JOC*Article*

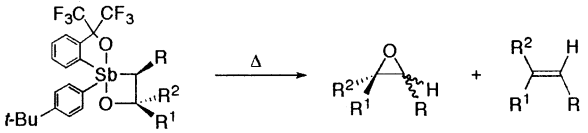
Syntheses, Structures, and Thermolyses of Pentacoordinate 1,2-Oxastibetanes: Potential Intermediates in the Reactions of Stibonium Ylides with Carbonyl Compounds

Yosuke Uchiyama, Naokazu Kano, and Takayuki Kawashima*

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

takayuki@chem.s.u-tokyo.ac.jp

Received October 3, 2005



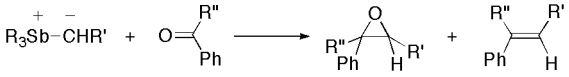
R = H, Ph; R^1, R^2 = Ph, CF_3

Pentacoordinate 1,2-oxastibetanes **14a**−**d**, which are formal [2 + 2]-cycloadducts of the reactions of stibonium ylides with carbonyl compounds, were successfully synthesized by the reactions of the corresponding bromo-2-hydroxyalkylstiboranes with NaH. The crystal structures of **14a** and **14c** were established by X-ray crystallographic analyses, showing their distorted trigonal bipyramidal structures and smaller C−Sb−O angles of the four-membered ring around antimony than the C−P−O angle of pentacoordinate 1,2-oxaphosphetane **3**. The ^{1}H, ^{13}C, and ^{19}F NMR spectra of **14a**−**d** are consistent with the trigonal bipyramidal structure in the solution state. Although **14a** did not decompose at all at 220 °C in *o*-xylene-d_{10}, the thermolyses of 3-phenyl-1,2-oxastibetane **14c** were carried out at 220 °C in *o*-xylene-d_{10} and at 140 °C in acetonitrile-d_3 to give the corresponding oxirane **28** with retention of configuration and cyclic stibinite **25**. The formation of **28** is explained by apical-equatorial ligand coupling around antimony via a polar transition state, which is more favorable than olefin formation. In contrast, the thermolyses of **14c** in the presence of LiBr and $LiBPh_4$ gave oxirane **29** with inversion of configuration and the olefin **30**, respectively. The formation of **29** and **30** is considered to proceed via an *anti*-betaine-type intermediate and hexacoordinate 1,2-oxastibetanide **36**, respectively. Selective formation of **28**, **29**, and **30** in the thermolyses of **14c**, which is regarded as an intermediate in the reaction of an α-phenyl-substituted stibonium ylide with a carbonyl compound, showed that the change of the reaction conditions controls the reactivity of a 1,2-oxastibetane compound.

Introduction

The Wittig reaction, the reaction of a phosphonium ylide with a carbonyl compound giving an olefin, is one of the most important organic transformations.[1] In contrast to the Wittig reaction, the reaction of a stibonium ylide with a carbonyl compound provides the corresponding olefin and/or oxirane, depending on the ylides and the substrates (Scheme 1).[2] The reaction of a stabilized stibonium ylide, which has a carbonyl group at the α-position of the antimony atom, with a carbonyl compound afforded the corresponding olefin as the sole product,[3] whereas a semistabilized stibonium ylide, which has a phenyl group on the α-carbon of the antimony atom, afforded both the olefin and the oxirane.[4] A nonstabilized stibonium ylide bearing no substituents was reacted with benzophenone to give an aldehyde via an oxirane.[5]

SCHEME 1



(1) (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (b) Edmonds, M.; Abell, A. In *Modern Carbonyl Olefination*; Takeda, T., Ed.; Wiley-VCH: Weinheim, Germany, 2004; pp 1−17.

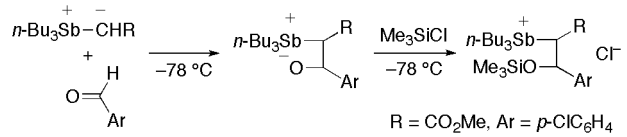
(2) Lloyd, D.; Gosney, I.; Ormiston, R. A. *Chem. Soc. Rev.* **1987**, *16*, 45.

(3) (a) Chen, C.; Huang, Y.-Z.; Shen, Y.; Liao, Y. *Heteroat. Chem.* **1990**, *1*, 49. (b) Liao, Y.; Huang, Y.-Z.; Zhang, L.-J.; Chen, C. *J. Chem. Res.* (*S*) **1990**, 388. (c) Matano, Y. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2703.

(4) Huang, Y.-Z.; Liao, Y.; Chen, C. *J. Chem. Soc., Chem. Commun.* **1990**, 85.

10.1021/jo0520700 CCC: $33.50
Published on Web 12/20/2005

SCHEME 2

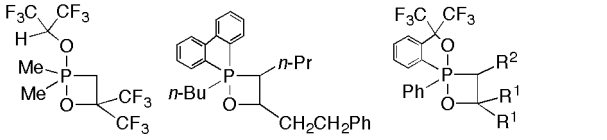


Extensive investigations on the mechanism of the Wittig reaction have been carried out, and pentacoordinate 1,2-oxaphosphetanes have been accepted as an intermediate by NMR studies.[6] In contrast, mechanistic studies on the reactions of a stibonium ylide with a carbonyl compound have been much less explored despite a variety of reactivities, and there has been no report of the isolation of an intermediate such as a pentacoordinate 1,2-oxastibetane and an *anti*-betaine. Indeed, there has been only one report of the trapping reaction of a betaine intermediate with chlorotrimethylsilane at −78 °C (Scheme 2).[3b] Another report used the results of theoretical calculations on the reaction mechanism to suggest different formation routes for the olefin and the oxirane.[7] The olefin was assumed to be formed by way of a pentacoordinate 1,2-oxastibetane as in the Wittig reaction, whereas the oxirane was assumed to be formed by the backside attack of oxide anion on the α-carbon atom of an *anti*-betaine intermediate as in the case of the Corey−Chaykovsky reaction, which is the reaction of a sulfonium ylide with a carbonyl compound to give an oxirane.[7,8]

We previously reported the oxirane formation reaction of highly coordinate 1,2-oxachalcogenetanes,[9] which are formal [2 + 2]-cycloadducts of chalcogenonium ylides with carbonyl compounds, and proposed the possibility of involvement of such 1,2-oxachalcogenetanes in the Corey−Chaykovsky reaction. These results encouraged us to explore the reactivities of pentacoordinate 1,2-oxastibetanes, which are antimony analogues of 1,2-oxaphosphetanes and 1,2-oxachalcogenetanes, to elucidate the relationship between 1,2-oxastibetanes and the reaction mechanism of olefin and/or oxirane formation in the reactions of a stibonium ylide with a carbonyl compound.

Pentacoordinate 1,2-oxastibetanes were considered to be thermally labile and unstable to moisture, as is the case of most pentacoordinate 1,2-oxaphosphetanes. Although most of the pentacoordinate 1,2-oxaphosphetanes are thermally labile, several examples such as **1** and **2** have been synthesized by taking advantage of some stabilizing groups (Chart 1).[10,11] One of the successful methods for stabilization of a pentacoordinate 1,2-oxaphosphetane is to introduce an electron-withdrawing group such as an electron-deficient alkoxy group and trifluoromethyl group on the phosphorus atom and/or the carbon atom at the 4-position.[10] Another method is to introduce a bidentate ligand on the phosphorus atom such as the 2,2′-biphenylylene group.[11] We previously reported the synthesis of isolable pentacoordinate 1,2-oxaphosphetanes **3**−**5**,[12] which are thermally stable and tolerant to moisture, by taking advantage of the Martin ligand.[13] The introduction of the Martin ligand has been found to stabilize the pentacoordinate 1,2-oxaphosphetanes effectively.

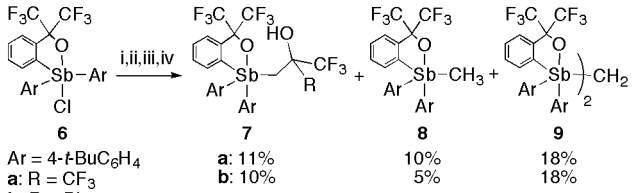
CHART 1. Examples of Spectroscopically Observed and Isolated Pentacoordinate 1,2-Oxaphosphetanes



1 **2**

3: $R^1 = CF_3$, $R^2 = H$
4: $R^1 = Ph$, $R^2 = H$
5: $R^1 = CF_3$, $R^2 = CO_2Me$

SCHEME 3 [a]



[a] Reagents and conditions: (i) *n*-BuTeCH$_2$Li (1.2 equiv), THF, −78 °C, 10 min; (ii) *n*-BuLi (1.2 equiv), THF, −78 °C, 10 min; (iii) $(F_3C)_2C{=}O$ or $Ph(F_3C)C{=}O$ (excess), THF, −78 °C to rt; (iv) H_3O^+.

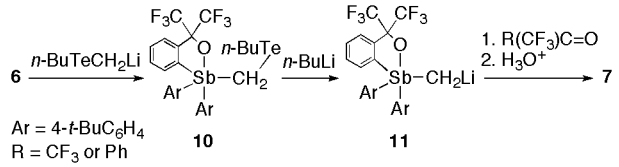
We previously reported the synthesis and thermolysis of pentacoordinate 3-phenyl-1,2-oxastibetanes bearing the Martin ligand as a preliminary communication.[14] In this report, we describe the syntheses, structures, and thermolyses of pentacoordinate 1,2-oxastibetanes in detail as well as the reaction mechanism for the thermolyses.

Results and Discussion

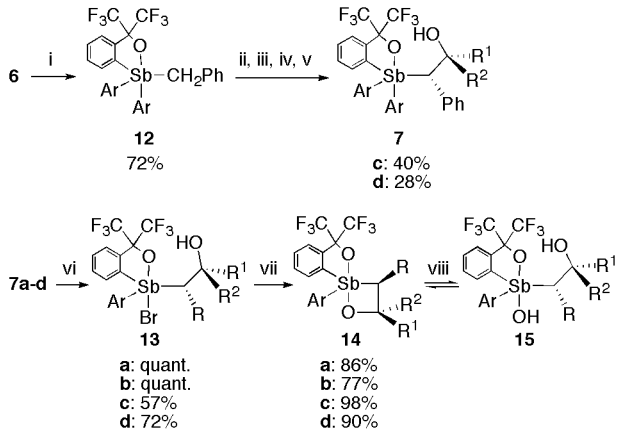
Syntheses. Pentacoordinate 1,2-oxastibetanes were synthesized by stepwise methods. Successive treatment of chlorostiborane **6** bearing the Martin ligand, which was prepared similarly to a reported procedure,[15] with lithium butyltelluromethylide (1.2 equiv), *n*-BuLi (1.2 equiv), hexafluoroacetone (denoted as HFA hereafter) (excess), and aqueous NH_4Cl gave the corresponding 2-hydroxyalkylstiborane **7a** (11%) together with diaryl(methyl)stiborane **8** (10%) and bis(stibonyl)methane **9** (18%) (Scheme 3).[16] A similar reaction with excess trifluoroacetophenone instead of HFA gave **7b** (10%), **8** (5%), and **9** (18%). Intramolecular hydrogen bonds between the hydroxy group and the oxygen atom of the Martin ligand were observed in the IR spectra of **7a** and **7b** (ν = 3073 and 3068 cm^{-1},

