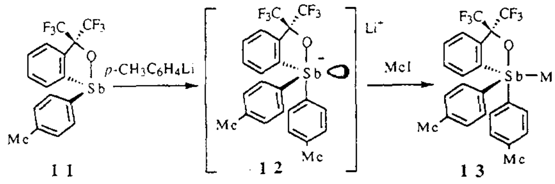


(4)

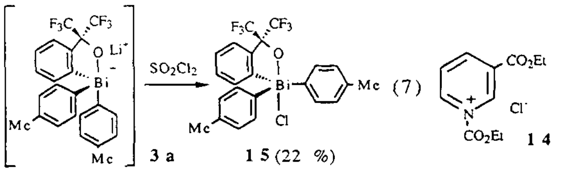
Attempted reactions of **3** with electrophiles revealed the poor nucleophilicity of the bismuth atom in this molecule. For example, reaction of **3a** with MeI at room temperature for 12 hours only gave **4** in 96% yield after treatment with water without *p*-xylene being obtained, which might have been expected to be formed as a coupling product from a pentacoordinate λ^5-bismuthane if the latter had been produced (Equation 5). The result is sharply in contrast with the behavior of the corresponding antimony compound. Reaction of the corresponding antimony compound **11** with MeI at room temperature for 20 hours gave the pentacoordinate product **13** in 43% yield [15,16], showing that the ate complex **12** was nucleophilic enough to react with MeI (Equation 6). Attempted reaction of **3a** with other electrophiles such as PhCOCl, $C_6H_4CH_2Br$, p-$CH_3C_6H_4Br$, and a pyridinium salt **14** proved to be in vain. However, reaction of **3a** with SO_2Cl_2 gave the pentacoordinate bismuth compound **15** [15,16], although in low yield (22%) (Equation 7).



(5)



(6)

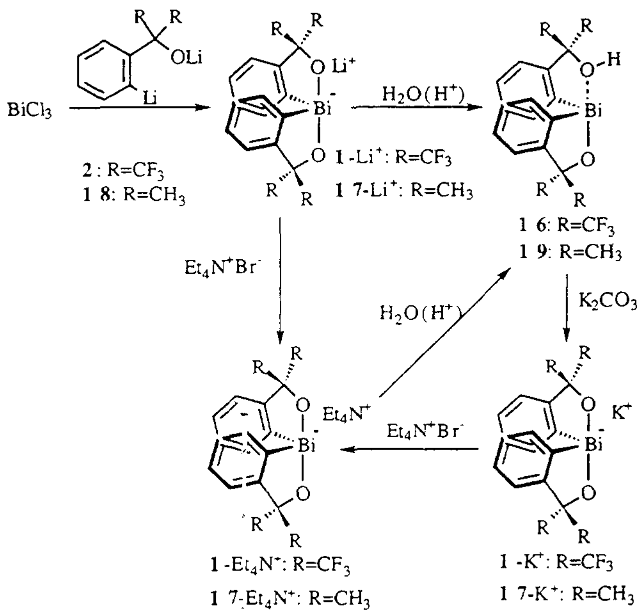


(7)

Therefore, it can be concluded that the presence of one Martin ligand was enough to give a thermodynamically stable 10-Bi-4 ate complex (**3**) but the stability of **3** toward moisture was not sufficient to permit its isolation.

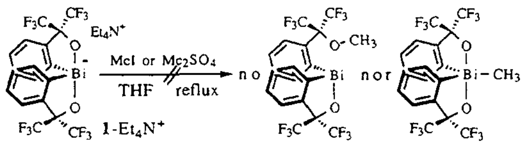
Synthesis and Reactions of 10-Bi-4 Organobismuth Ate Complexes (**1**) *Bearing Two Martin Ligands*

Reaction of 2 equiv of **2** with $BiCl_3$ gave almost pure **1**-Li^+ in 64% yield after recrystallization from acetone-ether. The **1**-Li^+ was fairly stable to atmospheric moisture but was unstable to chromatographic treatment (SiO_2) or to acids and gave protonated bismuth compound **16**, which afforded **1**-K^+ after treatment with K_2CO_3. Compound **1**-Li^+ or **1**-K^- was treated with $Et_4N^+Br^-$ to give the tetracoordinate bismuth complex **1**-Et_4N^+, which gave correct elemental analyses (Scheme 2). The structure of **1**-Et_4N^+ was confirmed by X-ray crystallographic analysis [9]. Similarly, **17**-Li^+ and **17**-Et_4N^+ could be prepared from **18**, but **17**-Et_4N^+ was unstable to atmospheric moisture, giving the protonated bismuth compound **19** in 66% yield (recrystallized from benzene-methanol) (Scheme 2). The structure of **19** was also determined by X-ray structural analysis [9].

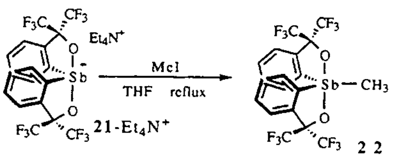


SCHEME 2

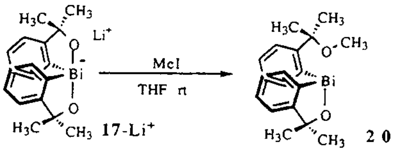
The lone pair electrons of **1**-Et_4N^+ were poorly reactive toward electrophilic reagents. Thus, **1**-Et_4N^+ did not react with MeI or Me_2SO_4 in refluxing THF during 12 hours (Equation 8). These results were sharply different from that of the corresponding 10-Sb-4 antimony complex **21**, which reacted with electrophilic reagents such as MeI, $PhCH_2Br$, or n-BuBr at the central antimony atom to give pentacoordinate compounds such as **22** (Equation 9) [15,16]. But nonfluorinated ate complex **17**-$Li^+(Na^+)$ reacted with MeI at the oxygen atom to give O-methylated product **20**, which was confirmed by ^1H NMR spectroscopy and X-ray crystallographic analysis [9].



