Synthesis and Structure of Six-Coordinated Organobismuth Compounds with Bidentate Ligands (12-Bi-6)

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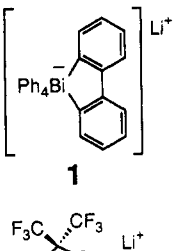
The thermally stable 12-Bi-6 compound **3**-Li$^+$, $\{(o\text{-}C_6H_4C(CF_3)_2O)_2\}Bi(p\text{-}CH_3C_6H_4)_2^-Li^+$, was synthesized. ^{19}F NMR of **3**-Li$^+$ showed a pair of quartets at room temperature but showed a singlet after addition of 12-crown-4 to the solution. The result indicated an important role of the Li$^+$ on the structure of the ate complex, and the structure of the Li salt was assigned as **3A**, bearing two cis oxygens, two cis *p*-tolyl groups, and two trans carbons at ligation sites about the central bismuth atom. The structure of the ate complex in the presence of 12-crown-4 was assigned as **3C**, bearing two cis oxygens, two trans *p*-tolyl groups, and two cis carbons at ligation sites. Compounds **3** were stable up to 150 °C, but the pair of quartets coalesced at 70 °C and the activation energy of the equilibrium between the CF_3 groups was calculated to be 18 kcal mol^{-1} at 70 °C. Bismuth–oxygen bond cleavage followed by pseudorotation was suggested for the coalescence. Compounds **3** were inert to electrophilic reagents such as *p*-(trifluoromethyl)benzoyl chloride. Water reacted with **3** to give an alcohol **17**. The alcohol was unstable at room temperature and cyclized with elimination of toluene to afford a 10-Bi-5 (**12**). Intramolecularly coordinated 12-Bi-6 compounds **18**, $(o\text{-}C_6H_4C(CF_3)_2O)BiAr_2(o\text{-}C_6H_4CR_2X)$ {Ar, R, X: **18a** $p\text{-}CH_3C_6H_4$, CF_3, CH_3O; **18b** $p\text{-}CF_3C_6H_4$, CF_3, CH_3O; **18c** $p\text{-}CH_3C_6H_4$, H, $(CH_3)_2N$; **18d** $p\text{-}CF_3C_6H_4$, H, $(CH_3)_2N$}, were synthesized, three of which were structurally determined by X-ray analysis. The structures were all cis geometry. The synthesis and stability of 12-Bi-6 ate complexes **5**, $(o\text{-}C_6H_4C(CF_3)_2O)Bi(p\text{-}CH_3C_6H_4)_3R^-Li^+$, were also described.

Introduction

Six-coordinated organobismuth(V) compounds (12-Bi-6) bearing carbon substituents have scarcely been reported due to instability of those compounds. For example, $Ph_6Bi^-Li^+$ has been synthesized from Ph_5Bi and PhLi,[1] but the ate complex was only stable at low temperatures. In addition, Hellwinkel reported formation of **1**,[2] which showed dissociation to form five-coordinated λ^5-bismuthane at room temperature. The only example of intramolecularly weakly coordinated 12-Bi-6 organobismuth(V) compounds, which were structurally determined by X-ray analysis, has been compound **2**.[3] The bond length between the bismuth and the nitrogen atom of **2** was 2.807(10) Å, which was very much shorter than the sum of the van der Waals radii (3.70 Å). Recently, we reported formation and some reactions of thermally stable 12-Bi-6 ate complexes (**3**)[4] by use of two molecules of five-membered ring ligands, the so-called Martin ligand (**4**).[5] Here we report the stability of ate complexes **5** bearing one molecule of **4** and the structural study of **3** by use of ^{19}F NMR. In addition, we prepared four intramolecularly coordinated neutral molecules of 12-Bi-6 (**18**), three of which were structurally determined by X-ray analysis.



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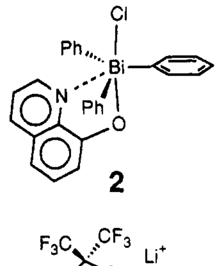

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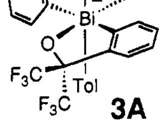
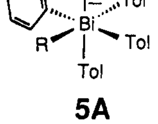


3A



5A

Results and Discussion

Synthesis and Stability of Six-Coordinated Bismuthate Complexes 5 Bearing One Molecule of 4. From our laboratory, formation of six-coordinated antimonate complex **7a** has been reported recently.[6] ^{19}F NMR of a mixture of 1 equiv of methyllithium with **8a** showed a pair of quartets for the nonequivalent CF_3 groups at −50 °C, which were assigned to **7aA**, and **7aA** isomerized to an equilibrium among three isomers **7aA**, **7aB**, and **7aC** (61:23:16) at room temperature. When the reaction mixture was quenched with water after stirring for 1 day at room temperature, five-coordinated compounds **8a** and **8b** were obtained in 5% and 90% yields, respectively (Scheme I).

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(1) Hellwinkel, D.; Kilthau, G. *Liebigs Ann. Chem.* **1967,** *705,* 66.

(2) Hellwinkel, D.; Bach, M. *Liebigs Ann. Chem.* **1968,** *720,* 198.

(3) Faragka, G.; Rivarola, E.; diBianca, F. *J. Organomet. Chem.* **1972,** *38,* 91. Barton, D. H. R.; Charpiot; B.; Dau, E. T. H.; Motherwell, W. B.; Pascard, C.; Pichon, C. *Helv. Chim. Acta* **1984,** *67,* 586.

(4) Akiba, K.-y.; Ohdoi, K.; Yamamoto, Y. *Tetrahedron Lett.* **1989,** *30,* 953.

(5) Perrozzi, 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.

(6) Yamamoto, Y.; Fujikawa, H.; Fujishima, H.; Akiba, K.-y. *J. Am. Chem. Soc.* **1989,** *111,* 2276. Akiba, K.-y.; Fujikawa, H.; Sunaguchi, Y.; Yamamoto, Y. *J. Am. Chem. Soc.* **1987,** *109,* 1245.