(5) Henry, M. C.; Wittig, G. *J. Am. Chem. Soc.* **1960**, *82*, 563.
(6) (a) Vedejs, E.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1973**, *95*, 5778. (b) Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 2823.
(7) Naito, T.; Nagase, S.; Yamataka, H. *J. Am. Chem. Soc.* **1994**, *116*, 10080.
(8) (a) Johnson, A. W.; LaCount, R. B. *J. Am. Chem. Soc.* **1961**, *83*, 417. (b) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1962**, *84*, 3782. (c) Aubé, J. In *Comprehensive Organic Synthesis*: *Selectivity, Strategy, and Efficiency in Modern Synthetic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, UK, 1991; pp 819−842.
(9) (a) Ohno, F.; Kawashima, T.; Okazaki, R. *J. Am. Chem. Soc.* **1996**, *118*, 697. (b) Kawashima, T.; Ohno, F.; Okazaki, R.; Ikeda, H.; Inagaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 12455. (c) Ohno, F.; Kawashima, T.; Okazaki, R. *Chem. Commun.* **1997**, 1671. (d) Ohno, F.; Kawashima, T.; Okazaki, R. *Chem. Commun.* **2001**, 463. (e) Kano, N.; Takahashi, T.; Kawashima, T. *Tetrahedron Lett.* **2002**, *43*, 6775.
(10) Ramirez, F.; Smith, C. P.; Pilot, J. F. *J. Am. Chem. Soc.* **1968**, *90*, 6726.
(11) Vedejs, E.; Marth, C. *Tetrahedron Lett.* **1987**, *28*, 3445.
(12) (a) Kawashima, T.; Kato, K.; Okazaki, R. *J. Am. Chem. Soc.* **1992**, *114*, 4008. (b) Kawashima, T.; Kato, K.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 869.
(13) 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*, 1049.
(14) Uchiyama, Y.; Kano, N.; Kawashima, T. *J. Am. Chem. Soc.* **2003**, *125*, 13346.
(15) (a) Akiba, K.-y.; Fujikawa, H.; Sunaguchi, Y.; Yamamoto, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1245. (b) Yamamoto, Y.; Fujikawa, H.; Fujishima, H.; Akiba, K.-y. *J. Am. Chem. Soc.* **1989**, *111*, 2276.
(16) Hiiro, T.; Atarashi, Y.; Kambe, N.; Fujiwara, S.; Ogawa, A.; Ryu, I.; Sonoda, N. *Organometallics* **1990**, *9*, 1355.

SCHEME 4



SCHEME 5 [a]



Ar = 4-*t*-BuC$_6$H$_4$, **a**: R = H, R^1,R^2 = CF$_3$, **b**: R = H, R^1,R^2 = CF$_3$,Ph, **c**: R = Ph, R^1 = Ph, R^2 = CF$_3$, **d**: R = Ph, R^1 = CF$_3$, R^2 = Ph

[a] Reagents and conditions: (i) PhCH$_2$MgCl (1.2 equiv), Et$_2$O, 0 °C, 2 h; (ii) LiTMP (2.2 equiv), benzene, rt, 12 h; (iii) Ph(F$_3$C)C═O (2.2 equiv), rt, 30 min; (iv) H_3O^+; (v) column chromatography (SiO_2); (vi) Br_2 (2.0 equiv), $CHCl_3$, rt, 1 h; (vii) NaH (4.0 equiv), THF, rt, 2 h; (viii) H_2O.

respectively). We propose a reaction mechanism for the formation of **7a**, **7b**, **8**, and **9**: Chlorostiborane **6** is first substituted nucleophilically by butyltelluromethylide to give butyltelluromethylstiborane **10** (Scheme 4), which undergoes Te−Li exchange with *n*-BuLi to give lithium stibonylmethylide **11**.[16] Addition reaction of stibonylmethylide **11** with the ketones followed by protonation gave **7a** or **7b**, whereas its hydrolysis and its addition to chlorostiborane **6** gave undesired products **8** and **9**, respectively.

Synthesis of (2-hydroxy-1-phenylalkyl)stiboranes **7c** and **7d** required a new synthetic method different from that used for the syntheses of **7a** and **7b** because the corresponding lithium butyltellurobenzylide was not available. Benzylstiborane **12**, which was easily prepared by the reaction of chlorostiborane **6** with benzylmagnesium chloride (1.2 equiv) in 72% yield, was reacted successively with lithium tetramethylpiperidide (denoted as LiTMP hereafter) (2.2 equiv) in benzene at room temperature for 12 h, trifluoroacetophenone (2.2 equiv), and aqueous NH_4Cl (Scheme 5). A mixture of the diastereomers of 2-hydroxyalkylstiboranes **7c** and **7d** was separated by column chromatography (SiO_2) to afford **7c** (40%) and **7d** (28%). The stereochemistry of **7c** and **7d** was deduced from the relative stereochemistry of the finally obtained 1,2-oxastibetane, whose structure was determined by X-ray crystallographic analysis (see below).

Treatment of 2-hydroxyalkylstiboranes **7a** and **7b** with bromine (1.2 equiv) in $CHCl_3$ resulted in quantitative formation of the corresponding bromo(2-hydroxyalkyl)stiboranes **13a** and **13b**, respectively (Scheme 5).[15,17] 4-Bromo-*tert*-butylbenzene was detected by ^{1}H NMR spectroscopy and GC-MS. Aromatic electrophilic substitution took place at the *ipso*-position of the aryl group attached to the antimony to give bromo(2-hydroxyalkyl)stiboranes **13a** and **13b**, as in the formation of chlorostiborane **6**.[15] The substitution of the aryl group instead of the alkyl group is in marked contrast to the reaction of diaryl(methyl)bismuthane bearing the Martin ligand with sulfuryl chloride and bromine giving diarylchloro- and diarylbromobismuthane, respectively.[15] Similarly to the syntheses of **13a** and **13b**, **7c** and **7d** were converted to bromo(2-hydroxyalkyl)stiboranes **13c** (57%) and **13d** (72%), respectively.

Treatment of bromo(2-hydroxyalkyl)stiboranes **13a**, **13b**, **13c**, and **13d** with excess NaH in THF provided the corresponding 1,2-oxastibetanes **14a** (86%), **14b** (77%), **14c** (98%), and **14d** (90%), respectively (Scheme 5). Although **14a** and **14c** were stable in air, **14b** and **14d** were somewhat unstable to moisture. In contrast to 1,2-oxastibetanes **14a** and **14c**, **14b** and **14d** came to equilibrium in $CDCl_3$ with hydroxystiboranes **15b** and **15d**, respectively, which were observed in the ^{1}H and ^{19}F NMR spectra. The equilibrium ratios of **14b** to **15b** in $CDCl_3$ were 1.8:1 at room temperature and 18:1 at 60 °C, suggesting that the dehydration of **15b** tends to proceed at higher temperature. These results indicated that the number and relative configuration of electron-withdrawing trifluoromethyl groups at the 4-position of 1,2-oxastibetane are important for the stability to water.

All the products **6**−**9** and **12**−**14** were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, FAB-MS, and elemental analyses. The stereochemistry of 1,2-oxastibetane **14c** was determined by X-ray crystallographic analysis (Figure 1). In contrast, **14b** and **14d** could not be isolated due to their instability to moisture and the equilibrium with **15b** and **15d**, respectively. Their stereochemistry at the 3-position of the 1,2-oxastibetane ring was inferred by analogy with spectral data for the 1,2-oxathietanes and comparison with those of **14c**.[9b] The yields of 1,2-oxastibetane **14b** and **14d** were estimated by ^{19}F NMR spectroscopy.

Another synthetic route to the pentacoordinate 1,2-oxastibetane is a direct reaction of a stibonium ylide with a ketone. Benzylstiborane **12** was allowed to react with bromine to afford benzylbromostiborane **16** (98%). Treatment of **16** with silver

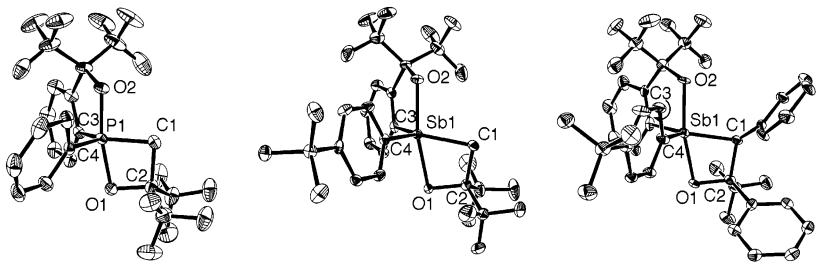
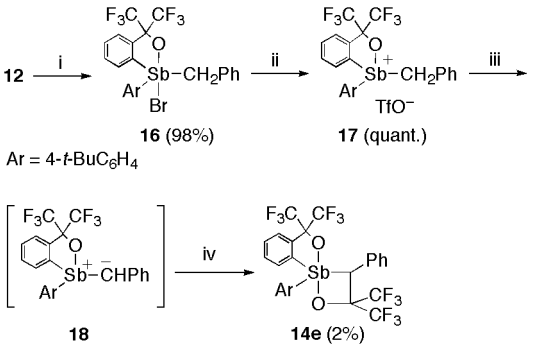


FIGURE 1. ORTEP drawings of 1,2-oxaphosphetane **3** (left) and 1,2-oxastibetanes **14a** (center) and **14c** (right) with thermal ellipsoid plots (50% probability). Hydrogen atoms are omitted for clarity.

SCHEME 6 [a]



[a] Reagents and conditions: (i) Br_2 (1.2 equiv), $CHCl_3$, rt, 0.5 h; (ii) AgOTf (1.2 equiv), THF, rt, 4 h; (iii) LiTMP (2.0 equiv), THF, −78 °C, 4 h; (iv) $(CF_3)_2C{=}O$ (excess).

TABLE 1. Crystallographic Data of 3, 14a, and 14c

	3	**14a**	**14c**
formula	$C_{19}H_{11}F_{12}O_2P$	$C_{23}H_{19}F_{12}O_2Sb$	$C_{34}H_{28}F_9O_2Sb$
FW	530.25	677.13	761.31
cryst System	triclinic	triclinic	monoclinic
a/Å	13.246(8)	10.691(3)	18.148(3)
b/Å	14.373(8)	12.257(4)	9.737(2)
c/Å	22.504(10)	19.324(7)	36.418(7)
α/deg	74.13(2)	102.894(6)	90
β/deg	82.51(2)	90.004(5)	98.600(8)
γ/deg	87.62(2)	91.278(5)	90
V/Å^3	4086(4)	2468(2)	3176.6(17)
space group	$P\bar{1}$	$P\bar{1}$	*C*2/*c*
Z	8	4	8
D_{calcd}/gcm^{-1}	1.724	1.823	1.590
*R*1 ($I > 2\sigma(I)$)	0.0820	0.0619	0.1016
*wR*2 (all data)	0.1489	0.0672	0.1799
GOF	1.069	1.097	1.427

triflate gave benzylstibonium triflate **17** (Scheme 6). Addition of LiTMP (2.0 equiv) to benzylstibonium triflate **17** at −78 °C in THF followed by bubbling of HFA (excess) afforded 3-phenyl-1,2-oxastibetane **14e** in 2% yield. The crude material contained mainly the benzylbutylstiborane and butyl(2-hydroxyalkyl)stiborane that were formed by the attack of *n*-BuLi, which was used to prepare LiTMP, on **17** or stibonium ylide **18** and **14e**, respectively.

X-ray Crystallographic Analyses. Single crystals of 1,2-oxaphosphetane **3** and 1,2-oxastibetanes **14a** and **14c** were obtained by recrystallization from hexane. X-ray crystallographic analyses of **3**, **14a**, and **14c** were performed to clarify the crystal structures and the relative configurations. The unit cell of **3** contains four independent molecules, which have similar conformations around the phosphorus atom, and that of **14a** contains two independent molecules. ORTEP drawings of **3** (one of four molecules), **14a** (one of two molecules), and **14c** are shown in Figure 1. Their crystallographic data, selected bond lengths, and angles are summarized in Tables 1 and 2.