(8)

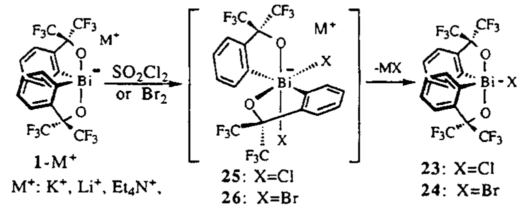


(9)



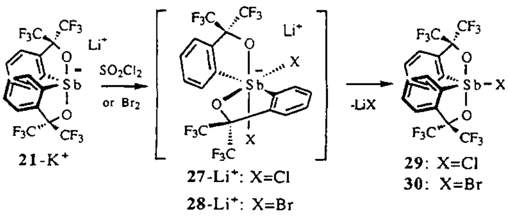
(10)

The reaction of strong electrophiles, such as sulfuryl chloride, with the lone pair electrons of **1**-K$^+$ took place in CH_2Cl_2 to afford λ^5-chlorobismuthane **23** almost quantitatively at room temperature (Equation 11). The reaction of **1**-K$^+$ with bromine also gave the corresponding λ^5-bromobismuthane **24** after recrystallization from ether. The pentacoordinate compounds **23** and **24** were sensitive to atmospheric moisture but could be recrystallized from ether to give colorless crystals. Compound **23** gave correct elemental analyses but **24** did not. It was found that, in the reaction of **1** with SO_2Cl_2 (or Br_2), the hexacoordinate intermediate **25** (or **26**) was observed before the formation of **23** (or **24**), respectively. The ^{19}F NMR spectrum of the crude product in these reactions showed a pair of quartets (δ −73.7, −74.7, J = 7.7 Hz for **25** and δ −72.7, −74.1, J = 8.3 Hz for **26** in acetone-d$_6$). However, these compounds were very unstable and lost one molecule of MCl or MBr to give **23** or **24**, respectively. The compounds **23** and **24** showed a singlet for the two CF_3 groups at room temperature (δ −73.9 for **25** in acetone-d$_6$ and δ −75.4 for **26** in $CDCl_3$). In contrast, the antimony analogues **27**-Et$_4$N$^+$ and **28**-Et$_4$N$^+$ were stable enough to allow isolation, and the structure of **27**-Et$_4$N$^+$ was confirmed by X-ray crystallographic analysis (Equation 13) [16].

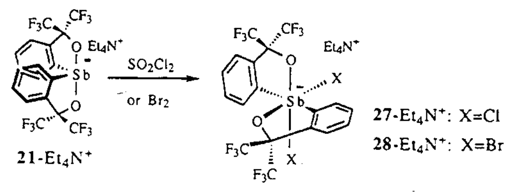


(11)

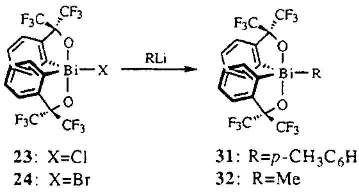
It is interesting to note that the halogen group in **23** or **24** could be substituted by treatment with p-$CH_3C_6H_4Li$ or MeLi at −78°C for 1 hour to give the corresponding pentacoordinate compounds **31** and **32** in 49% and 15% yields, respectively (Equation 14).



(12)

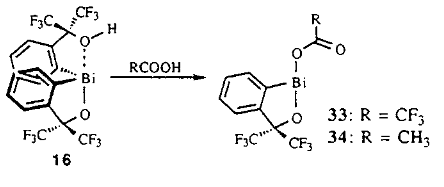


(13)



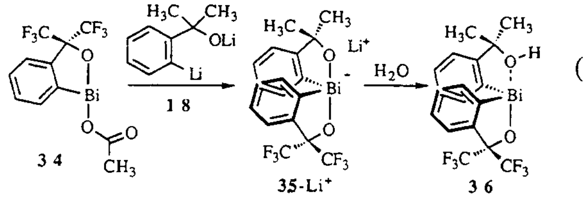
(14)

As described earlier, the compound **1**-Et$_4$N$^+$ was unstable to acids and gave protonated bismuth compound **16**. Further exposure of **16** to trifluoroacetic acid and acetic acid for 5 hours at rt gave **33** (95%) and **34** (97%), respectively. Thus, one of the ligands was replaced by a trifluoroacetate and an acetate group, respectively. This reaction is similar to that of **4** with the acids, but the rate of protonolysis of **16** was slower than that of **4**. An excess of trifluoroacetic acid led to elimination of the second ligand in **33**, but **34** was stable to excess acetic acid.



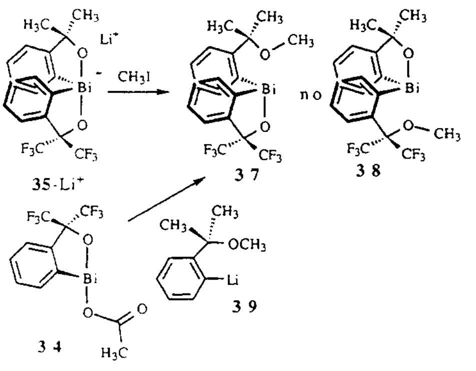
(15)

The synthesis of unsymmetrical spirobismuth compound **35**-Li$^+$ could be carried out by using **34**. The compound **35**-Li$^+$ was unstable to atmospheric moisture and gave **36** (Equation 16). The ^{19}F NMR spectrum of **36** showed one pair of quartets in contrast to that of **16**, which showed a singlet. The result suggests that configuration of **36** might be rigid at rt (vide infra).