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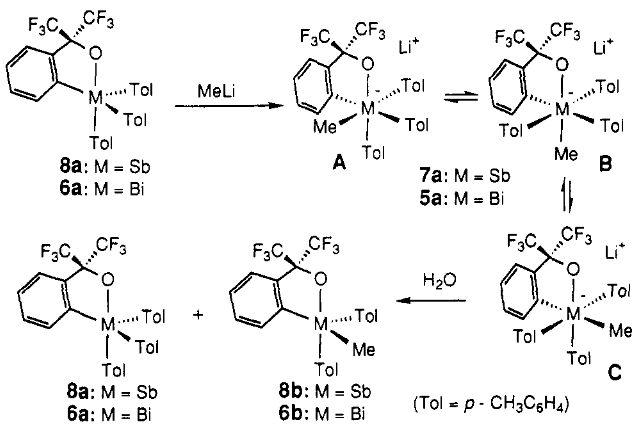
Scheme I

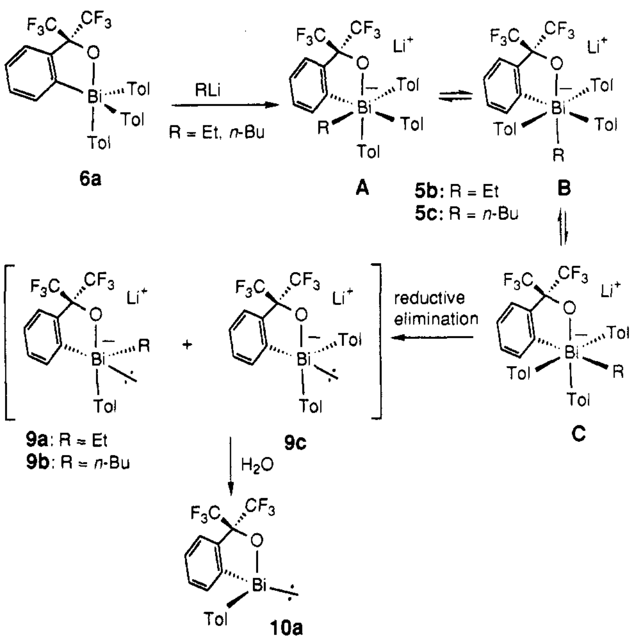


Reaction of 1,1,1-tris(*p*-methylphenyl)-3,3-bis(trifluoromethyl)-3*H*-2,1λ^5-benzoxabismole (**6a**)[7] with 1 equiv of methyllithium was carried out at 0 °C, and the mixture was quenched with water after stirring for 1.5 h at room temperature. Five-coordinated compounds **6a** and **6b** were obtained in good yields (10% and 70%, respectively) by TLC (SiO_2; ethyl acetate:*n*-hexane = 1:9). The result is consistent with that of the corresponding antimony analogue; thus, six-coordinated bismuthate complexes **5a** were possibly formed in this case. Only 20% of **6a**, however, was recovered after the mixture was stirred for 1 day, and **6b** could not be detected at all. This indicated that the six-coordinated bismuthate complexes **5a** (**5aA** + **5aB** + **5aC**) were not as stable as six-coordinated antimonate complexes **7a** (**7aA** + **7aB** + **7aC**) and gradually decomposed at room temperature by an unknown mechanism.

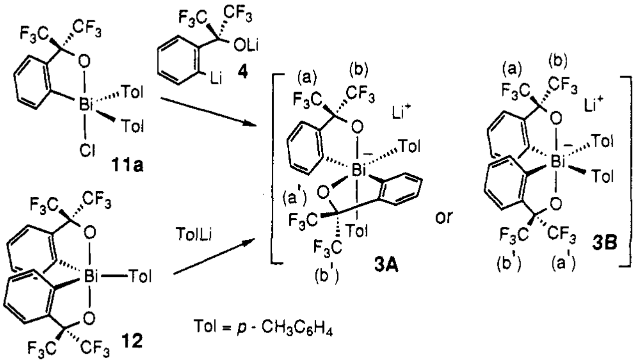
Reaction of ethyllithium or *n*-butyllithium with **6a** did not give the expected five-coordinated compounds of type **6** even when the reaction was quenched at −78 °C after 1 h. Instead, three-coordinated 1-(*p*-methylphenyl)-3,3-bis(trifluoromethyl)-3*H*-2,1λ^5-benzoxabismole (**10a**)[7] was obtained in 86% and 90% yields, respectively. The possible explanation of the result is as follows: the initially formed six-coordinated bismuthate complexes **5b** and **5c** were quite unstable, and reductive elimination took place to give unstable four-coordinated bismuth compounds **9**, which afforded the three-coordinated compound **10a** after quenching with water (Scheme II). Indeed, formation of **9a** (or **9b**) by the addition of 1 equiv of ethyllithium (or butyllithium) to **10a** was confirmed at −50 °C by ^{19}F NMR. **10a** was recovered in good yield by quenching the above reference reaction mixtures with water.[8]

Synthesis, Structure, and Reactions of Six-Coordinated Bismuthate Complexes 3 Bearing Two Molecules of 4. In order to stabilize six-coordinated bismuthate complexes, Martin ligand **4** was used as a nucleophile toward λ^5-chlorobismuthane **11a** (Scheme III).[7] Thus, **4** prepared from bis(trifluoromethyl)benzyl alcohol (0.12 mL, 0.72 mmol), *n*-BuLi (1.00 mL, 1.55 mmol), and *N,N,N′,N′*-tetramethylethylenediamine (0.03 mL, 0.20 mmol) was added to **11a** in 2 mL of THF at −78 °C. After 10 min of stirring at −78 °C, ca. 0.4 mL of the solution was transferred to an NMR tube by using a double ended needle (sample 1). Then the remaining solution was warmed to