The X-ray crystallographic analyses of **14a** and **14c**, similarly to that of **3**, showed their distorted trigonal bipyramidal (TBP) structures with two oxygen atoms at the apical positions and three carbon atoms at the equatorial positions in the crystalline state. The relative configuration of the phenyl group at the 3-position of **14c** is cis to both the 4-*tert*-butylphenyl group and the phenyl group at the 4-position of the 1,2-oxastibetane ring.

The O1−Sb1−O2 bond angles of both **14a** [166.2(1)°] and **14c** [165.4(2)°] deviated from linearity. Such a deviation is a common structural feature of hypervalent compounds containing a four-membered ring.[9,12,14] The C1−Sb1−C4 bond angle of **14c** [120.4(3)°] is somewhat wider than that of **14a** [115.7(1)°] because of the steric repulsion between the phenyl group at the 3-position of the 1,2-oxastibetane ring and the 4-*tert*-butylphenyl group on the antimony atom of **14c**. Judging from the torsion angles of Sb1−C1−C2−O1 [8.6(3)° for **14a** and 1.1(5)° for **14c**] and the sum of the interior angles of the 1,2-oxastibetane ring [359.0° for **14a** and 360.0° for **14c**], the 1,2-oxastibetane ring of **14c** is almost planar, while that of **14a** slightly deviates from planarity.

TABLE 2. Selected Bond Lengths (Å) and Angles (deg) of 3, 14a, and 14c

	3 (Pn = P)	**14a** (Pn = Sb)	**14c** (Pn = Sb)
Pn1−O1	1.779(2)	2.075(2)	2.059(5)
Pn1−O2	1.722(2)	2.024(2)	2.039(5)
Pn1−C1	1.827(3)	2.118(3)	2.132(7)
Pn1−C3	1.805(3)	2.080(3)	2.103(8)
Pn1−C4	1.814(3)	2.086(3)	2.110(7)
C1−C2	1.541(4)	1.543(4)	1.587(10)
O1−C2	1.408(3)	1.406(4)	1.437(8)
O1−Pn1−O2	168.5(1)	166.17(9)	165.4(2)
O1−Pn1−C1	76.5(1)	68.2(1)	69.8(2)
O1−Pn1−C3	93.4(1)	95.7(1)	99.4(3)
O1−Pn1−C4	94.4(1)	97.5(1)	97.9(2)
O2−Pn1−C1	92.9(1)	101.4(1)	97.4(2)
O2−Pn1−C3	88.9(1)	82.1(1)	81.3(3)
O2−Pn1−C4	94.6(1)	95.3(1)	94.7(2)
C1−Pn1−C3	124.9(1)	122.7(1)	122.9(3)
C1−Pn1−C4	117.2(1)	115.7(1)	120.4(3)
C3−Pn1−C4	117.5(1)	121.0(1)	116.5(3)
Pn1−C1−C2	89.3(2)	89.7(2)	89.0(4)
Pn1−O1−C2	95.7(2)	95.4(2)	96.3(4)
C1−C2−O1	98.4(2)	105.7(3)	104.9(5)

The C1−Sb1−O1 [68.2(1)°] angle of **14a** is smaller than the corresponding angles [76.5(1)°] of **3**, indicating that the structure of **14a** is more distorted from the ideal TBP structure than that of **3**. The large distortion of **14a** results from the longer pnictogen Pn−O and Pn−C bond lengths of **14a** (Pn = Sb) than those of **3** (Pn = P) corresponding to the atomic radius of the central atom (P:1.10 Å, Sb:1.41 Å).[18]

NMR Studies. In the ^{1}H NMR spectra of 1,2-oxastibetanes **14a**−**d**, signals due to the ortho protons of the Martin ligand relative to the antimony atom were observed at a lower field (δ_H 8.02−8.21) than those of other aryl protons, as observed with other hypervalent compounds with a TBP structure bearing the Martin ligand.[9,12,14] In the ^{19}F NMR spectra, **14a**−**d** showed a pair of quartets due to the CF_3 groups of the Martin ligand. These spectral features of **14a**−**d** are consistent with the TBP structures in the crystalline state.

When the single crystals of 3-phenyl-1,2-oxastibetane **14c** were dissolved in $CDCl_3$, the solution initially showed only one set of signals, at δ −79.3 (s, 3F), −76.8 (q, $^4J_{FF}$ = 8.2 Hz, 3F), and −74.3 (q, $^4J_{FF}$ = 8.2 Hz, 3F) in the ^{19}F NMR spectra. After the sample was allowed to stand at room temperature for 1 h, a new set of signals at δ −78.0 (s, 3F), −75.5 (q, $^4J_{FF}$ = 9.4 Hz, 3F), and −74.4 (q, $^4J_{FF}$ = 9.4 Hz, 3F) together with the original signals were observed in the ^{19}F NMR spectra. The integral ratio (the new peaks:the original peaks = 1:4) subsequently remained unchanged at room temperature. In the ^{1}H

(17) Chen, X.; Ohdoi, K.; Yamamoto, Y.; Akiba, K.-y. *Organometallics* **1993**, *12*, 1857.
(18) Emsley, J. In *The Elements*, 3rd ed.; Oxford University Press: New York, 1998; pp 22−23, 152−153.

SCHEME 7

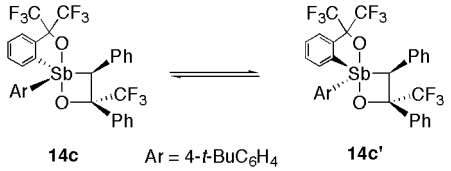
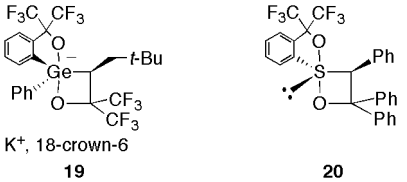


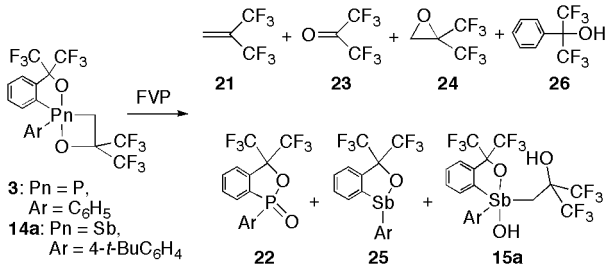
CHART 2. Examples of the Compounds that Epimerize: 1,2-Oxagermetanide 19 (left) and 1,2-Oxathietane 20 (right)



NMR spectra, the chemical shift due to the ortho proton of the Martin ligand (δ_H 8.41) of the newly generated compound was observed at a lower field than that of **14c** (δ_H 8.19). The large inequality of the two quartets in the ^{19}F NMR spectra and the downfield shift of the ortho proton in the ^{1}H NMR spectra of the new compound are consistent with the epimer **14c′** without a change of configuration at the 3- and 4-positions of the 1,2-oxastibetane ring, which is in equilibrium with **14c** in solution (Scheme 7). Another candidate for the newly generated compound is the pseudorotamer bearing a carbon atom of the four-membered ring at the apical position, which was observed in pentacoordinate 1,2-azaphosphetidines and some pentacoordinate 1,2-oxaphosphetanes,[19,20] though it is excluded by inconsistency with the downfield shift of the ortho proton in the ^{1}H NMR spectra. Pentacoordinate 1,2-oxagermetanide **19**[21] and tetracoordinate 1,2-oxathietane **20**[9a] also showed such an equilibrium with the epimers under thermal conditions (Chart 2). These epimerization reactions are considered to proceed via pseudorotation.

Flash Vacuum Pyrolysis (FVP) of 1,2-Oxastibetane 14a and Its Reaction Mechanism. Thermolyses of 1,2-oxastibetanes were attempted to obtain some experimental information about the mechanism of the reactions of a stibonium ylide with a carbonyl compound because the pentacoordinate 1,2-oxastibetanes were expected to be intermediates in the olefin formation reaction. However, neither **14a** nor **14b** decomposed in *o*-xylene-d_{10} upon heating, even at 220 °C. Their thermal stability contrasted with the thermolysis of 1,2-oxaphosphetane **3** in toluene-d_8 at 200 °C for 11 h giving olefin **21** (65%) and cyclic phosphinate **22** (65%) with recovery of **3** (35%).[12] Flash vacuum pyrolyses[22] of **14a** and **3** were carried out at a much higher temperature. All products were detected by ^{1}H NMR, ^{19}F NMR, and GC-MS and their yields were determined by ^{19}F NMR spectroscopy. Upon heating at 500 °C with nitrogen flow for 6 h, **3** decomposed entirely (Scheme 8 and Table 3). The decomposition products of **3** were olefin **21** (55%), cyclic phosphinate **22** (85%), and hexafluoroacetone **23** (5%). In contrast, 1,2-oxastibetane **14a** was recovered in 45% yield in its FVP under similar conditions. The products of the FVP of **14a** were olefin **21** (4%), oxirane **24** (15%), cyclic stibinite **25** (13%), hexafluorocumyl alcohol **26** (1%), and hydroxystiborane **15a** (6%). It is interesting that the FVP of 1,2-oxastibetane **14a** gave oxirane **24** and cyclic stibinite **25**, whereas that of 1,2-oxaphosphetane **3** gave neither oxirane **24** nor the corresponding cyclic phosphinite at all. Hydroxystiborane **15a** was probably obtained by hydrolysis of **14a**.

SCHEME 8 [a]

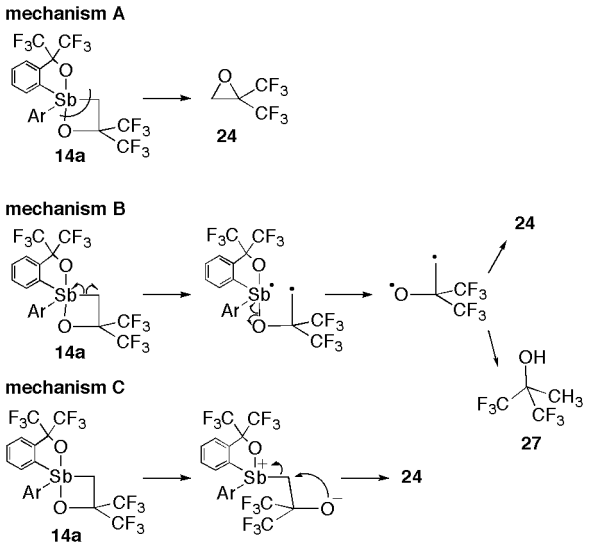


[a] FVP condition: 500 °C, 1 × 10^{-1} Torr, N_2 flow.