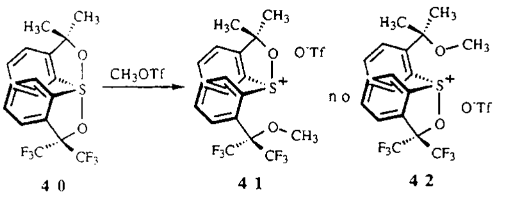


(16)

Reaction of **35**-Li$^+$ with MeI was interesting in view of the regioselectivity of methylation. In fact, only one isomer **37** was obtained after the reaction of **35**-Li$^-$ with MeI at room temperature for 12 hours (Equation 17). The structure of compound **37** was confirmed by X-ray structural analysis (vide infra) and by an independent synthesis from the reaction of **34** with **39**.



(17)



(18)

It is interesting to compare this result with the reported methylation of the sulfurane analogue **40** [19]. Compound **40** reacted with MeOTf to give **41**. The site of the attack in **40** was the oxygen atom of the hexafluoroalkoxy group. The regioselectivity of the attack in **40** has been explained in two ways: (i) in the starting material **40**, the resonance structure **40b** was much more dominant than **40a** (depicted in 19). This concept was supported by the large difference in the lengths of the S–O bonds (a: 1.713, b: 1.955 Å) of **40**; (ii) the stability of the product **41** from the reaction at the fluoroalkoxy oxygen would be much larger than that of **42**, because the positive charge of the product alkoxysulfonium ion is placed adjacent to the less electronegative alkoxy group in **41**. Based on these arguments, the reversed regioselectivity of the methylation toward **35**-Li$^+$ could also be essentially explained. In the case of the reaction of the bismuth anion **35**-Li$^+$, the electronically neutral products such as **37** or **38** should be formed, and the difference in stability of the two products between **37** and **38** is not as large as that of **41** and **42**. In addition, the difference in contribution between the resonance structures **35a** and **35b** should not be as large as that between **40a** and **40b** because the former resonance structures do not need to stabilize any cationic site at all. Therefore, electrophilic attack of **35**-Li$^+$ took place at the alkoxy oxygen, which should be essentially more nucleophilic than the fluoroalkoxy oxygen because of the electron-donating effect of the nonfluorinated alkyl group.

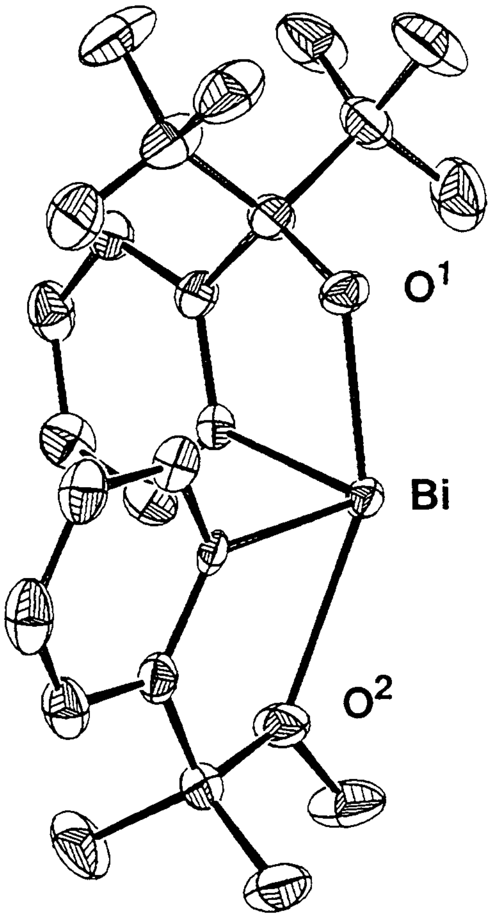
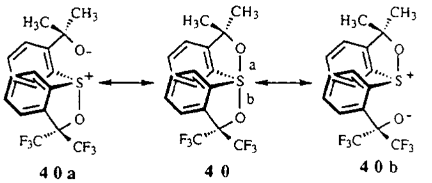


FIGURE 1 ORTEP drawing of **37**. Vibrational ellipsoids are scaled to enclose 30% of the electron density. Hydrogen atoms are omitted for clarity.



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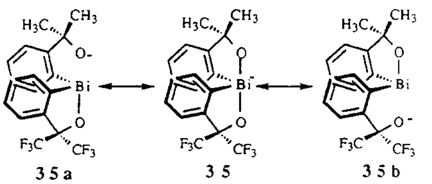
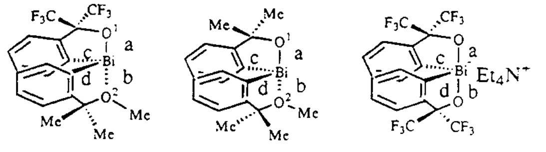


(20)

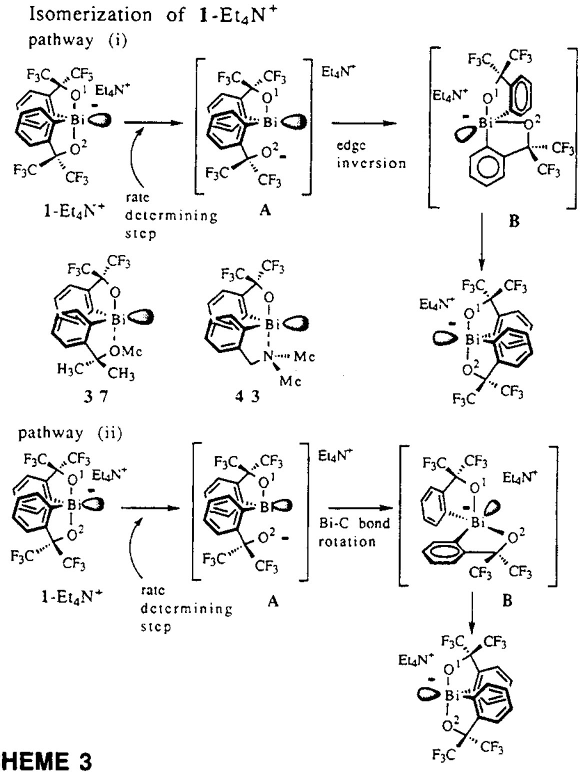
Crystal Structure of 37

Crystals of **37** suitable for X-ray analysis were obtained by recrystallization from ether. The ORTEP diagram is shown in Figure 1. The analysis clearly showed that methylation had taken place at the oxygen atom of the nonfluorinated alkoxy group. The geometry about bismuth was a distorted trigonal-bipyramid structure with an apical O–Bi–O bond, where the carbon atoms adjacent to bismuth occupy the equatorial plane. The structure was