Scheme II



Scheme III



room temperature and was stirred for 24 h and ca. 0.4 mL of the mixture was transferred to another NMR tube (sample 2). ^{19}F NMR spectra (376 MHz) of both samples showed the same spectra at 0 °C, i.e., a pair of quartets (δ −76.0 and −76.4 ppm) at 0 °C, suggesting the formation of a six-coordinated ate complex **3A** or **3B**, in which each pair of CF_3 (a = a′, b = b′) should be magnetically identical. The pair of quartets coalesced at 70 °C to become a sharp singlet, which was stable up to 150 °C. The same quartets were observed again when the solution was cooled to 0 °C. Therefore, the ate complex **3A** or **3B** should be the thermodynamically most stable isomer. It is noteworthy here that the same pair of quartets was observed in the ^{19}F NMR spectrum at −50 °C immediately after *p*-$CH_3C_6H_4Li$ was added to a solution of bicyclic compound **12** at −78 °C. The activation energy of the equilibration was calculated from the ^{19}F NMR coalescence temperature to be 18 kcal mol^{-1} at 70 °C. The isomerization of the ate complexes may proceed through an intramolecular Bi–O bond cleavage assisted by the lithium cation followed by pseudorotation of the resulting 10-Bi-5 intermediate and recyclization, similar to that of 12-Sb-6 compound (Scheme IV).[6]

Both structures for the six-coordinated ate compounds **3A** and **3B** can comply with the presence of a pair of quartets in ^{19}F NMR. In order to distinguish between **3A** and **3B** the preparative reaction was repeated and 12-crown-4 was added in order to deprive the ate complex of

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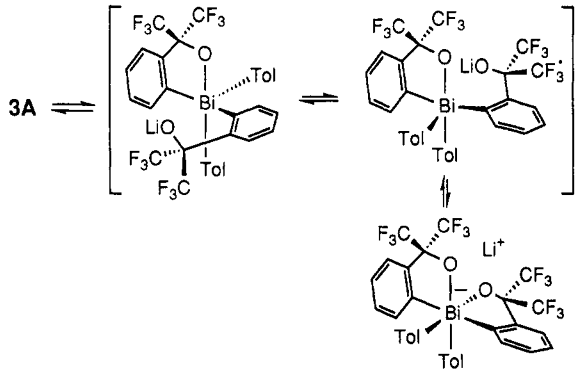
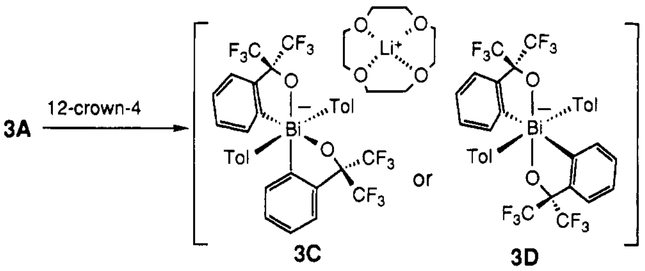
[7] Chen, X.; Ohdoi, K.; Yamamoto, Y.; Akiba, K.-y. *Organometallics* **1993**, *12*, 1857. Akiba, K.-y.; Ohdoi, K.; Yamamoto, Y. *Tetrahedron Lett.* **1988**, *29*, 3817.

[8] Chen, X.; Yamamoto, Y.; Akiba, K.-y. Unpublished results.

Scheme IV

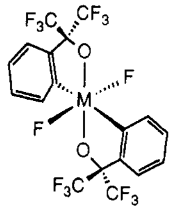


Scheme V

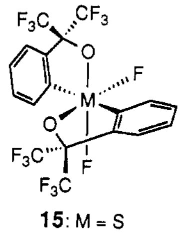


the lithium ion. The ^{19}F NMR spectrum of the resulting solution gave a sharp singlet just after the addition, and it was thermally stable up to 150 °C (Scheme V). This result suggested that the complex prepared without the 12-crown-4 contained the lithium ion complexed to two cis oxygen atoms, a result which showed **3A** as the correct structure, excluding **3B**.

Two structures **3C** and **3D**, in which four CF_3 groups are magnetically equivalent, are possible for the isomer obtained when 12-crown-4 was used in the synthesis. We cannot distiguish between structures **3C** and **3D** experimentally. However, in our laboratory, ab initio calculation was carried out on models of six-coordinated antimony compounds such as *cis*-$H_4SbF_2^-$ and *trans*-$H_4SbF_2^-$. And the *cis*-$H_4SbF_2^-$ was found to be considerably more stable than the trans one (5.2 kcal mol^{-1}).[6] In addition, all-trans six-coordinated sulfur compound **13**[9] or tellurium compound **14**,[10] obtained as the kinetically favored isomer, was reported to isomerize to cis-fused **15** or **16**, respectively. Thus, the **3C** bearing two cis oxygen atoms should be a thermodynamically preferred isomer to **3D** bearing trans oxygen atoms.