TABLE 3. Results of FVP of 1,2-Oxaphosphetane 3 and 1,2-Oxastibetane 14a

	yields (%)							
	recovery	**21**	**22**	**23**	**24**	**25**	**26**	**15a**
3 (Pn = P)	0	55	85	5	0	0	0	0
14a (Pn = Sb)	45	4	0	0	15	13	1	6

SCHEME 9. Formation Mechanisms of Oxirane 24 by FVP of 14a



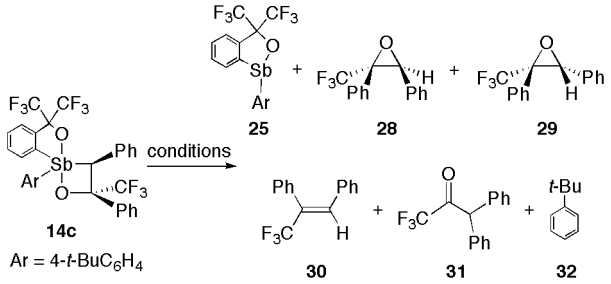
There are three possibilities for the formation mechanism of oxirane **24**: the ligand coupling reaction through the formal apical-equatorial coupling (mechanism A), the radical mechanism (mechanism B), and the intramolecular attack of the oxide anion of an *anti*-betaine intermediate on the carbon atom attached to the antimony atom (mechanism C) (Scheme 9). The Sb−O (314 kJ/mol) and Sb−C (215 kJ/mol) bond energies are smaller than the P−O (407 kJ/mol) and P−C (264 kJ/mol) bond energies,[18] respectively, and homolytic cleavage could occur easily. But, if the reaction proceeded through the radical pathway as in the case of 1,2-oxatelluretane,[9e] the corresponding alcohol **27** should be obtained by hydrogen abstraction. The absence of the formation of **27** suggests that **24** is unlikely to be formed

(19) Kawashima, T.; Soda, T.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1096.
(20) Kojima, S.; Sugino, M.; Matsukawa, S.; Nakamoto, M.; Akiba, K.-y. *J. Am. Chem. Soc.* **2002**, *124*, 7674.
(21) Kawashima, T.; Nishiwaki, Y.; Okazaki, R. *J. Organomet. Chem.* **1995**, *499*, 143.
(22) (a) Yamamoto, Y.; Akiba, K.-y. In *Chemistry of Hypervalent Compounds*; Akiba, K.-y., Ed.; Wiley: New York, 1998; Chapter 9, pp 279−294. (b) Akiba, K.-y. *Pure Appl. Chem.* **1996**, *68*, 837.

TABLE 4. Thermolyses of 3-Phenyl-1,2-oxastibetane 14c under Various Conditions

	conditions				yields (%)						
entry	solvent	temp/°C	time/h	additive	**14c**	**25**	**28**	**29**	**30**	**31**	**32**
1	*o*-xylene-d_{10}	220	17	none	5	89	90	0	0	5	5
2	*o*-xylene-d_{10}	140	48	none	98	2	2	0	0	0	0
3	CD_3CN	140	9	none	98	2	2	0	0	0	0
4	CD_3CN	140	48	none	52	48	46	0	0	0	0
5	CD_3CN	140	112.5	none	19	80	80	0	0	1	1
6	CD_3CN	140	10	LiBr	12	88	10	71	0	0	0
7	CD_3CN	140	10	LiI	56	44	18	19	0	0	0
8	CD_3CN	140	43	$(n\text{-Bu})_4NBr$	68	32	13	18	2	0	0
9	CD_3CN	140	43	$(n\text{-Bu})_4NI$	61	39	33	<1	<1	0	0
10	CD_3CN	140	10	$LiBPh_4$·3DME	10	<1	<1	<1	85	0	0

SCHEME 10



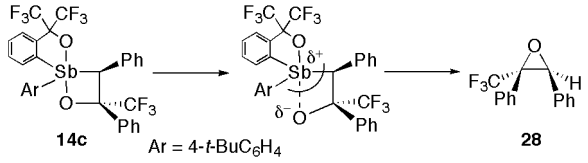
by the radical reaction though mechanism B cannot be ruled out completely due to the low total yields of identified products. Furthermore, the reaction is unlikely to proceed via an *anti*-betaine (mechanism C), because the polar state is highly unstable in the gas phase even though the Sb−O bond of **14a** is more polar than the P−O bond of **3**. Thus, we think that the oxirane is formed via mechanism A, although it cannot be determined unambiguously.

Thermolyses of 1,2-oxastibetane 14c. Thermolyses of 1,2-oxastibetane **14c** bearing a phenyl group on the 3-position of the 1,2-oxastibetane ring were investigated to determine the stereochemistry of the oxirane formation reactions of a pentacoordinate 1,2-oxastibetane and to get some information about the reaction mechanism. The results are summarized in Scheme 10 and Table 4. Thermolysis of **14c** in *o*-xylene-d_{10} at 220 °C for 17 h gave the corresponding oxirane **28** (90%) with retention of relative configuration and stibine **25** (89%) in high yields (entry 1). Neither oxirane **29** with inversion of configuration nor olefin **30** were formed at all, whereas trace amounts of rearranged ketone **31** and *tert*-butylbenzene **32** were formed. Relative thermal instability of **14c** and the simple results of the thermolysis are in contrast to the FVP of 1,2-oxastibetane **14a**. Furthermore, the reaction rates for the thermolysis of **14c** depend on the solvents used. Upon heating at 140 °C for 48 h, 48% of **14c** was converted in CD_3CN to give **28** (46%), whereas only 2% of **14c** was converted in *o*-xylene-d_{10} to give **28** (2%) (entries 2 and 4). These results show that a polar solvent accelerates the thermolysis of **14c** and that **28** forms faster in CD_3CN than in *o*-xylene-d_{10}.

Thermolyses of **14c** in the presence of LiBr and LiI as the additive in CD_3CN at 140 °C for 10 h provided **28** in 10% and 18% yields, respectively (entries 6 and 7), which are better yields than that in the absence of any additives (2%) (entry 3). These results suggested that the counteranions of lithium salts affect the yields of **28** in the thermolyses of **14c**.

Use of LiBr and $(n\text{-Bu})_4NBr$ as the additive in the thermolysis of **14c** gave better yields of **29** than that of LiI and $(n\text{-Bu})_4NI$ (entries 6−9). The use of lithium salts gave much better yields

SCHEME 11



of **29** than that of tetrabutylammonium salts despite the short reaction time. In contrast, the thermolysis of **14c** alone gave no **29** (entry 5). These results indicate that both lithium cation and bromide anion are important for the formation of oxirane **29** with inversion of configuration in the thermolyses of **14c**.

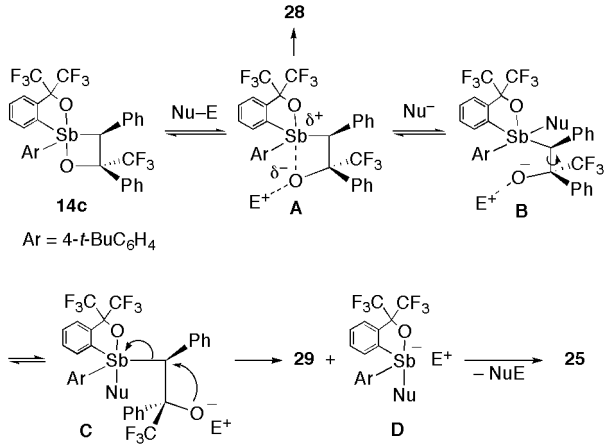
The thermolysis of **14c** in the presence of $(n\text{-Bu})_4NBr$ or $(n\text{-Bu})_4NI$ provided a trace amount of olefin **30**, which was not obtained at all in the reactions with LiBr and LiI (entries 6−9). Interestingly, olefin **30** was obtained in good yield (85%) in the thermolysis of **14c** in the presence of $LiBPh_4$·3DME complex (entry 10). The counterpart of **30**, compounds bearing both antimony and the Martin ligand such as **25**, could not be obtained as compounds identified by NMR spectroscopy and mass spectrometry.

Plausible Mechanism for the Formation of Oxiranes 28 and 29. The formation of oxirane **28** with retention of configuration is explained by the formal apical−equatorial ligand coupling on the antimony atom because the stereochemistry was retained in the formation of **28** from **14c** alone (Scheme 11). The apical−equatorial ligand coupling is symmetry forbidden and the apical−apical or equatorial−equatorial coupling is symmetry allowed, according to the Woodward−Hoffmann rule.[23] In a theoretical calculation on the reaction pathway of the H_2 elimination of a series of PnH_5 (Pn = P, As, Sb, and Bi) species, PnH_5 (Pn = P, As, and Sb) undergo the equatorial−equatorial ligand coupling, whereas pentahydrobismuthane undergoes polar apical−equatorial ligand coupling.[23] Although the apical−equatorial ligand coupling reactions of stiboranes **14c** in thermal conditions are considered to be unfavorable, such a ligand coupling may occur if the reaction proceeds via a polar transition state similar to that expected by the theoretical calculation on the reaction pathway of pentahydrobismuthane.[23] In the thermolyses of **14c**, the transition state to give **28** should be more stabilized by the polar Sb−O bond, which is much more polar than the Sb−H bond of the pentahydrostiborane. The clearly observed solvent effect in the thermolysis of **14c** supports that the reaction proceeded via a polar transition state (Scheme 11).

The plausible mechanisms for the formation of oxiranes **28** and **29** in the thermolyses of **14c** in the presence of additives

(23) Moc, J.; Morokuma, K. *J. Am. Chem. Soc.* **1995**, *117*, 11790.

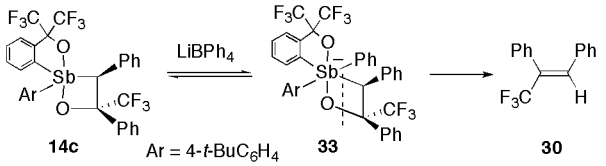
SCHEME 12



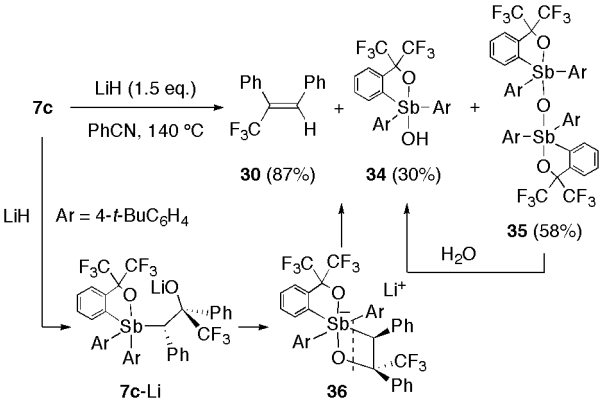
are summarized in Scheme 12. A Lewis acid, such as the lithium cation, coordinates to the oxygen of the Sb−O bond of **14c** to give a polar transition state **A**, which easily gives oxirane **28** by ligand coupling at antimony. A nucleophile such as the bromide ion attacks the antimony atom of **A**, and the Sb−O bond cleaves to afford **B**. Both the cation−oxygen interaction and the attack on antimony by the nucleophile promote cleavage of the Sb−O bond. After the C−C bond rotation to form intermediate **C**, attack of the oxide anion of **C** on the carbon atom next to the antimony and elimination of stiborate **D** gives oxirane **29**. Elimination of the salt, NuE, from **D** yields stibine **25**. Therefore, the thermolysis of **14c** to give oxirane **28** was accelerated in the presence of LiBr or LiI compared with that without salts under similar conditions. In contrast, the yields of oxirane **28** decreased in the thermolyses of **14c** in the presence of ammonium salts and $LiBPh_4$·3DME, because the interaction between the antimony and the counteranion is more predominant than the $E^+\cdots O$ interaction and the polar transition state **A**, which leads to **B**, is destabilized. Both the $E^+\cdots O$ interaction and the nucleophilic attack of the nucleophile on the antimony atom are important for the formation of oxirane **29**. The ratio of **29** to **28** is higher in the presence of a lithium salt than an ammonium salt as the additive. Furthermore, the ratio is higher in the thermolysis with LiBr than with LiI. The former fact is explained by noting that Sb−O bond cleavage proceeds more easily because there is the $Li^+\cdots O$ interaction. The latter fact is explained by noting that the reverse reaction of **B** to **A** is retarded because of the poor leaving ability of the bromide anion compared with the iodide anion. Thus, both lithium cation and bromide anion play important roles in the formation of oxirane **29** with inversion of configuration.