TABLE 1 A Comparison of Bond Distances (Å) and Bond Angles (Deg) for Similar Compounds **37**, **20**, and **1**-Et_4N^+



	37	20	1-Et_4N^+
a	2.193(7)	2.134(7)	2.306(5)
b	2.536(8)	2.566(9)	2.273(5)
c	2.24 (1)	2.242(10)	2.237(8)
d	2.25 (1)	2.241(9)	2.249(7)
ab	155.2(3)	157.3(3)	159.7(2)
cd	94.4(4)	92.1(4)	94.1(3)
ac	76.3(3)	77.4(3)	74.8(2)
bd	69.5(3)	67.6(3)	73.8(2)
ad	92.3(3)	88.9(3)	91.0(2)
bc	88.0(3)	94.5(3)	92.6(2)



SCHEME 3

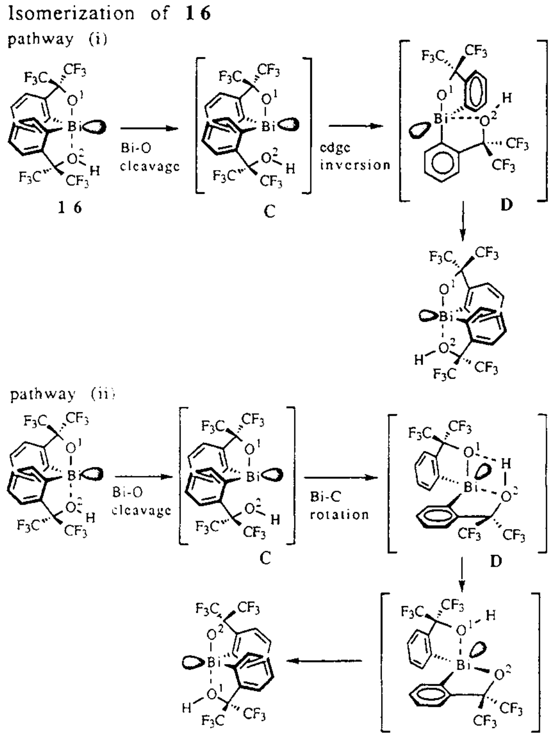
similar to those of **1**-Et_4N^+, **19**, and **20** [9]. Selected data on the molecular geometry of **37** together with those of **1**-Et_4N^+ and **20** are summarized in Table 1.

In compound **37**, the O(2) atom in the methoxy group was found to coordinate to the Bi atom with a Bi–O(2) distance of 2.536 Å, while the other Bi–O(1) bond length was 2.193 Å. The Bi–O(2) distance was longer than that of a normal single bond (ca. 2.1 Å) but was much shorter than the sum of van der Waals radii (ca. 3.67 Å) [20], and it was thus considered that the O(1)–Bi–O(2) bond is a hypervalent bond. It is interesting to note that the Bi–O(2) distance of **20** was 2.566 Å, which was 0.030 Å longer than that of **37**; in contrast, the Bi–O(1) distance of **20** was 0.059 Å shorter than that of **37**. These results indicate that the interaction between O(2) and the central bismuth atom was stronger in **37** than that in **20**, because the electronegative CF_3 substituents in **37** attached to the carbon atom next to the apical O(1) are effective in delocalizing the negative charge. These results are consistent with the property of the hypervalent three-center four-electron bond [18,21]. Apical bond distances were greatly affected by the electronegativity of the other apical group in comparison with the effect of the equatorial substituents.

*Dynamic NMR Study on Compounds **1**-Et_4N^+, **1**-Et_3NH^+, **16**, and **36***

The coalescence of the gem-CF_3 groups of **1**-Et_4N^+ could be observed at 130°C in benzonitrile and at 135°C in pyridine by ^{19}F NMR. The energies of activation at the above temperatures are 19.5 kcal mol^{-1} (130°C in PhCN) and 19.1 kcal mol^{-1} (135°C in pyridine), respectively. The effect of the nucleophilicity of pyridine was not significant in comparison with that of noncoordinated **4** ($\Delta G^{\neq}_{373}$ = 17.8 kcal mol^{-1} in pyridine-d_5 at 100°C, and the coalescence was not observed up to 170°C in benzonitrile), intramolecularly coordinated bismuth compounds **37** ($\Delta G^{\neq}_{398}$ = 18.6 kcal mol^{-1} in DMSO-d_6 at 125°C, and the coalescence temperature >170°C in *o*-dichlorobenzene), or **43** ($\Delta G^{\neq}_{313}$ = 14.6 kcal mol^{-1} in pyridine-d_5, $\Delta G^{\neq}_{398}$ = 20.5 kcal mol^{-1} in toluene-d_8). The inversion at the bismuth atom of **37** and **43** was greatly accelerated by nucleophilic solvents and was consistent with the edge inversion mechanism [11]. Since the activation energy of **1**-Et_4N^+ in nucleophilic pyridine was almost the same as that in benzonitrile, the edge inversion mechanism should not be operative in **1**-Et_4N^+. Instead, the Bi–O bond cleavage should become the rate-determining step for **1**-Et_4N^+. The higher barrier (19.1 kcal mol^{-1}) for **1** than that (14.6 kcal mol^{-1}) for **43** in pyridine-d_5 is consistent with the expectation that the Bi–O bond of **1** is much stronger than the Bi–N interaction in **43**. Two mechanisms are possible for the isomerization of **1** after the Bi–O bond cleavage: (i) usual edge inversion via **A** to form T-shaped intermediate **B** stabilized by internal oxygen anion; (ii) Bi–C bond rotation of **A** which results in the formation of the same intermediate **B**. We do not have evidence for discrimination between the two mechanisms. We think the latter pathway may be easier because only Bi–C(Ar) rotation is necessary for the isomerization (Scheme 3).