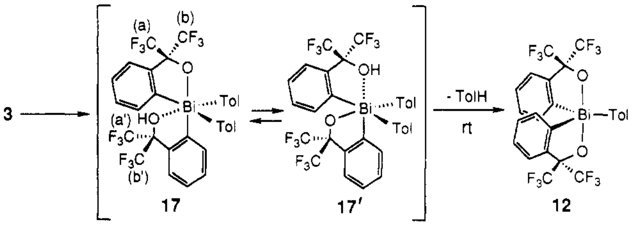
13: M = S
14: M = Te



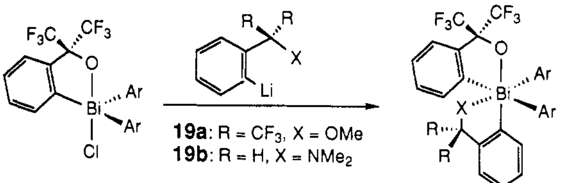
15: M = S
16: M = Te

The remarkable stability of the ate complexes was also observed in the reaction of **3** with electrophiles. For example, 2.1 equiv of *p*-(trifluoromethyl)benzoyl chloride did not react with **3** even under refluxing in THF for 40 h. In the presence of 12-crown-4, *p*-chlorobenzoyl chloride did not react with **3** even after 13 h of stirring at room temperature and refluxing in THF for 4.5 h. At present only protons (such as water) reacted with **3** to give an alcohol **17**. The alcohol (**17**) was unstable at room temperature, and cyclization with elimination of toluene afforded a bicyclic compound **12** quantitatively (Scheme VI). However, **17** could be isolated in almost pure form by use of flash column chromatography (SiO_2) at ca. −20 °C. The ^{19}F NMR showed a singlet (δ −74.5 ppm ($CDCl_3$)) at 0 °C, i.e., rapid bond switching between the bismuth and the oxygen taking place by intramolecular prototropy between the two oxygen atoms (**17** $\rightleftarrows$ **17′**). At −90 °C, however, a 470-MHz ^{19}F NMR spectrum showed four broad quartets (**17**, two pairs of quartets: a $\neq$ a′, b $\neq$ b′) with equal integral ratios, indicating that the bond switching was frozen and the oxygen atom of the hydroxy group coordinated toward the central bismuth atom to form a six-coordinated structure. It should be different from the structures of the ate complexes **3** (**3A**, **3B**) in which ^{19}F NMR showed a pair of quartets without 12-crown-4. Therefore, in order to confirm the structure of **17** potentially six-coordinated bismuth complexes **18** each bearing an intramolecularly coordinating group were synthesized and the X-ray structural analysis was carried out for **18b**, **18c**, and **18d**.

Scheme VI



Scheme VII



19a: R = CF_3, X = OMe
19b: R = H, X = NMe_2

11a: Ar = *p*-$CH_3C_6H_4$
11b: Ar = *p*-$CF_3C_6H_4$

18a: Ar = *p*-$CH_3C_6H_4$, R = CF_3, X = OMe
18b: Ar = *p*-$CF_3C_6H_4$, R = CF_3, X = OMe
18c: Ar = *p*-$CH_3C_6H_4$, R = H, X = NMe_2
18d: Ar = *p*-$CF_3C_6H_4$, R = H, X = NMe_2

Synthesis and Crystal Structures of Six-Coordinated Bismuth Complexes 18 Bearing an Intramolecularly Coordinating Ligand. Five-coordinated chlorobismuthane **11a** and **11b** could be used for the preparation of potentially six-coordinated bismuth compounds **18** (Scheme VII). These compounds were stable to atmospheric moisture and could be purified by column chromatography (SiO_2). Crystals of **18b**, **18c**, and **18d** suitable for X-ray analysis were obtained by recrystallization from acetonitrile. The structures are very similar in these compounds, and the ORTEP diagrams are shown in Figures 1–3. Selected bond lengths and bond angles are listed in Table I. The distance between the oxygen of the methoxy group and the central bismuth atom in **18b** is 2.741(5) Å, which is very much shorter than the sum of van der Waals radii (ca. 3.67 Å). And the distances 2.85(1) Å in **18c** and 2.878(8) Å in **18d** between the nitrogen of the *N*,*N*-dimethylamino group in **18c** and **18d** are also very

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(9) Michalak, R. S.; Martin, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 5634.
(10) Michalak, R. S.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7529.

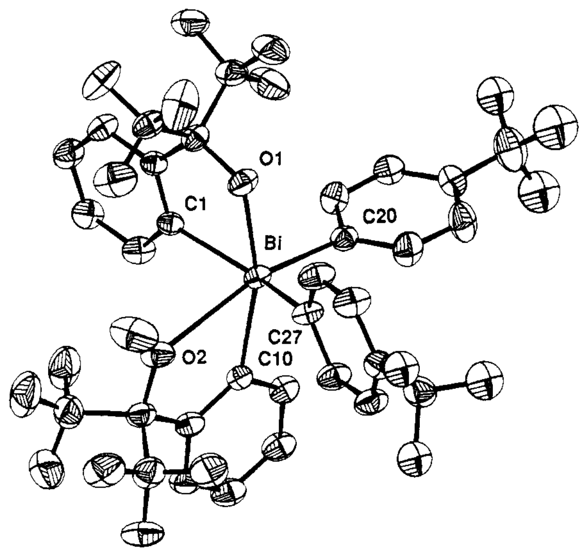


Figure 1. ORTEP diagram (30% probability ellipsoids) for **18b**.

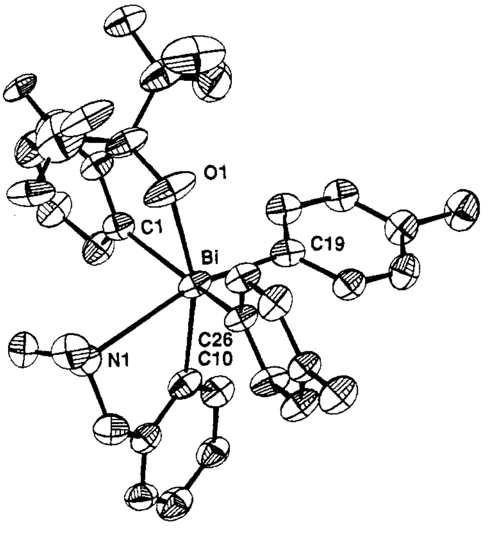


Figure 2. ORTEP diagram (30% probability ellipsoids) for **18c**.