Plausible Mechanism for the Formation of Olefin 30. Formation of olefin **30** in the thermolyses of **14c** with $(n\text{-Bu})_4NBr$ and $(n\text{-Bu})_4NI$ and the lack of formation in thermolyses with LiBr and LiI indicate the importance of the character of the cation of the additives for the formation of **30**. Because the tetrabutylammonium ion is inert toward oxygen compared with lithium ion, the olefin formation is independent of both the cation−oxygen interaction and the Sb−O bond cleavage. Moreover, the high yield of **30** in the thermolysis of **14c** with $LiBPh_4$·3DME should be mentioned. In this case, the $Li^+\cdots O$ interaction is not effective for the formation of **30** because the lithium cation should interact with DME, which is included in commercially available $LiBPh_4$. As mentioned above, other products containing antimony and the Martin ligand were obtained as a complex mixture and could not be identified by

SCHEME 13



SCHEME 14



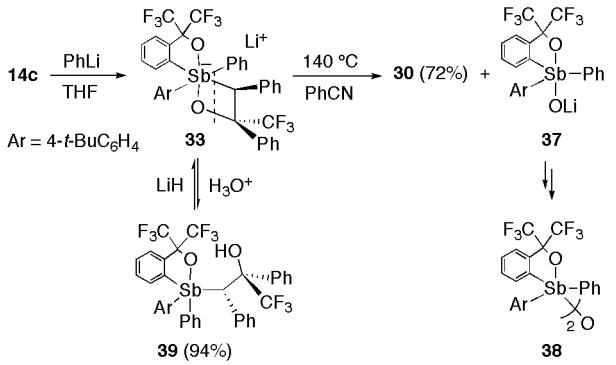
^1H and ^{19}F NMR spectroscopy. The FAB-MS of the reaction mixture showed a peak at *m*/*z* 573, which is attributable to a fragment ion of the antimony compound ($R_FSbPhAr$: R_F = the Martin ligand, Ar = 4-*t*-BuC_6H_4). This result strongly suggests that a phenyl group was transferred from tetraphenylborate onto the antimony atom of **14c** to generate the corresponding hexacoordinate phenyl-1,2-oxastibetanide **33**, which gave olefin **30** (Scheme 13). The formation of olefin **30** would proceed via cleavage of the Sb−C and C−O bonds of the 1,2-oxastibetane ring. Transformation of the equatorial (sp^2) bonds of **14c** to the weaker hypervalent bonds of a hexacoordinate compound **33** would enable the olefin formation reaction. A similar hexacoordinate antimony intermediate has been postulated in the formation of an olefin bearing an electron-withdrawing group from an α-stiboranylcarbanion and benzaldehyde, while hexacoordinate species bearing a 1,2-oxastibetane ring have never been observed.[24,25]

Formation of Hexacoordinate 1,2-Oxastibetanides and Their Reactivity. To clarify whether the hexacoordinate species gives the corresponding olefin or not, hexacoordinate 1,2-oxastibetanides were synthesized by other methods. The 2-hydroxyalkylstiborane **7c** was heated with 1.5 equiv of LiH at 140 °C for 6 h to give olefin **30** (87%) together with hydroxystiborane **34** (30%) and bis(stiboranyl)oxide **35** (58%) (Scheme 14). Therefore, we considered that olefin **30** and hydroxystiborane **34** were obtained by decomposition of hexacoordinate 1,2-oxastibetanide **36** that was generated from **7c**-Li (Scheme 14). Formation of only one isomer of **36** was detected by ^{19}F NMR spectroscopy of the reaction solution at δ −73.6 (s, 3F), −76.4 (q, $^4J_{FF}$ = 8.5 Hz, 3F), and −77.0 (q, $^4J_{FF}$ = 8.5 Hz, 3F), showing that there was only one isomer,

(24) Kojima, S.; Takagi, R.; Akiba, K.-y. *J. Am. Chem. Soc.* **1997**, *119*, 5970.

(25) (a) Matsukawa, S.; Kojima, S.; Kajiyama, K.; Yamamoto, Y.; Akiba, K.-y.; Re, S.; Nagase, S. *J. Am. Chem. Soc.* **2002**, *124*, 13154. (b) Kawashima, T.; Watanabe, K.; Okazaki, R. *Tetrahedron Lett.* **1997**, *38*, 551. (c) Kojima, S.; Akiba, K.-y. *Tetrahedron Lett.* **1997**, *38*, 547. (d) Kojima, S.; Kawaguchi, K.; Akiba, K.-y. *Tetrahedron Lett.* **1997**, *38*, 7753. (e) Bojin, M. L.; Barkallah, S.; Evans, S. A., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 1549.

SCHEME 15



though the stereochemistry is not clear. Considering that the oxygen atom of the four-membered ring is located at the opposite side of the oxygen atom of the Martin ligand in the most stable isomer of hexacoordinate 1,2-oxaphosphetanides,[25c] the oxygen atoms of **36** are presumed to be located similarly. Elimination of olefin **30** from **36** and successive hydrolysis of the counterpart should give hydroxystiborane **34**, and its dehydrative dimerization should give **35**. Compounds **34** and **35** are in equilibrium, and attempted separation of **34** and **35** by gel permeation chromatography was unsuccessful.

Moreover, the reaction of pentacoordinate 1,2-oxastibetane **14c** with PhLi in THF at 0 °C provided the mixture (3:1) of two diastereomers of **33**, which were detected by ^{19}F NMR spectroscopy (Scheme 15). Exchange of the solvent of the reaction mixture from THF to PhCN and successive thermolysis gave olefin **30** and lithium stibonyloxide **37**, which was protonated and dimerized with dehydration to give **38**. The FAB-MS of the reaction mixture showed peaks at *m*/*z* 1163 and 573, which are attributable to [**38** + H]$^+$ and the fragment ion of R_FSbPhAr, respectively. Hydrolysis of **33** provided 2-hydroxyalkylstiborane **39** in good yield and the reaction of **39** with LiH gave **33**, which was detected by ^{19}F NMR spectroscopy, quantitatively. These results suggest the intermediacy of a hexacoordinate 1,2-oxastibetanide, though the stereochemistry except at the 3- and 4-positions of the oxastibetane ring is not clear (Scheme 15).

Conclusion

We have described the syntheses, structures, and thermolyses of the pentacoordinate 1,2-oxastibetanes with and without a phenyl group at the 3-position on the 1,2-oxastibetane ring, which are considered as formal [2 + 2]-cycloadducts of the reaction of a stibonium ylide and a carbonyl compound. In fact, the reaction of the stibonium benzylide with HFA gave the corresponding pentacoordinate 1,2-oxastibetane. The 1,2-oxastibetane without a phenyl group at the 3-position did not decompose even at 220 °C in *o*-xylene-d_{10}, whereas the 3-phenyl-1,2-oxastibetane decomposed under similar conditions to give the corresponding oxirane with retention of configuration as the sole product, in sharp contrast to the result of the thermolysis of the 1,2-oxaphosphetane bearing the Martin ligand. Thermolysis of the 3-phenyl-1,2-oxastibetane in the presence of LiBr and $LiBPh_4$·3DME gave selectively the oxirane with inversion of configuration and the corresponding olefin as the main product, respectively. These results showed that 3-phenyl-1,2-oxastibetanes thermally decompose to give both the oxirane and the olefin and that the phenyl group at the 3-position decreases the thermal stability of the 1,2-oxastibetanes. When the oxirane is formed, either the apical−equatorial ligand coupling of the 1,2-oxastibetane or the decomposition of an *anti*-betaine intermediate would take place. The X-ray analyses revealed that the endocyclic C−Sb−O angles around the antimony atoms of 1,2-oxastibetanes **14a** and **14c** are smaller than the endocyclic C−P−O angle of **3**, resulting in the easier ligand coupling reaction around the antimony atoms than the 1,2-oxaphosphetanes, giving the oxirane with retention of configuration. In contrast, when the olefin is obtained, the reaction must proceed via the hexacoordinate 1,2-oxastibetanide. Taking into consideration the results of the thermolyses of the pentacoordinate 1,2-oxastibetanes, they can be regarded as potential intermediates in the reaction of a stibonium ylide with a carbonyl compound.

Experimental Section

1,1-Bis[4-(*tert*-butyl)phenyl]-3,3-bis(trifluoromethyl)-1-(2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl)-3*H*-2,1-benzoxastibole (7a). To a solution of 1,1-bis[4-(*tert*-butyl)phenyl]-1-chloro-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastibole (**6**) (381 mg, 0.573 mmol) in THF (10 mL) was added at −78 °C a THF solution (5 mL) of lithium butyltelluromethylide, which was prepared from bis(butyltelluro)methane (269 mg, 0.701 mmol) and *n*-BuLi (0.50 mL, 0.77 mmol) at −78 °C for 10 min. After the reaction mixture was stirred for 10 min, *n*-BuLi (0.50 mL, 0.77 mmol) was added to it at −78 °C and the reaction mixture was further stirred for 10 min. HFA gas, which was generated by dehydration of HFA·3H_2O (2.0 mL, 14 mmol), was bubbled to the reaction solution at −78 °C for 2 h, and the solution was warmed slowly to room temperature. The mixture was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were washed with H_2O and brine and dried with $MgSO_4$. After removal of the solvent, the residue was separated by wet column chromatography (WCC) (SiO_2, hexane/CH_2Cl_2 = 4/1) and HPLC ($CHCl_3$) to give **7a** (60 mg, 0.074 mmol, 13%), 1,1-bis[4-(*tert*-butylphenyl)]-1-methyl-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastibole (**8**) (36 mg, 0.056 mmol, 10%), and bis{1,1-bis[4-(*tert*-butyl)phenyl]-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastibolyl}methane (**9**) (175 mg, 0.136 mmol, 24%).[27]
7a: colorless crystals (EtOH), mp 200−201 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 18H), 2.90 (s, 2H), 7.44 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.48−7.50 (m, 5H), 7.56 (d, $^3J_{HH}$ = 8.3 Hz, 4H), 7.63 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.91 (br d, $^3J_{HH}$ = 7.3 Hz, 1H), 8.59 (br s, 1H, O*H*); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 29.4 (s, *C*H_2), 31.1 (s, *C*H_3), 34.9 (s), 74.8 (sept, $^2J_{CF}$ = 30 Hz), 78.3 (sept, $^2J_{CF}$ = 29 Hz), 123.4 (q, $^1J_{CF}$ = 289 Hz), 123.6 (q, $^1J_{CF}$ = 291 Hz), 126.4 (s), 126.9 (s), 128.3 (br s), 129.7 (s), 130.4 (s), 132.2 (s), 134.5 (s), 134.8 (s), 137.3 (s), 154.4 (s); ^{19}F NMR (254 Hz, $CDCl_3$) δ −78.4 (s, 6F), −75.0 (s, 6F); MS (FAB) *m*/*z* 811 (M + H$^+$, 50), 57 (100%); IR (KBr, cm^{-1}) 3081 (w), 2968 (w), 2871 (w), 1699 (s), 1590 (w), 1558 (w), 1507 (w), 1493 (w), 1464 (w), 1388 (w), 1364 (s), 1271 (vs), 1189 (vs), 1144 (s), 1120 (s), 1064 (w), 1011 (m); IR ($CHCl_3$, cm^{-1}) 3073 (w), 2966 (w), 2906 (w), 2871 (w), 1589 (s), 1493 (w), 1464 (w), 1387 (w), 1303 (w), 1275 (m), 1236 (w), 1216 (vs), 1207 (m), 1193 (m), 1167 (w), 1144 (w), 1119 (w), 1060 (w), 1010 (w). Anal. Calcd for $C_{33}H_{33}F_{12}O_2Sb$: C, 48.85; H, 4.10. Found: C, 48.92; H, 4.19.