Similar discussions can be valid for **16**. The ex-



SCHEME 4

change of the gem-CF_3 groups can be achieved by the following routes: (i) the edge inversion mechanism similar to **1**, that is, Bi–O^2 bond cleavage to give **C** followed by recoordination of the O^2 atom to the empty *p*-orbital at the T-shaped bismuth in the transition state (**D**); and (ii) the Bi–C bond rotation in **C** to give **D** followed by an intramolecular exchange of the proton between Bi–O^2 and Bi–O^1. The process is similar to the mechanism shown for **1**-Et_4N^+.

The low activation barrier ($\Delta G^{\ne}_{293}$ = 13.4 kcal mol^{-1} in acetone-d_6) for **16** in comparison with that for **1** ($\Delta G^{\ne}_{413}$ = 19.5 kcal mol^{-1} in benzonitrile) indicates that process (ii) takes place. In addition, addition of Et_3N to **16** (which should form **1**-Et_3NH^+) was found to raise the activation barrier ($\Delta G^{\ne}_{393}$ = 18.3 kcal mol^{-1}), which is consistent with process (ii), because the proton transfer should be interfered by Et_3N and the energy barrier of **16** should become almost the same as that of **1**-Et_4N^+. If process (i) were to take place, the addition of nucleophilic Et_3N should have lowered the edge activation barrier or should not have changed the barrier at all as in compound **1**. Furthermore, spectroscopic behavior and the energy barrier for isomerization of **36** support pathway (ii). Thus, ^1H NMR spectra of **36** showed two different protons ortho to the Bi atom, one of which was downfield in comparison with **19** (from δ 8.08 in **19** to δ 8.30 in **36**) and the other upfield (δ 7.70). The corresponding two protons in **16** and **1** shifted to downfield from those of **19** (δ 8.25 in **16**, δ 8.28 in **1**-Et_4N^+). Since the chemical shift was reported to be due to the influence of polarization of the hypervalent 3c–4e bond [22], these results indicate that the structure of compounds **16**, **1**, and **19** have symmetrical geometry, and in compound **36**, the proton may be localized at the site of the nonfluorinated alkoxy group. Therefore, the rate of proton transfer for **36** in pathway (ii) should be slower than that for **16**. In fact, the activation barrier for the isomerization of **36** was found to be very high ($\Delta G^{\ne}_{408}$ = 18.8 kcal mol^{-1} in DMSO-d_6) in comparison with that of **16** ($\Delta G^{\ne}_{293}$ = 13.4 kcal mol^{-1} in acetone-d_6). The result is consistent with pathway (ii).

EXPERIMENTAL

Melting points were taken on a Yanagimoto micromelting point apparatus and were uncorrected. ^1H NMR (400 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on a JEOL EX-400 spectrometer. ^1H 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 ^1H 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.

Reaction of 4 *with Lithium Reagents* (*p*-$CH_3C_6H_4Li$, *n*-*BuLi*)

To a solution of **4** (100.2 mg, 0.18 mmol) in THF (3 mL) *p*-$CH_3C_6H_4Li$ (0.15 mL, 0.27 mmol in ether) was added at −78°C. The ^{19}F NMR spectrum of the mixture showed a singlet at −78°C, which did not change even after the mixture was warmed to 0°C. When water was added to the mixture, only a pair of the characteristic quartets for **4** was observed.

To a solution of **4** (112 mg, 0.21 mmol) in THF (3 mL) *n*-BuLi (0.18 mL, 0.30 mmol in hexane) was added at −78°C. The ^{19}F NMR spectrum of the mixture showed a pair of quartets, which is different from that of **4** at −78°C. When water was added to the mixture at −50°C, only a pair of the characteristic quartets for **4** was observed. After the mixture was warmed to rt, no **4** was recovered. In the reaction of **4** with excess of *n*-BuLi (3 equiv), no **4** was recovered after the mixture was kept for 2 hours at −50°C and was treated with water.

Reaction of 3a *with MeI and* $PhCH_2Br$

To a solution of ate complex **3a** in THF, prepared from the reaction of **4** (104.5 mg, 0.19 mmol) with 1.5 equiv of *p*-$CH_3C_6H_4Li$ (0.16 mL, 0.27 mmol), an excess amount (ca. 10 equiv) of MeI was added at

0°C. The mixture was stirred for 15 hours at 0°C – rt and was treated with water. The compound **4** was recovered in 96% yield. To a solution of **3a** in THF, prepared from the reaction of **4** (100.4 mg, 0.18 mmol) with 1.5 equiv of *p*-$CH_3C_6H_4Li$ (0.16 mL, 0.27 mmol), an excess amount (ca. 10 equiv) of $PhCH_2Br$ was added at 0°C. The mixture was stirred overnight at 0°C – rt and was treated with water. The compound **4** was recovered in 100% yield.