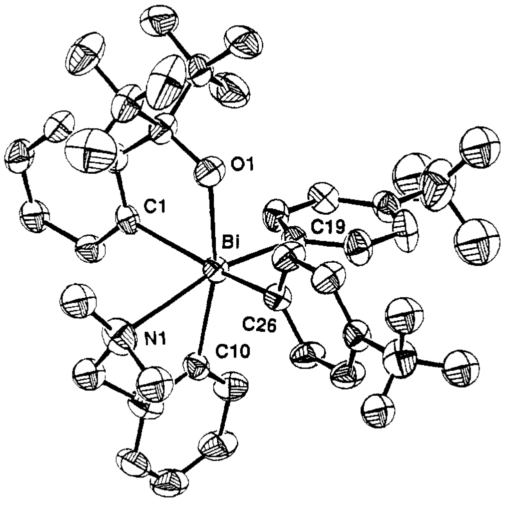
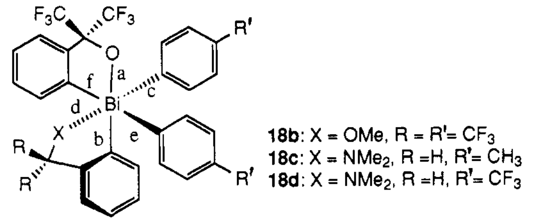


Figure 3. ORTEP diagram (30% probability ellipsoids) for **18d**.

much shorter than the sum of van der Waals radii (3.7 Å). Thus, the coordination of the OMe (or NMe_2) group effectively forms a six-coordinated 12-Bi-6 compound. It should be noted that the structure of **17** suggested for the alcohol was essentially the same as the structure of **18** and was different from the structures of covalently bound ate complexes **3** (**3A, 3B, 3C, 3D**). The result clearly indicated that the favored structure in the six-coordinated compounds was very sensitive to several factors such as charge, countercation, nucleophilic coordination, and so on.

Table I. Selected Bond Lengths and Angles for 18b, 18c, and 18d



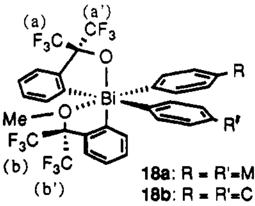
	18b	18c	18d
	Bond Lengths (Å)		
a	2.275 (6)	2.313 (9)	2.292 (8)
b	2.290 (8)	2.26 (1)	2.27 (1)
c	2.214 (7)	2.25 (1)	2.230 (8)
d	2.741 (5)	2.85 (1)	2.878 (8)
e	2.219 (7)	2.219 (9)	2.228 (8)
f	2.222 (7)	2.20 (1)	2.23 (1)
	Bond Angles (deg)		
ab	162.6 (2)	162.2 (5)	165.4 (3)
cd	165.1 (2)	163.2 (3)	165.9 (4)
ef	148.1 (3)	151.3 (4)	149.3 (3)
fc	103.7 (2)	98.5 (4)	102.3 (4)
ce	100.2 (3)	100.9 (4)	100.2 (3)
ed	79.5 (2)	80.5 (4)	80.5 (3)
df	82.7 (2)	86.9 (4)	82.6 (3)
ac	94.9 (2)	102.5 (3)	96.5 (3)
ae	83.0 (2)	82.4 (3)	82.6 (3)
ad	99.8 (2)	94.3 (4)	97.6 (3)
af	74.2 (2)	74.5 (3)	74.5 (3)
bc	101.9 (3)	94.2 (4)	97.1 (3)
be	98.3 (3)	100.4 (4)	100.0 (3)
bd	63.6 (3)	69.1 (4)	69.0 (3)
bf	97.1 (3)	99.0 (4)	97.5 (4)

NMR observations in solution were consistent with the structures in the solid state. For example, the ^{19}F NMR (CD_2Cl_2) spectra of **18a** and **18b** showed two nonequivalent pairs of quartets (four quartets) for the CF_3 groups of the Martin ligand and the link at low temperatures although a singlet was observed at room temperature. Coalescence temperatures and activation parameters are listed in Table III. The solvent effect was not apparent among dichloromethane-d_2, toluene-d_8, and acetone-d_6. It should be noted that the coalescence of the methyl protons at the NMe_2 group of **18c** and **18d** could be measured in acetone-d_6 and the activation free energy was estimated to be 11.5 kcal mol^{-1} ($\Delta\nu$ = 22 Hz) at −45 °C in **18c** and 11.4 kcal mol^{-1} ($\Delta\nu$ = 15 Hz) at −50 °C in **18d**. Thus, the activation energies for the exchange of the amino Me groups are identical with those for the exchange processes of the CF_3 groups of the Martin ligand of **18c** and **18d**, as described in Table III. Since the exchange of the methyl protons at the NMe_2 group can only take place by the dissociation of the Bi–N bond, the rate-limiting step of all the processes can be assigned as the dissociation of the Bi–N bond and rapid rotation around the Bi–C(Ar) bond should take place to effect the exchange of the Me groups and also the CF_3 groups (Scheme VIII). Therefore, the slightly higher energy for **18d** in comparison with **18c** seems to reflect an increase of the strength of the Bi–N bond due to the stronger electron-withdrawing ability of the *p*-$CF_3C_6H_4$

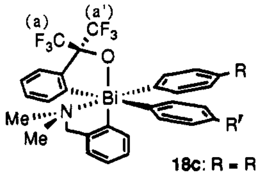
Table II. Crystal Data for 18b, 18c, and 18d