1,1-Bis[4-(*tert*-butyl)phenyl]-1-(2-hydroxy-2-phenyl-3,3,3-trifluoropropyl)-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastibole (7b).
7b: colorless crystals (EtOH), mp 201−202 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (s, 9H), 1.39 (s, 9H), 3.27 (d, $^2J_{HH}$ = 12.5 Hz, 1H), 3.36 (d, $^2J_{HH}$ = 12.5 Hz, 1H), 6.97−7.00 (m, 3H), 7.06−

(26) Marvel, C. S.; Johnston, H. W.; Meier, J. W.; Mastin, T. W.; Whitson, J.; Himel, C. M. *J. Am. Chem. Soc*. **1944**, *66*, 914.

(27) The yields of **7a**, **8**, and **9** were calculated assuming that 1 mol of **6** gives 1 mol of **7a** and **8**, and 0.5 mol of **9**, respectively.

7.10 (m, 3H), 7.14 (dt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.9 Hz, 2H), 7.34−7.39 (m, 3H), 7.40−7.50 (m, 4H), 7.57 (td, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.1 Hz, 1H), 7.71 (br s, 1H, O*H*), 7.92 (br d, $^3J_{HH}$ = 7.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 31.1 (s), 31.2 (s), 32.0 (s, *C*H_2), 34.7 (s), 34.9 (s), 74.9 (q, $^2J_{CF}$ = 29 Hz), 78.3 (sept, $^2J_{CF}$ = 29 Hz), 123.4 (q, $^1J_{CF}$ = 290 Hz), 124.0 (q, $^1J_{CF}$ = 290 Hz), 125.6 (s), 125.6 (q, $^1J_{CF}$ = 287 Hz), 125.9 (s), 126.2 (s), 126.7 (s), 127.6 (s), 127.9 (s), 128.0 (s), 128.4 (s), 129.0 (s), 130.3 (s), 131.9 (s), 133.1 (s), 134.6 (s), 134.7 (s), 135.4 (s), 137.4 (s), 138.5 (s), 153.6 (s), 153.8 (s); ^{19}F NMR (254 Hz, $CDCl_3$) δ −81.5 (s, 3F), −74.8 (q, $^2J_{FF}$ = 9.0 Hz, 3F), −74.1 (q, $^2J_{FF}$ = 9.0 Hz, 3F); MS (FAB) *m*/*z* 819 ($M + H^+$, 45), 629 ($M^+ - CH_2C(CF_3)OH$, 100%); IR (KBr, cm^{-1}) 3068 (w), 2971 (m), 2907 (w), 2871 (w), 2832 (w), 1589 (w), 1552 (w), 1492 (w), 1465 (w), 1449 (w), 1388 (w), 1364 (s), 1269 (s), 1223 (m), 1202 (m), 1176 (s), 1159 (vs), 1142 (m), 1122 (w), 1105 (w), 1054 (m). Anal. Calcd for $C_{38}H_{38}F_9O_2Sb$: C, 55.70; H, 4.67. Found: C, 55.62; H, 4.68.

1-Benzyl-1,1-bis[4-(*tert*-butyl)phenyl]-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastibole (12). To magnesium turnings (70 mg, 2.9 mmol) in Et_2O (5 mL) was added dropwise an ethereal solution (5 mL) of benzyl chloride (0.31 mL, 2.7 mmol) over 1 h under reflux and the mixture was stirred at room temperature for 1 h. To the reaction mixture was added an ethereal solution (15 mL) of chlorostiborane **6** (1.62 g, 2.44 mmol). After the reaction mixture was stirred at room temperature overnight, it was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were washed with H_2O, aqueous Na_2CO_3, and brine and dried with $MgSO_4$. After removal of the solvent, the residue was washed with hexane to give **12** (1.37 g, 78%) as a white solid. **12**: colorless crystals (hexane), mp 142−143 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 1.30 (s, 18H), 3.98 (s, 2H), 7.00 (br s, 5H), 7.08 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.26 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 7.31 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 7.39 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.57 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.94 (br d, $^3J_{HH}$ = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 31.2 (s), 34.7 (s), 35.2 (s), 78.6 (sept, $^2J_{CF}$ = 29 Hz), 125.5 (q, $^1J_{CF}$ = 283 Hz), 125.6 (s), 126.0 (s), 127.7 (s), 128.2 (s), 129.0 (s), 129.8 (s), 130.0 (s), 131.2 (s), 131.4 (s), 134.67 (s), 134.70 (s), 135.4 (s), 138.6 (s), 153.2 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ −74.9 (s, 6F); MS (FAB) *m*/*z* 721 ($M + H^+$, 18), 629 ($M^+ - PhCH_2$, 100%). Anal. Calcd for $C_{36}H_{37}F_6OSb$: C, 59.93; H, 5.17. Found C, 59.66; H, 5.23.

1,1-Bis[4-(*tert*-butyl)phenyl]-1-(2-hydroxy-1,2-diphenyl-3,3,3-trifluoropropyl)-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastiboles (7c and 7d). To a solution of tetramethylpiperidine (0.39 mL, 2.20 mmol) in benzene (5 mL) was added *n*-BuLi (1.50 mL, 2.10 mmol) at room temperature and the mixture was stirred at room temperature for 0.5 h. To the reaction mixture was added a benzene solution (15 mL) of benzylstiborane **12** (720 mg, 1.00 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 12 h, a benzene solution (1 mL) of trifluoroacetophenone (390 mg, 2.24 mmol) was added to the reaction solution and the solution was stirred at room temperature for 0.5 h. The mixture was treated with aqueous NH_4Cl and extracted with $CHCl_3$. The organic layer was washed with H_2O and brine and dried with $MgSO_4$. After removal of the solvent, the residue was separated by WCC (hexane/$CHCl_3$ = 1/1) to give **7c** (360 mg, 40%) and **7d** (248 mg, 28%). **7c**: colorless crystals (EtOH/$CHCl_3$ = 4/1), mp 251−252 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 1.16 (s, 9H), 1.42 (s, 9H), 4.37 (s, 1H), 6.50 (d, $^2J_{HH}$ = 8.5 Hz, 2H), 6.99−7.12 (m, 9H), 7.44 (br d, $^2J_{HH}$ = 7.3 Hz, 2H), 7.53 (dt, $^3J_{HH}$ = 7.3 Hz, 1H), 7.57−7.60 (m, 6H), 7.66 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 7.88 (br d, $^3J_{HH}$ = 7.5 Hz, 1H), 8.59 (s, 1H, O*H*); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 31.0 (s), 31.3 (s), 34.6 (s), 34.9 (s), 64.9 (s), 77.6 (m), 78.1 (q, $^2J_{CF}$ = 27 Hz), 123.4 (q, $^1J_{CF}$ = 291 Hz), 124.0 (q, $^1J_{CF}$ = 290 Hz), 125.1 (s), 126.5 (q, $^1J_{CF}$ = 289 Hz), 126.3 (s), 127.4 (s), 127.5 (s), 127.76 (s), 127.83 (s), 128.1 (s), 130.3 (s), 130.6 (s), 130.8 (s), 131.4 (s), 133.8 (s), 134.3 (s), 134.5 (s), 134.8 (s), 135.3 (s), 135.4 (s), 136.1 (s), 136.6 (s), 137.3 (s), 153.18 (s), 153.24 (s); ^{19}F NMR (470 Hz, $CDCl_3$) δ −77.0 (m, 3F), −74.6 (q, $^4J_{FF}$ = 9.4 Hz, 3F), −73.6 (m, 3F); MS (FAB) *m*/*z* 895 ($M + H^+$, 6), 629 ($M^+ - CH_2C(CF_3)OH$, 100%); IR (KBr, cm^{-1}) 3145 (w, OH), 3072 (m), 2965 (w), 2905 (w), 2870 (w), 1589 (w), 1552 (w), 1493 (w), 1455 (w), 1396 (w), 1386 (w), 1364 (w), 1300 (w), 1266 (vs), 1226 (m), 1201 (m), 1183 (vs), 1166 (m), 1134 (w), 1114 (m), 1078 (w). Anal. Calcd for $C_{44}H_{42}F_9O_2Sb$: C, 59.01; H, 4.73. Found: C, 58.75; H, 4.84. **7d**: colorless crystals (EtOH), mp 174−175 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.34 (s, 9H), 4.54 (s, 1H), 6.58 (m, 3H), 6.96−7.01 (m, 6H), 7.12 (t, $^2J_{HH}$ = 7.3 Hz, 1H), 7.28−7.36 (m, 7H), 7.50 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 7.79−7.83 (m, 4H), 7.97 (s, 1H, O*H*); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 31.0 (s), 31.2 (s), 34.6 (s), 34.8 (s), 62.9 (s), 77.8 (sept, $^2J_{CF}$ = 29 Hz), 79.5 (q, $^2J_{CF}$ = 27 Hz), 123.5 (q, $^1J_{CF}$ = 291 Hz), 124.3 (q, $^1J_{CF}$ = 290 Hz), 125.2 (q, $^1J_{CF}$ = 289 Hz), 125.3 (s), 125.4 (s), 125.48 (s), 125.55 (s), 127.1 (s), 127.6 (s), 127.8 (s), 128.7 (s), 129.3 (s), 130.1 (s), 131.3 (s), 133.1 (s), 134.4 (s), 134.6 (s), 134.95 (s), 135.01 (s), 135.2 (s), 135.3 (s), 136.7 (s), 140.1 (s), 153.0 (s), 153.1 (s); ^{19}F NMR (470 Hz, $CDCl_3$) δ −74.1 (q, $^4J_{FF}$ = 9.4 Hz, 3F), −73.5 (s, 3F), −73.1 (q, $^4J_{FF}$ = 9.4 Hz, 3F); MS (FAB) *m*/*z* 895 ($M + H^+$, 6), 629 ($M^+ - CH_2C(CF_3)OH$, 100%); IR (KBr, cm^{-1}) 3429 (w, OH), 3218 (w), 3069 (w), 3030 (w), 2965 (w), 2906 (w), 2871 (w), 1631 (w), 1590 (w), 1495 (w), 1464 (w), 1444 (w), 1387 (w), 1363 (w), 1264 (w), 1239 (m), 1223 (m), 1203 (m), 1184 (m), 1141 (m), 1114 (m), 1061 (w), 1032 (w), 1010 (w). Anal. Calcd for $C_{44}H_{42}F_9O_2Sb$: C, 59.01; H, 4.73. Found: C, 58.84; H, 4.84.