Reaction of **3a** *with* SO_2Cl_2

To a solution of **3a** in THF, prepared from the reaction of **4** (107 mg, 0.197 mmol) with 1.5 equiv of *p*-$CH_3C_6H_4Li$ (0.17 mL, 0.29 mmol), sulfuryl chloride (SO_2Cl_2) (0.02 mL, 0.249 mmol) was added with stirring at 0°C. The mixture was stirred for 4 hours and was treated with water. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. After filtration, the solvent was evaporated and the residue was purified by TLC (SiO_2, EtOAc/*n*-hexane = 1/3) to give **15** [17,18]: 28.7 mg, 21.8%. Mp 186–189°C (benzene-ethanol). ^1H NMR ($CDCl_3$) 2.38 (s, 6H), 7.43 (d, J = 8 Hz, 4H), 7.60–8.05 (m, 3H), 8.17 (d, J = 8 Hz, 4H), 8.73 (d, J = 7 Hz, 1H); ^{19}F NMR ($CDCl_3$) −74.1 (s, 6F). Anal. calcd for $C_{23}H_{18}F_6OClBi$: C, 41.30; H, 2.71. Found: C, 41.07; H, 2.70.

Preparation of **1**-Et_4N^+

A solution of a dilithiated reagent (**2**), which was prepared from bis(trifluoromethyl)benzyl alcohol (1 mL, 5.98 mmol), *n*-BuLi (12.4 mmol in 8.0 mL of hexane), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA: 0.2 mL, 1.21 mmol), and a small amount (ca. 1.5 mL) of THF [10], was added dropwise to a cold (−78°C) stirred solution of $BiCl_3$ (0.94 g, 2.99 mmol) in 15 mL of THF. The mixture was stirred for 5 hours at −78°C and was treated with water. Almost pure **1**-Li^+ was obtained in 64% yield after recrystallization from acetone-ether. Treatment of **1**-Li^+ with Et_4N^+Br gave **1**-Et_4N^+ in almost quantitative yield. **1**-Et_4N^+. Mp 167–168°C. ^1H NMR (acetone-d_6) 1.38 (tt, J = 7.3, 1.9 Hz, 12H), 3.47 (q, J = 7.3 Hz, 8H), 7.22–7.70 (m, 6H), 8.23–8.33 (m, 2H); ^{19}F NMR (acetone-d_6) −74.5 (q, J = 8.8 Hz, 6F), −77.4 (q, J = 8.8 Hz, 6F). Anal. calcd for $C_{26}H_{28}F_{12}NO_2Bi$: C, 37.92; H, 3.43; N, 1.70. Found: C, 38.10; H, 3.36; N, 1.46.

1-[o-(1,1,1,3,3,3-Hexafluoropropyl-2-oxy)phenyl]-3,3-bis(trifluoromethyl)-3H-2,1-benzoxabismole (**16**)

A solution of a dilithiated reagent (**2**), which was prepared from bis(trifluoromethyl)benzyl alcohol (5 mL, 29.9 mmol), *n*-BuLi (60 mmol in 40.0 mL of hexane), and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA: 1 mL, 6.6 mmol), was added dropwise to a cold (−78°C) stirred solution of $BiCl_3$ (9.43 g, 29.9 mmol) in 50 mL of THF. The mixture was stirred for 5 hours at −78°C and was treated with water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. After filtration, the solvent was evaporated, and the residue was purified by chromatographic treatment (SiO_2) to give protonated compound **16** in 78% yield. **16**: Mp 100–102°C (dec). ^1H NMR (acetone-d_6) 7.29 (td, J = 5.8, 1.4 Hz, 2H), 7.50 (td, J = 5.8, 1.4 Hz, 2H), 7.61–7.68 (m, 2H), 8.25 (dd, J = 5.8, 1.4 Hz, 2H); ^{19}F NMR (acetone-d_6) −76.3 (brs, 12F). Anal. calcd for $C_{18}H_9F_{12}O_2Bi$: C, 31.14; H, 1.30. Found: C, 31.12; H, 1.90.

1-[o-(2-Propyloxy)phenyl]-3,3-dimethyl-3H-2,1-benzoxabismole (**19**)

A solution of a dilithiated reagent (**18**), which was prepared from dimethylbenzyl alcohol (5 mL, 35.8 mmol), *n*-BuLi (82.5 mmol in 50.0 mL of hexane), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA: 1.0 mL, 6.6 mmol), and a small amount (ca. 1 mL) of THF, was added dropwise to a cold (−78°C) stirred solution of $BiCl_3$ (5.63 g, 17.9 mmol) in 100 mL of THF. The mixture was stirred for 5 hours at −78°C and was treated with aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$. After filtration, the solvent was evaporated and the residue was recrystallized from benzene-methanol to give colorless crystals of **19**: 5.65 g, 66%. Mp 227–228°C (dec). ^1H NMR ($CDCl_3$) 1.75 (s, 12H), 7.11–7.50 (m, 6H), 8.08 (d, J = 7.3 Hz, 2H). Anal. calcd for $C_{18}H_{21}O_2Bi$: C, 45.20; H, 4.43. Found: C, 45.13; H, 4.88.

Reaction of **17**-Li^+ *or* **17**-Na^+ *with MeI*

A solution of a dilithiated reagent (**18**), which was prepared from dimethylbenzyl alcohol (5 mL, 35.8 mmol) as described earlier, was added dropwise to a cold (−78°C) stirred solution of $BiCl_3$ (5.63 g, 17.9 mmol) in 50 mL of THF. The mixture was stirred for 5 hours at −78°C and MeI (4 mL, 64.4 mmol) was added. The mixture was allowed to warm to rt and was treated with water. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$. After filtration, the solvent was evaporated and the residue was recrystallized from benzene-methanol to give colorless crystals of **20**: 5.74 g, 67%. Mp 200–202°C. ^1H NMR ($CDCl_3$) 1.58 (s, 12H), 3.74 (s, 3H), 7.10–7.70 (m, 7H), 8.20–8.40 (m, 1H). Anal. calcd for $C_{19}H_{23}O_2Bi$: C, 46.35; H, 4.71. Found: C, 46.72; H, 4.74.