	18b	**18c**	**18d**
formula	$C_{33}H_{19}F_{18}O_2Bi$	$C_{32}H_{30}F_6ONBi$	$C_{32}H_{24}F_{12}ONBi$
mol wt	998.46	767.56	875.51
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
cryst dimens, mm	0.50 × 0.50 × 0.35	0.70 × 0.45 × 0.25	0.40 × 0.30 × 0.10
a, Å	10.980(2)	18.515(4)	95.41(4)
b, Å	12.266(1)	10.590(2)	12.793(4)
c, Å	13.125(2)	16.501(5)	13.127(5)
α, deg	99.82(1)	90	95.41(3)
β, deg	101.14(1)	113.15(2)	101.63(3)
γ, deg	98.20(1)	90	109.75(3)
V, Å^3	1680.5(4)	2975(1)	1616(1)
Z	2	4	2
D_{calc}, g cm^{-3}	1.97	1.72	1.80
abs coeff (ν), cm^{-1}	51.42	57.75	53.47
$F(000)$	956	1496	844
radiation; λ, Å	Mo Kα; 0.710 73	Mo Kα; 0.710 73	Mo Kα; 0.710 73
temp, °C	23 ± 1	23 ± 1	23 ± 1
$2\theta_{max}$, deg	50	50	50
scan rate, deg/min	14.0	10.0	4.0
linear decay, %		30	30
no. of data collcd	$\pm h,+k,\pm l$	$\pm h,+k,+l$	$+h,\pm k,\pm l$
total no. of data collcd, unique, obsd	6316, 5919, 5322 ($I > 3\sigma(I)$)	6166, 5260, 3900 ($I > 3\sigma(I)$)	6120, 5689, 4653 ($I > 3\sigma(I)$)
R_{int}	0.02	0.13	0.02
no. of params refined	544	376	421
R, R_w, S	0.043, 0.051, 1.33	0.056, 0.083, 1.04	0.054, 0.049, 1.59
max shift in final cycle	5.61	0.11	0.26
final diff map, max, e/Å^3	1.65	1.87	1.41

Table III. Coalescence Temperatures and Activation Parameters for 18a–18d



18a: R = R'=Me
18b: R = R'=CF$_3$



18c: R = R'=Me
18d: R = R'=CF$_3$

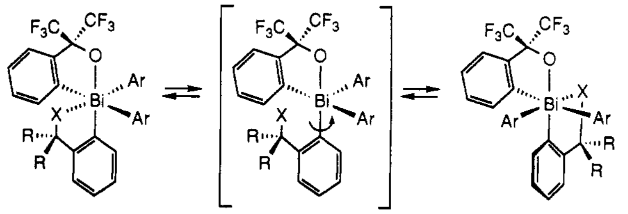
compd	solvent	probe	$\Delta\nu$ (Hz)	T_c (°C)	$\Delta G^{\neq}$ (kcal mol^{-1})
18a	CD_2Cl_2	(a)–(a′)	64.4	−40	11.2
		(b)–(b′)	ca. 17.6	−67	ca. 10.4
		R–R′	ca. 11.0	−67	ca. 11.0
	toluene-d_8	(a)–(a′)	57.1	−36	11.5
		(b)–(b′)	51.7	−42	11.2
		R–R′	10.0	−54	11.3
18b	CD_2Cl_2	(a)–(a′)	67.5	−45	11.0
		(b)–(b′)	24.8	−50	11.2
		R–R′	ca. 4.1	−65	ca. 11.1
	toluene-d_8	(a)–(a′)	77.5	−37	11.3
		(b)–(b′)	ca. 45.5	−62	ca. 10.3
		R–R′	17.6	−52	11.2
18c	CD_2Cl_2	(a)–(a′)	52.2	−36	11.5
		R–R′	7.0	−48	11.8
	acetone-d_6	(a)–(a′)	30.9	−40	11.6
		R–R′	11.7	−45	11.8
18d	CD_2Cl_2	(a)–(a′)	75.9	−24	12.0
		R–R′	4.1	−48	12.1
	acetone-d_6	(a)–(a′)	34.1	−30	12.0
		R–R′	14.5	−50	11.4

group compared to the p-$CH_3C_6H_4$ group although the Bi–N bond shortening was not apparent in the X-ray structures.

Experimental Section

Melting points were taken on a Yanagimoto micro melting 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.

Scheme VIII



Solvents and Reagents. The preparation of lithium 1,1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propoxide (4) from n-BuLi, 10% N,N,N',N'-tetramethylethylenediamine (TMEDA), and the corresponding alcohol followed the published procedure.[5] 3,3-Bis(trifluoromethyl)-1,1,1-tris(p-methylphenyl)-3H-2,1λ^5-benzoxabismole (**6a**), 3,3-bis(trifluoromethyl)-1-methyl-1,1-bis(p-methylphenyl)-3H-2,1λ^5-benzoxabismole (**6b**), 3,3-bis(trifluoromethyl)-1-p-methylphenyl-3H-2,1λ^5-benzoxabismole (**10**), 3,3-bis(trifluoromethyl)-1-chloro-1,1-bis(p-methylphenyl)-3H-2,1λ^5-benzoxabismole (**11a**), and 3,3-bis(trifluoromethyl)-1-chloro-1,1-bis[p-(trifluoromethyl)phenyl]-3H-2,1λ^5-benzoxabismole (**11b**) were reported.[7] Tetrahydrofuran (THF) and diethyl ether were distilled from sodium–benzophenone.

Reaction of 6a with Lithium Reagents. (a) Reaction of 6a with MeLi. (i) To a solution of **6a** (341 mg, 0.471 mmol) in 15 mL of THF was added 0.345 mL of methyllithium (1.365 M ether solution) at 0 °C with stirring under Ar. The reaction mixture was quenched with water, after stirring for 1.5 h at room temperature, to give **6a** (33.6 mg, 9.9%) and **6b** (212.4 mg, 69.6%), which were separated by TLC (ethyl acetate:n-hexane = 1:9). (ii) To a solution of **6a** (341 mg, 0.471 mmol) in 15 mL of THF was added 0.345 mL of methyllithium (1.365 M ether solution) at 0 °C with stirring under Ar. The reaction mixture was quenched with water, after stirring for 1 day at room temperature, to give **6a** (69.0 mg, 20.2%).