1-Bromo-1-[4-(*tert*-butyl)phenyl]-3,3-bis(trifluoromethyl)-1-(2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl)-3*H*-2,1-benzoxastibole (13a). To a solution of 2-hydroxyalkylstiborane **7a** (127 mg, 0.156 mmol) in $CHCl_3$ (5 mL) was added dropwise a solution of bromine (0.04 mL, 0.8 mmol) in $CHCl_3$ (1 mL) at 0 °C for 10 min in the dark, and the mixture was stirred at room temperature for 0.5 h. After removal of the solvent, the residue was washed with hexane to give **13a** (118 mg, 100%) as a white solid. **13a**: colorless crystals (hexane), mp 141−145 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 1.31 (s, 9H), 3.20 (d, $^2J_{HH}$ = 13.7 Hz, 1H), 3.66 (m, 1H), 6.48 (br s, 1H, O*H*), 7.56 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.73 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 7.78 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 7.86 (br d, $^3J_{HH}$ = 7.6 Hz, 1H), 8.07 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 8.45 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 31.0 (s, *C*H_3), 35.0 (s), 43.0 (s, *C*H_2), 74.9 (sept, $^2J_{CF}$ = 31 Hz), 80.8 (sept, $^2J_{CF}$ = 30 Hz), 122.7 (q, $^1J_{CF}$ = 288 Hz), 122.8 (q, $^1J_{CF}$ = 288 Hz), 123.2 (br q, $^1J_{CF}$ = 288 Hz), 127.0 (s), 127.7 (s), 127.8 (s), 128.6 (s), 131.7 (s), 133.5 (s), 133.8 (s), 135.0 (s), 135.8 (s), 156.4 (s); ^{19}F NMR (254 Hz, $CDCl_3$) δ −79.0 (br q, $^4J_{FF}$ = 9.4 Hz, 3F), −77.9 (q, $^4J_{FF}$ = 9.4 Hz, 3F), −75.5 (br q, $^4J_{FF}$ = 9.4 Hz, 3F), −74.7 (q, $^4J_{FF}$ = 9.4 Hz, 3F); MS (FAB) *m*/*z* 757 ($M + H^+$, 4), 677 (M^+ − Ar, 100%); IR (KBr, cm^{-1}) 3224 (w), 3077 (w), 2967 (w), 2872 (w), 1699 (s), 1652 (w), 1558 (w), 1490 (w), 1463 (w), 1447 (w), 1397 (s), 1305 (m), 1272 (vs), 1242 (s), 1195 (vs), 1148 (s), 1117 (m), 1059 (w), 1050(w), 1007 (m); IR ($CHCl_3$, cm^{-1}) 3274 (w), 3074 (w), 2968 (w), 1653 (w), 1558 (w), 1489 (w), 1463 (w), 1444 (w), 1396 (w), 1364 (w), 1304 (m), 1277 (m), 1237 (m), 1223 (s), 1215 (s), 1200 (s), 1147 (m), 1117 (w), 1050 (w), 1008 (w). Anal. Calcd for $C_{23}H_{20}BrF_{12}O_2Sb$: C, 36.44; H, 2.66. Found: C, 36.66; H, 2.93.

1-Bromo-1-[4-(*tert*-butyl)phenyl]-1-(2-hydroxy-2-phenyl-3,3,3-trifluoropropyl)-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastibole (13b). 13b: colorless crystals (hexane), mp 143−145 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 1.27 (s, 9H), 3.69 (d, $^2J_{HH}$ = 12.7 Hz, 1H), 3.82 (d, $^2J_{HH}$ = 12.7 Hz, 1H), 5.52 (br s, 1H, O*H*), 7.03−7.05 (m, 3H), 7.24 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.46−7.48 (m, 2H), 7.57 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.69 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 7.73 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 7.84 (br d, $^3J_{HH}$ = 7.6 Hz, 1H), 8.43 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 31.0 (s, *C*H_3), 34.8 (s), 49.3 (s, *C*H_2), 75.8 (q, $^2J_{CF}$ = 30 Hz), 80.8 (sept, $^2J_{CF}$ = 30 Hz), 122.9 (q, $^1J_{CF}$ = 289 Hz), 123.4 (q, $^1J_{CF}$ = 288 Hz), 124.9 (q, $^1J_{CF}$ = 287 Hz), 126.5 (s), 126.6 (s), 126.9 (s), 127.5 (s), 128.1 (s), 129.0 (s),

129.1 (s), 131.5 (s), 133.2 (s), 133.8 (s), 135.2 (s), 136.0 (s), 136.2 (s), 155.2 (s): ^{19}F NMR (254 MHz, $CDCl_3$) δ −81.6 (s, 3F), −75.3 (q, $^4J_{FF}$ = 9.1 Hz, 3F), −74.5 (br q, $^4J_{FF}$ = 9.1 Hz, 3F); IR (KBr, cm^{-1}) 3411 (m), 3073 (w), 2964 (m), 2906 (w), 2870 (w), 1634 (w), 1587 (w), 1490 (w), 1463 (w), 1451 (w), 1396 (s), 1365 (w), 1305 (m), 1272 (vs), 1232 (s), 1214 (vs), 1192 (vs), 1166 (s), 1147 (s), 1120 (m), 1102 (w), 1074 (w), 1059 (w), 1050 (w), 1007 (w); MS (FAB) *m*/*z* 765 ($M + H^+$, 10), 513 (100%). Anal. Calcd for $C_{28}H_{25}F_{12}O_2Sb$: C, 43.89; H, 3.29. Found C, 43.81; H, 3.32.

1-Bromo-1-[4-(*tert*-butyl)phenyl]-1-(2-hydroxy-1,2-diphenyl-3,3,3-trifluoropropyl)-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastibole (13c). Major isomer of **13c**: colorless crystals (hexane/$CHCl_3$ = 1/1), mp 199−200 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (s, 9H), 5.47 (s, 1H), 6.47 (br s, 1H), 6.84−6.91 (m, 2H), 7.07−7.24 (m, 8H), 7.54 (br d, $^2J_{HH}$ = 7.1 Hz, 2H), 7.66−7.69 (m, 2H), 7.77−7.82 (m, 3H), 8.62 (d, $^2J_{HH}$ = 7.8 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 30.9 (s), 34.6 (s), 74.1 (s), 79.9 (q, $^2J_{CF}$ = 28 Hz), 80.5 (sept, $^2J_{CF}$ = 31 Hz), 122.7 (q, $^1J_{CF}$ = 289 Hz), 123.0 (q, $^1J_{CF}$ = 289 Hz), 123.4 (q, $^1J_{CF}$ = 286 Hz), 125.5 (s), 125.8 (s), 126.4 (s), 127.0 (s), 127.4 (s), 127.9 (s), 128.2 (s), 128.3 (s), 128.5 (s), 131.6 (s), 132.1 (s), 132.6 (s), 133.9 (s), 134.3 (s), 134.6 (s), 134.8 (s), 135.8 (s), 154.6 (s); ^{19}F NMR (470 Hz, $CDCl_3$) δ −77.69 to −77.68 (m, 3F), −74.08 (q, $^4J_{FF}$ = 9.9 Hz, 3F), −73.63 to −73.60 (m, 3F); MS (FAB) *m*/*z* 842 ($C_{34}H_{39}{}^{81}BrF_6O_2Sb^+$, 2), 186 (100%); IR (KBr, cm^{-1}) 3398 (s), 3352 (m), 3071 (m), 3028 (w), 2963 (w), 2906 (w), 2869 (w), 1635 (w), 1587 (w), 1493 (m), 1454 (w), 1441 (w), 1424 (w), 1397 (m), 1364 (m), 1350 (m), 1301 (m), 1286 (s), 1267 (vs), 1236 (vs), 1187 (vs), 1157 (vs), 1144 (vs), 1103 (vs), 1078 (m), 1061 (m). Anal. Calcd for $C_{34}H_{29}BrF_9O_2Sb$: C, 48.49; H, 3.47. Found: C, 48.28; H, 3.64. Minor isomer of **13c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (s, 9H), 5.13 (s, 1H), 6.84−6.91 (m, 3H), 7.07−7.24 (m, 8H), 7.40 (br d, $^2J_{HH}$ = 7.6 Hz, 1H), 7.54 (br d, $^2J_{HH}$ = 7.1 Hz, 1H), 7.66−7.69 (m, 2H), 7.77−7.82 (m, 3H), 8.62 (d, $^2J_{HH}$ = 7.8 Hz, 1H); ^{19}F NMR (470 Hz, $CDCl_3$) δ −76.26 to −76.25 (m, 3F), −74.64 (br s, 3F), −74.11 to −74.05 (m, 3F).

1-Bromo-1-[4-(*tert*-butyl)phenyl]-1-(2-hydroxy-1,2-diphenyl-3,3,3-trifluoropropyl)-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastibole (13d). Major isomer of **13d**: colorless crystals (hexane/$CHCl_3$ = 5/1), mp 160−161.5 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (s, 9H), 5.35 (s, 1H), 5.67 (br s, 1H), 6.91 (br, 1H), 7.10−7.13 (m, 5H), 7.19 (t, $^2J_{HH}$ = 7.4 Hz, 1H), 7.31−7.39 (m, 3H), 7.43−7.46 (m, 1H), 7.47−7.64 (m, 3H), 7.64−7.79 (m, 4H); ^{19}F NMR (470 Hz, $CDCl_3$) δ −75.1 (br s, 3F), −74.6 (br s, 3F), −73.3 (br s, 3F); MS (FAB) *m*/*z* 842 ($C_{34}H_{39}{}^{81}BrF_6O_2Sb^+$, 1), 186 (100%); IR (KBr, cm^{-1}) 3324 (w), 3065 (w), 3039 (w), 2965 (w), 2871 (w), 1633 (w), 1585 (w), 1491 (w), 1449 (w), 1396 (w), 1302 (w), 1270 (m), 1241 (m), 1226 (m), 1184 (vs), 1142 (m), 1108 (m), 1076 (m), 1050 (m). Anal. Calcd for $C_{34}H_{29}BrF_9O_2Sb$: C, 48.49; H, 3.47. Found: C, 48.58; H, 3.48. Minor isomer of **13d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (s, 9H), 5.55 (s, 1H), 5.67 (br s, 1H), 6.91 (br, 1H), 7.10−7.13 (m, 5H), 7.19−7.39 (m, 4H), 7.43−7.46 (m, 1H), 7.47−7.64 (m, 3H), 7.64−7.79 (m, 4H); ^{19}F NMR (470 Hz, $CDCl_3$) δ −74.4 (s, 3F), −74.1 (q, $^4J_{FF}$ = 9.9 Hz, 3F), −72.34 to −72.35 (m, 3F).

1-[4-(*tert*-Butyl)phenyl]-3,3,4′,4′-tetrakis(trifluoromethyl)-spiro{2,1-benzoxastibole-1(3*H*),2′λ^5-[1,2]oxastibetane} (14a). To a suspension of NaH (48 mg, 1.2 mmol) in THF (1 mL) was added a solution of bromo(2-hydroxyalkyl)stiborane **13a** (250 mg, 0.33 mmol) in THF (6 mL) at room temperature and the mixture was stirred for 2 h. After the reaction mixture was filtered through Celite, THF was removed in vacuo, and the residue was separated by preparative gel permeation liquid chromatography (GPLC) ($CHCl_3$) to give 1,2-oxastibetane **14a** (86%) as a colorless solid. **14a**: colorless crystals (hexane); mp 148−150 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (s, 9H), 4.09 (d, $^2J_{HH}$ = 14.1 Hz, 1H), 4.41 (d, $^2J_{HH}$ = 14.1 Hz, 1H), 7.62 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.71−7.74 (m, 2H), 7.89 (br d, $^3J_{HH}$ = 7.0 Hz, 1H), 7.92 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 8.02 (dd, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.8 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 31.0 (s, CH_3), 35.2 (s), 50.0 (s, CH_2), 76.0 (sept, $^2J_{CF}$ = 31 Hz), 82.1 (sept, $^2J_{CF}$ = 30 Hz), 123.2 (q, $^1J_{CF}$ = 288 Hz), 123.3 (q, $^1J_{CF}$ = 288 Hz), 123.8 (q, $^1J_{CF}$ = 286 Hz), 124.0 (q, $^1J_{CF}$ = 286 Hz), 125.1 (s), 127.3 (s), 127.4 (s), 128.1 (s), 131.4 (s), 132.9 (s), 133.5 (s), 134.0 (s), 136.9 (s), 157.2 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ −78.4 (q, $^4J_{FF}$ = 8.8 Hz, 3F), −77.5 (q, $^4J_{FF}$ = 8.8 Hz, 3F), −76.8 (q, $^4J_{FF}$ = 8.5 Hz, 3F), −74.4 (q, $^4J_{FF}$ = 8.5 Hz, 3F); MS (FAB) *m*/*z* 677 ($M + H^+$, 89), 57 (100%). Anal. Calcd for $C_{23}H_{19}F_{12}O_2Sb$: C, 40.80; H, 2.83. Found C, 40.82; H, 2.97.