To a solution of **19** (124.9 mg, 0.26 mmol) in THF (10 mL) was added NaH. After filtration, an excess amount of MeI (0.05 mL, 0.8 mmol) was added at rt and the mixture was stirred for 15 hours. The crude product was recrystallized from benzene-methanol to give colorless crystals of **20**: 99.3 mg, 77%.

Reaction of **1**-*Et_4N^+ with Me_2SO_4*

To a solution of **1**-Et_4N^+ (79.2 mg, 0.096 mmol) in THF (2 mL) Me_2SO_4 (0.05 mL, 0.53 mmol) was added at rt, and the mixture was heated under reflux for 15 hours and was treated with water. Colorless crystals of **16** were obtained in quantitative yield. No methylation product was obtained.

To a suspension of **1**-Et_4N^+, **1**-Li^+, **1**-K^+, **1**-K^+ + 18-crown-6 (0.14–0.35 mmol) in THF (10 mL) MeI or Me_2SO_4 (0.5–1.6 mmol) was added at rt. The mixture was heated under reflux for 18 hours and was quenched with water. Colorless crystals of **16** were obtained in quantitative yield. No methylation product was obtained.

Reaction of **1** *with SO_2Cl_2*

To a CH_2Cl_2 (10 mL) suspension of **1**-K^+, prepared from **16** (100 mg, 0.14 mmol) and K_2CO_3 in acetone, was added an excess amount of SO_2Cl_2 (0.05 mL, 0.65 mmol) at 0°C. The mixture was stirred for 1 hour at rt and the solvent was removed. Recrystallization of the residue from ether gave **23** (97.5 mg) in 90% yield. Mp 225–227°C. ^1H NMR (acetone-d_6) 7.90–8.40 (m, 6H), 8.69–8.82 (m, 2H); ^{19}F NMR (acetone-d_6) −73.9 (s, 12F). Anal. calcd for $C_{18}H_8F_{12}O_2ClBi$: C, 29.67; H, 1.11. Found: C, 29.89; H, 0.92.

To a suspension of **1**-Et_4N^+ (109 mg, 0.13 mmol) in 10 mL of CH_2Cl_2 was added excess Br_2 (0.05 mL, 0.52 mmol) at 0°C. The mixture was stirred for 5 minutes and the solvent was removed. Recrystallization of the residue from ether gave **24** (84 mg, 0.11 mmol) in 84% yield. Mp 200–204°C. ^1H NMR ($CDCl_3$) 7.70–8.20 (m, 6H), 8.38–8.50 (m, 2H); ^{19}F NMR ($CDCl_3$) −75.4 (s, 12F).

The ^1H NMR and ^{19}F NMR spectra of the crude products in these reactions showed the presence of intermediates, thus hexacoordinate are complexes (**25** and **26**) with two halogen atoms could be observed. The products were very sensitive to atmospheric moisture and could not be purified.

25: ^1H NMR (acetone-d_6) 7.60–8.20 (m, 6H), 8.80–9.00 (m, 2H); ^{19}F NMR (acetone-d_6) −73.7 (q, J = 7.7 Hz, 6F), −74.7 (q, J = 7.7 Hz, 6F). **26**: ^1H NMR (acetone-d_6) 7.74–7.95 (m, 6H), 8.82–8.92 (m, 2H); ^{19}F NMR (acetone-d_6) −72.7 (q, J = 8.3 Hz, 6F), −74.1 (q, J = 8.3 Hz, 6F).

Reaction of **24** *with p-$CH_3C_6H_4Li$*

To a solution of **24** in THF (10 mL), which was prepared from the residue of the reaction of **1**-Et_4N^+ (187.6 mg, 0.228 mmol) with an excess amount of Br_2 (0.02 mL, 0.39 mmol) at 0°C in CH_2Cl_2 for 5 minutes, *p*-$CH_3C_6H_4Li$ (0.3 mL, 0.296 mmol) in THF was added with stirring at −78°C. The mixture was treated with water after it had been stirred overnight at rt, and the crude product was purified by TLC (*n*-hexane-EtOAc = 9:1) to give colorless crystals of **31**: 88.2 mg, 49.3%. Mp 130–132°C. ^1H NMR ($CDCl_3$) 2.39 (s, 3H), 7.50–8.20 (m, 12H); ^{19}F NMR ($CDCl_3$) −74.0 (q, J = 8.4 Hz, 6F), −75.2 (q, J = 8.4 Hz, 6F). Anal. calcd for $C_{25}H_{15}F_{12}O_2Bi$: C, 38.28; H, 1.93. Found: C, 38.21; H, 1.95.

Reaction of **23** *with MeLi*

To an ether (10 mL) solution of **23**, which was prepared from the residue of the reaction of **1**-Et_4N^+ (546.8 mg, 0.77 mmol) with an excess amount of SO_2Cl_2 (0.7 mL, 1.18 mmol) at 0°C in CH_2Cl_2, MeLi (0.8 mL, 0.88 mmol) was added with stirring at 0°C. The mixture was treated with water after 4 hours, and the crude products were subjected to TLC to give colorless crystals of **32**: 108.6 mg, 15.3%. Mp 190–192°C (dec). ^1H NMR ($CDCl_3$) 1.84 (s, 3H), 7.23 (dd, J = 6.8, 7.3 Hz, 2H), 7.61 (dd, J = 7.8, 7.3 Hz, 2H), 7.66 (d, J = 7.8 Hz, 2H), 8.08 (d, J = 8.3 Hz, 2H); ^{19}F NMR ($CDCl_3$) −74.9 (q, J = 8.4 Hz, 6F), −76.2 (q, J = 8.4 Hz, 6F).