(b) Reaction of 6a with Ethyllithium. To a stirred solution of **6a** (117.6 mg, 0.16 mmol) in 1 mL of THF was added dropwise

EtLi (0.24 mmol in 0.5 mL of ether) at −78 °C. The mixture was stirred for 1 h at −78 °C and was quenched with aqueous NaCl. After workup, the crude product could be purified by TLC (SiO_2, *n*-hexane:AcOEt = 1:1). The main product was the compound **10a** (75.7 mg, yield 86.1%).

(c) **Reaction of 6a with *n*-Butyllithium.** To a stirred solution of **6a** (565.7 mg, 0.78 mmol) in 5 mL of THF was added dropwise *n*-BuLi (1.09 mmol in 0.7 mL of *n*-hexane) at −78 °C. The mixture was stirred for 1 h at −78 °C and was quenched with aqueous NaCl. After workup, the crude product could be purified by TLC (SiO_2, *n*-hexane:AcOEt = 3:1). The main product was the compound **10a** (382 mg, yield 90.3%).

1,1-Bis(*p*-methylphenyl)-1-[2-(2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl)phenyl]-3,3-bis(trifluoromethyl)-3*H*-2,1λ^5-benzoxabismole (17). The dilithiated reagent (**4**), which was prepared from bis(trifluoromethyl)benzyl alcohol (0.35 mL, 2.09 mmol), *n*-BuLi (4.65 mmol in 3.0 mL of hexane), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA: 0.075 mL, 0.50 mmol), and a small amount (ca. 0.3 mL) of THF, was added dropwise to a cold (−78 °C) stirred solution of **11a** (1.02 g, 1.53 mmol) in 9 mL of THF. The mixture was stirred for 10 h at −78 °C and quenched with aqueous NaCl at −70 °C. The aqueous layer was extracted with cold ether. The combined organic layer was dried over $MgSO_4$. After filtration, the solvent was evaporated at low temperatures, and the residue was purified by flash column chromatography (ethyl acetate:*n*-hexane = 1:6) at −20 °C to 0 °C to give **17**: 1.28 g, 95.8%. ^{1}H NMR (acetone-d_6, −20 °C) δ 2.36 (s, 6 H), 7.2–8.1 (m, 16 H); ^{1}H NMR ($CDCl_3$, room temperature) δ 2.35 (s, 6 H), 7.1–8.1 (m, 16 H); ^{19}F NMR (acetone-d_6, −20 °C) δ −72.8 (s, 12 F); ^{19}F NMR ($CDCl_3$, room temperature) −74.5 (s, 12 F); ^{19}F NMR (ether, −80 °C, 470 MHz) δ −72.0 to −72.5 (brs, 3 F), −73.3 to −73.7 (brs, 3 F), −73.7 to −74.1 (brs, 3 F), −74.4 to −74.7 (brs, 3 F); ^{19}F NMR (ether, −50 °C, 470 MHz) δ −73.5 (brs, 12 F).

Preparation of the Six-Coordinated Ate Complex (3). (a) The dilithiated reagent (**4**), which was prepared from bis(trifluoromethyl)benzyl alcohol (0.12 mL, 0.72 mmol), *n*-BuLi (1.55 mmol in 1.0 mL of hexane), and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA: 0.03 mL, 0.20 mmol), was diluted in 3 mL of THF and was added dropwise to a cold (−78 °C) stirred solution of **11a** (351 mg, 0.53 mmol) in 2 mL of THF. After 15 min of stirring at −78 °C, ca. 0.4 mL of the solution was transferred to an NMR tube by using a double ended needle (sample 1). Then, the remaining solution was warmed to room temperature and was stirred for 24 h (sample 2). The remaining solution from sample 2 was stirred further for 21 h and an excess of 12-crown-4 was added to the NMR tube (sample 3). ^{19}F NMR of samples 1 and 2 showed the same spectra at 0 °C (br q: −76.0, −76.4 ppm). The pair of quartets coalesced at 70 °C ($\Delta\nu$ = 14.9 Hz) to become a singlet, which was stable up to 150 °C. The same quartets were observed again when the solution was cooled to 0 °C. ^{19}F NMR of sample 3 showed only a sharp singlet. ^{19}F NMR of all the samples became a sharp singlet when water was added.

(b) To a solution of **12** (386 mg, 0.49 mmol) in THF (1.8 mL) was added (*p*-methylphenyl)lithium (0.53 mmol, 0.34 mL) in ether at −78 °C. The mixture was stirred for 30 min at −78 °C and ca. 0.4 mL of the solution was transferred to an NMR tube by using a double ended needle at that temperature. ^{19}F NMR of the solution at −50 °C showed the same spectrum as that by procedure a.

1,1-Bis(*p*-methylphenyl)-1-[2-(2,2,2-trifluoro-1-methoxy-1-(trifluoromethyl)ethyl)phenyl]-3,3-bis(trifluoromethyl)-3*H*-2,1λ^5-benzoxabismole (18a). A solution of *o*-$C_6H_4(I)C(CF_3)_2OMe$ (0.86 mL, 4.24 mmol) was added dropwise to *n*-BuLi (4.50 mmol in 2.9 mL of hexane) in 1 mL of THF at −78 °C with stirring. The reaction mixture was stirred at the temperature for 1 h, followed by dilution in 11 mL of THF and the solution was added to a cold solution of **11a** (2.33 g, 3.48 mmol) in 12 mL of THF. The mixture was allowed to warm from −78 to +5 °C for 12.5 h and was quenched with aqueous NaCl. After workup, compound **18a** could be purified by column chromatography (*n*-hexane:AcOEt = 5:1) to give colorless crystals (0.92 g, yield 29.7%). Mp: 232-234 °C. ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 6 H), 3.2–3.4 (m, 3 H), 7.0–8.1 (m, 16 H). ^{19}F NMR ($CDCl_3$): δ −66.6 (s, 6 F), −73.4 (s, 6 F). Anal. Calcd for $C_{33}H_{25}F_{12}O_2Bi$: C, 44.51; H, 2.83. Found: C, 44.40; H, 2.78.