Reaction of **16** *or* **19** *with Acids*

To a suspension of **16** (0.14 mmol) in ether (10 mL) was added 1.2 equiv of acetic acid (0.02 mL, 0.34 mmol) with stirring at 0°C. The mixture was stirred for 5 hours at rt. The resulting insoluble product was separated from the mixture by filtration, washed with ether, and dried under vacuum with heating. The pure **33** (68 mg, 0.13 mmol) was obtained in 95% yield. The crystalline **33** with one molecule of acetic acid as solvent of crystallization was confirmed by elemental analysis. Anal. calcd for $C_{11}H_7F_6O_3Bi + C_2H_4O_2$: C, 27.38; H, 1.94. Found: C, 27.75; H, 1.98. The same sample was further dried under vacuum at 100°C for 3 hours. The colorless powder of **33** without acetic acid was obtained. **33**: mp 267–269°C (dec). ^1H NMR (acetone-d_6) 1.86 (s, 3H), 7.53–7.72 (m, 1H), 7.93–8.25 (m, 2H), 8.52–8.63 (m, 1H); ^{19}F NMR (acetone-d_6) −74.8 (s, 6F). Anal. calcd for $C_{11}H_7F_6O_3Bi$: C, 25.90; H, 1.38. Found: C, 26.04; H, 1.37.

The similar reaction between compound **19** (0.35 mmol) and trifluoroacetic acid (0.03 mL, 0.39 mmol) in ether (10 mL) was carried out for 5 hours at rt. The resulting insoluble product was separated from the mixture by filtration, washed with ether, and dried under vacuum with heating. The pure **34** (190 mg, 0.34 mmol) was obtained in 97% yield. **34**: mp 185–186°C (recrystallized from acetone-ether). ^1H NMR (acetone-d_6) 7.62–7.78 (m, 1H), 8.04–8.41 (m, 2H), 8.64–8.78 (m, 1H). ^{19}F NMR (acetone-d_6) −74.0 (s, 3F), −74.5 (s, 6F). Anal. calcd for $C_{11}H_4F_9O_3Bi$: C, 23.96; H, 0.89. Found: C, 23.67; H, 0.78.

Preparation of **35**

To a suspension of **34** (1.46 g, 2.86 mmol) in THF (20 mL) was added dropwise the dilithiated reagent **2** at −78°C. The mixture was allowed to warm to rt and was treated with water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. After filtration, the solvent was evaporated, and the residue was recrystallized from ether to give colorless crystals of **36**: 0.67 g, 40.1%. ^1H NMR (acetone-d_6) 1.55 (s, 6H), 7.25–7.90 (m, 7H), 8.12–8.20 (m, 1H); ^{19}F NMR (acetone-d_6) −73.8 (q, J = 8.8 Hz, 3F), −77.6 (q, J = 8.8 Hz, 3F). **36** was treated with K_2CO_3 and Et_4N^+Br to give tetracoordinate bismuth complex **35**-Et_4N^+[^{19}F NMR (acetone-d_6) −72.9 (q, J = 8.8 Hz, 3F), −75.8 (q, J = 8.8 Hz, 3F)], but this compound was very sensitive to atmospheric moisture and **36** was recovered after treatment with water.

Reaction of **35** *with MeI*

To a suspension of **34** (4.16 g, 8.55 mmol) in THF (50 mL) was added dropwise at −78°C the dilithiated reagent **18**, which was prepared from dimethylbenzyl alcohol (1 mL, 7.14 mmol), *n*-BuLi (15.5 mmol in 10.0 mL of hexane), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA: 0.2 mL, 1.3 mmol), and a small amount (ca. 0.5 mL) of THF. The mixture was stirred for 5 hours at −78°C, and an excess amount of MeI (1 mL, 16.1 mmol) was added. The mixture was stirred overnight and was treated with water. The crude product was recrystallized from ether to give colorless crystals of **37**: 2.53 g, 59%. Mp 234–235°C. ^1H NMR ($CDCl_3$) 1.56–1.63 (m, 6H), 3.80 (s, 3H), 7.10–7.90 (m, 7H), 8.10–8.22 (m, 1H); ^{19}F NMR ($CDCl_3$) −72.6 (q, J = 8.6 Hz, 6F), −75.9 (q, J = 8.6 Hz, 6F). Anal calcd for $C_{19}H_{17}F_6O_2Bi$: C, 38.40; H, 2.82. Found: C, 38.01; H, 2.85.

Crystal Structure of **37**

A crystal suitable for X-ray structure determination was mounted on a Mac Science MXC3 diffractometer and was irradiated with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å) for data collection. Formula: $C_{19}H_{17}F_6O_2Bi$, monoclinic space group $P2_1/n$, a = 1780.7(4), b = 1100.2(3), c = 1042.3(2) pm, β = 106.68(2)°; T = 25°C, Z = 4, FW = 600.31, D_c = 2.04 g/cm^3 μ = 87.69 cm^{-1}. Crystal description: a colorless plate (0.80 × 0.80 × 0.30) grown by ether evaporation from a solution of **37**. Lattice parameters were determined by least-squares fitting of 36 reflections with $31° < 2\theta < 35°$. A total of 4957 reflections were collected ($3° < 2\theta < 55°$). With 3620 unique reflections of intensity greater than 3.0 σ (corrected for absorption [23] and extinction [24]), the structure was solved by a direct method using a program, Monte Carlo-Multan [25]. Refinement on F was carried out by full-matrix least-squares. All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the refinement on calculated positions (C–H = 1.0 Å) riding on their carrier atoms with isotropic thermal parameters. The final R factors were 0.056, Rw = 0.070. The final difference Fourier showed the largest residual density to be 3.77 e/Å^3 (near the central bismuth atom). All the computations were carried out on a Titan-750 computer.

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SUPPLEMENTARY MATERIAL AVAILABLE

A complete description of the X-ray crystallographic structure determinations on **37** has been deposited with Cambridge Crystallographic Data Centre.

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