1,1-Bis[*p*-(trifluoromethyl)phenyl]-1-[2-(2,2,2-trifluoro-1-methoxy-1-(trifluoromethyl)ethyl)phenyl]-3,3-bis(trifluoromethyl)-3*H*-2,1λ^5-benzoxabismole (18b). A solution of *o*-$C_6H_4(I)C(CF_3)_2OMe$ (519.7 mg, 1.35 mmol) in 7 mL of ether was added dropwise to *n*-BuLi (1.35 mmol in 0.87 mL of hexane) at −78 °C with stirring. The reaction mixture was stirred at the temperature for 1 h, and the solution was added to a cold solution (−78 °C) of **11b** (829.1 mg, 1.07 mmol) in 3 mL of ether. The mixture was allowed to warm from −78 to −30 °C for 5 h and was quenched with aqueous NH_4Cl. After workup, compound **18b** could be purified by column chromatography (*n*-hexane:AcOEt = 10:1) to give colorless crystals (1.01 g, yield 94.8%). Mp: 239–241 °C. ^{1}H NMR (toluene-d_8): δ 3.1–3.3 (m, 3 H), 6.7–8.2 (m, 16 H). ^{19}F NMR (toluene-d_8): δ −61.2 (s, 6 F), −66.2 (s, 6F), −72.5 (s, 6 F). Anal. Calcd for $C_{33}H_{19}F_{18}O_2Bi$: C, 39.70; H, 1.92. Found: C, 39.92; H, 1.98.

1,1-Bis(*p*-methylphenyl)-1-[2-((*N,N*-dimethylamino)methyl)phenyl)-3,3-bis(trifluoromethyl)-3*H*-2,1λ^5-benzoxabismole (18c). A solution of dimethylbenzylamine (0.27 mL, 1.80 mmol) in 2 mL of ether was added dropwise to *n*-BuLi (2.09 mmol in 1.35 mL of hexane) at −10 °C with stirring. The reaction mixture was stirred at room temperature for 10 h, and the solution was added to a cold solution (−10 °C) of **11a** (1.00 g, 1.50 mmol) in 10 mL of THF. After 1.5 h at −10 °C, the mixture was allowed to warm to room temperature for 13 h and was quenched with 5% aqueous $NaHCO_3$. After workup, the compound **18c** could be purified by column chromatography (*n*-hexane:AcOEt = 4:1) to give colorless crystals (0.97 g, yield 84.4%). Mp: 227-229 °C. $_1$H NMR ($CDCl_3$): δ 1.48 (s, 6 H), 2.33 (s, 6H), 3.22 (s, 2 H), 7.0–8.1 (m, 16 H). ^{19}F NMR ($CDCl_3$): δ −73.5 (s, 6 F). Anal. Calcd for $C_{32}H_{30}F_6NOBi$: C, 50.07; H, 3.94; N, 1.82. Found: C, 50.28; H, 3.98; N, 1.95.

1,1-Bis[*p*-(trifluoromethyl)phenyl]-1-[2-((*N,N*-dimethylamino)methyl)phenyl]-3,3-bis(trifluoromethyl)-3*H*-2,1λ^5-benzoxabismole (18d). A solution of dimethylbenzylamine (0.24 mL, 1.60 mmol) in 2 mL of ether was added dropwise to *n*-BuLi (1.78 mmol in 1.15 mL of hexane) at −10 °C with stirring. The reaction mixture was stirred at room temperature for 10 h. After dilution in 5 mL of ether, the solution was added to a cold solution (−10 °C) of **11b** (0.99 g, 1.28 mmol) in 7 mL of THF. After 10 min at −10 °C, the mixture was allowed to warm to room temperature for 9 h and was quenched with 5% aqueous $NaHCO_3$. After workup, the compound **18d** could be purified by column chromatography (*n*-hexane:AcOEt = 10:1) to give colorless crystals (0.83 g, yield 74.2 %). Mp: 219–222 °C. ^{1}H NMR ($CDCl_3$): δ 1.56 (s, 6 H), 3.31 (s, 2 H), 7.3–8.2 (m, 16 H). ^{19}F NMR ($CDCl_3$): δ −62.4 (s, 6 F), −73.9 (s, 6 F). Anal. Calcd for $C_{32}H_{24}F_{12}NOBi$: C, 43.90; H, 2.76; N, 1.60. Found: C, 44.10; H, 2.75; N, 1.41.

Crystallographic Studies. Crystal Structure of 18b, 18c, and 18d. 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 31 reflections for **18b**, 22 for **18c**, and 22 for **18d** reflections with 32° < 2θ < 35°, 32° < 2θ < 35°, and 31° < 2θ < 35° for **18b**, **18c**, and **18d**, respectively. Data were collected with the ω scan mode. All data were corrected for absorption[11] and extinction.[12] The structures were solved by a direct method with a program, Monte Carlo-Multan.[13] Refinement on *F* was carried out by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms in **18b**, **18c**, and **18d** were included in the refinement on calculated

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(11) Furusaki, A. *Acta Crystallogr.* **1979**, *A35*, 220.
(12) Katayama, C. *Acta Crystallogr.* **1986**, *A42*, 19.
(13) Coppens, P.; Hamilton, W. C. *Acta Crystallogr.* **1970**, *A26*, 71.

positions (C–H = 1.0 Å) riding on their carrier atoms with isotropic thermal parameters. The CF_3 groups in *p*-$CF_3C_6H_4$ in **18b** and **18d** and the CH_2NMe_2 group in **18d** were disordered; these were treated by refining the occupancies of the group in two possible configurations. All the computations were carried out on a Titan-750 computer.

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Supplementary Material Available: ORTEP diagrams and tables of crystal data, positional and thermal parameters, and complete interatomic distances and angles for **18b**, **18c**, and **18d** (51 pages). Ordering information is given on any current masthead page.

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