1-[4-(*tert*-Butyl)phenyl]-4-phenyl-3,3,4′-tris(trifluoromethyl)-spiro{2,1-benzoxastibole-1(3*H*),2′λ^5-[1,2]oxastibetane} (14b). **14b**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.27 (s, 9H), 4.58 (d, $^2J_{HH}$ = 13.0 Hz, 1H), 4.41 (d, $^2J_{HH}$ = 13.0 Hz, 1H), 7.29−8.00 (m, 12H), 8.12−8.14 (m, 1H); ^{19}F NMR (254 MHz, $CDCl_3$) δ −81.0 (s, 3F), −76.9 (q, $^4J_{FF}$ = 8.1 Hz, 3F), −74.2 (q, $^4J_{FF}$ = 8.1 Hz, 3F); MS (FAB) *m*/*z* 685 ($M + H^+$, 11), 513 (100%). **15b**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.34 (s, 9H), 4.18 (d, $^2J_{HH}$ = 13.2 Hz, 1H), 4.46 (d, $^2J_{HH}$ = 13.2 Hz, 1H), 7.29−8.00 (m, 12H), 8.03−8.10 (m, 1H); ^{19}F NMR (254 MHz, $CDCl_3$) δ −79.9 (q, $^4J_{FF}$ = 8.8 Hz, 3F), −76.7 (q, $^4J_{FF}$ = 8.4 Hz, 3F), −74.3 (q, $^4J_{FF}$ = 8.4 Hz, 3F).

1-[4-(*tert*-Butyl)phenyl]-3′,4′-diphenyl-3,3,4′-tris(trifluoromethyl)spiro{2,1-benzoxastibole-1(3*H*),2′λ^5-[1,2]oxastibetane} (14c). **14c**: colorless crystals (hexane); mp 189−190 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (s, 9H), 6.09 (s, 1H), 6.65 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.94 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 7.04 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.16−7.19 (m, 5H), 7.30 (br d, $^3J_{HH}$ = 6.4 Hz, 2H), 7.55 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.68 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 7.74 (t, $^3J_{HH}$ = 7.1 Hz, 1H), 7.87 (br d, $^3J_{HH}$ = 7.3 Hz, 1H), 8.19 (d, $^3J_{HH}$ = 7.4 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 31.1 (s, *C*H$_3$), 35.1 (s), 78.7 (s, *C*H), 81.7 (q, $^2J_{CF}$ = 28 Hz), 82.1 (sept, $^2J_{CF}$ = 30 Hz), 123.38 (q, $^1J_{CF}$ = 288 Hz), 123.41 (q, $^1J_{CF}$ = 288 Hz), 124.5 (q, $^1J_{CF}$ = 288 Hz), 126.2 (s), 126.4 (s), 127.1 (s), 127.3 (s), 127.4 (s), 127.8 (s), 128.2 (s), 128.3 (s), 128.5 (s), 130.1 (s), 131.3 (s), 132.3 (s), 132.4 (s), 133.5 (s), 134.1 (s), 136.5 (s), 137.2 (s), 156.4 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ −79.3 (s, 3F), −76.8 (q, $^4J_{FF}$ = 8.2 Hz, 3F), −74.3 (q, $^4J_{FF}$ = 8.2 Hz, 3F); MS (FAB) *m*/*z* 761 ($M + H^+$, 8), 187 (100%). Anal. Calcd for $C_{34}H_{28}F_9O_2Sb$: C, 53.64; H, 3.71. Found C, 53.68; H, 3.89. X-ray crystallographic analysis of **14c** revealed that 4-(*tert*-butyl)phenyl and two phenyl groups of the 1,2-oxastibetane ring are cis to each other. **14c′**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 9H), 6.34 (s, 1H), 6.55 (d, $^3J_{HH}$ = 7.2 Hz, 2H), 6.85 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 6.93−7.20 (m, 3H), 7.30−7.31 (m, 4H), 7.58−7.66 (m, 3H), 7.73 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 8.01 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 8.41 (d, $^3J_{HH}$ = 8.4 Hz, 1H); ^{19}F NMR (470 MHz, $CDCl_3$) δ −78.0 (s, 3F), −75.5 (q, $^4J_{HH}$ = 9.4 Hz, 3F), −74.4 (q, $^4J_{HH}$ = 9.4 Hz, 3F).

1-[4-(*tert*-Butyl)phenyl]-3′,4′-diphenyl-3,3,4′-tris(trifluoromethyl)spiro{2,1-benzoxastibole-1(3*H*),2′λ^5-[1,2]oxastibetane} (14d). **14d**: colorless solids; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.37 (s, 9H), 5.89 (s, 1H), 6.93−7.39 (m, 6H), 7.48−7.76 (m, 9H), 8.08 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 8.21 (d, $^3J_{HH}$ = 7.5 Hz, 1H); ^{19}F NMR (254 MHz, $CDCl_3$) δ −76.8 (q, $^4J_{FF}$ = 7.9 Hz, 3F), −74.3 (q, $^4J_{FF}$ = 7.9 Hz, 3F), −72.5 (s, 3F); MS (FAB) *m*/*z* 761 ($M + H^+$, 8), 187 (100%). **15d**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.29 (s, 9H), 5.95 (s, 1H), 6.85−7.30 (m, 6H), 7.34−7.57 (m, 9H), 7.95 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 8.29 (d, $^3J_{HH}$ = 7.5 Hz, 1H); ^{19}F NMR (470 MHz, $CDCl_3$) δ −76.8 (q, $^4J_{FF}$ = 8.2 Hz, 3F), −74.6 (q, $^4J_{FF}$ = 8.2 Hz, 3F), −73.2 (s, 3F).

1-Benzyl-1-bromo-1-[4-(*tert*-butyl)phenyl]-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastibole (16). To a solution of benzylstiborane **12** (73 mg, 0.10 mmol) in CCl_4 (4 mL) was added dropwise a solution of bromine (12 mL, 0.20 mmol) in CCl_4 (1 mL) at 0 °C in the dark. After the mixture was stirred at room temperature for 30 min, the solvent was removed and the residue was washed with hexane to give **16** (65 mg, 98%) as a colorless solid. **16**: colorless crystals (hexane), mp 132−133.5 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (s, 9H), 4.13 (d, $^2J_{HH}$ = 11.3 Hz, 1H), 4.28 (d, $^2J_{HH}$ = 11.3 Hz, 1H), 7.18−7.20 (m, 3H), 7.25−7.27 (m, 2H), 7.37 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.68−7.76 (m, 4H), 7.85 (br d, $^3J_{HH}$ = 7.5

Hz, 1H), 8.55 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 31.0 (s), 34.8 (s), 47.8 (s, *C*H_2), 80.6 (sept, $^2J_{CF}$ = 30 Hz), 123.4 (q, $^1J_{CF}$ = 289 Hz), 123.6 (q, $^1J_{CF}$ = 289 Hz), 126.0 (s), 127.4 (s), 127.5 (s), 128.5 (s), 130.0 (s), 130.1 (s), 131.0 (s), 131.3 (s), 132.1 (s), 132.7 (s), 134.5 (s), 135.5 (s), 137.4 (s), 155.3 (s); ^{19}F NMR (254 Hz, $CDCl_3$) δ −75.7 (q, $^2J_{FF}$ = 8.9 Hz, 3F), −74.7 (q, $^2J_{FF}$ = 8.9 Hz, 3F); MS (FAB) *m*/*z* 668 (M^+ + H^+, 5), 91 (100%). Anal. Calcd for $C_{26}H_{24}BrF_6OSb$: C, 46.74; H, 3.62. Found: C, 46.64; H, 3.77.

1-Benzyl-1-[4-(*tert*-butyl)phenyl]-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastibonium Trifluoromethanesulfonate (17). A mixture of benzylbromostiborane **16** (410 mg, 0.615 mmol) and AgOTf (210 mg, 0.734 mmol) in THF (10 mL) was stirred at room temperature for 2 h, and filtered through Celite. Removal of the solvent gave **17** (452 mg, 100%) as a colorless oil. **17**: colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 1.26 (s, 9H), 4.26 (d, $^2J_{HH}$ = 14.9 Hz, 1H), 4.54 (d, $^2J_{HH}$ = 14.9 Hz, 1H), 7.23−7.27 (m, 3H), 7.33 (d, $^3J_{HH}$ = 6.2 Hz, 2H), 7.44 (s, 4H), 7.79 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 7.83 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 7.91 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 8.35 (d, $^3J_{HH}$ = 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 30.9 (s), 35.0 (s), 41.7 (s, *C*H_2), 82.2 (sept, $^2J_{CF}$ = 29 Hz), 119.3 (q, $^1J_{CF}$ = 319 Hz, Tf), 123.0 (q, $^1J_{CF}$ = 288 Hz), 125.4 (s), 127.2 (s), 127.8 (s), 127.9 (s), 128.3 (s), 129.0 (s), 129.6 (s), 130.1 (s), 132.7 (s), 133.5 (s), 133.8 (s), 134.8 (s), 138.3 (s), 156.8 (s); ^{19}F NMR (254 Hz, $CDCl_3$) δ −77.2 (s, 3F), −75.6 (q, $^2J_{FF}$ = 8.0 Hz, 3F), −75.2 (q, $^2J_{FF}$ = 8.0 Hz, 3F); MS (FAB) *m*/*z* 587 (M^+ − TfO, 21), 91 (100%).

1-[4-(*tert*-Butyl)phenyl]-3′-phenyl-3,3,4′,4′-tris(trifluoromethyl)spiro{2,1-benzoxastibole-1(3*H*),2′λ^5-[1,2]oxastibetane} (14e). To a solution of stibonium triflate **17** (196 mg, 0.270 mmol) in THF (5 mL) was added at −78 °C a THF solution (3 mL) of LiTMP, which was prepared from tetramethylpiperidine (0.18 mL, 1.00 mmol) and *n*-BuLi (0.65 mL, 1.0 mmol) at −78 °C for 10 min. After the reaction mixture was further stirred for 10 min, HFA gas, which was generated by dehydration of HFA·3H_2O (1.5 mL, 11 mmol), was bubbled to the reaction solution at −78 °C for 2 h, and the solution was warmed slowly to room temperature. The mixture was treated with aqueous NH_4Cl and extracted with Et_2O. The extracts were washed with H_2O and brine and dried with $MgSO_4$. After removal of the solvent, the residue was separated by GPLC ($CHCl_3$) and preparative thin-layer chromatography (PTLC) (SiO_2, hexane/CH_2Cl_2 = 1/1) to give a mixture containing **14e** (4.2 mg, 2%). **14e**: ^1H NMR (270 MHz, $CDCl_3$) δ 6.06 (s, 1H), other aliphatic and aromatic signals could not be assigned; ^{19}F NMR (254 Hz, $CDCl_3$) δ −71.9 (q, $^2J_{FF}$ = 9.1 Hz, 3F), −74.3 (q, $^2J_{FF}$ = 8.1 Hz, 3F), −76.8 (q, $^2J_{FF}$ = 8.9 Hz, 3F), −77.0 (q, $^2J_{FF}$ = 8.6 Hz, 3F); MS (FAB) *m*/*z* 753 (M + H).

1-[4-(*tert*-Butyl)phenyl]-1-(2-hydroxy-1,2-diphenyl-3,3,3-trifluoropropyl)-1-phenyl-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxastibole (39). To a solution of **14c** (11 mg, 0.014 mmol) in THF (0.5 mL) was added PhLi (2.28 M, 7.0 μL, 0.016 mmol) at room temperature and the mixture was stirred at room temperature for 1 h. The mixture was treated with aqueous NH_4Cl and extracted with Et_2O. The organic layer was washed with brine and dried with $MgSO_4$. After removal of the solvent, the residue was separated by PTLC (hexane/$CHCl_3$ = 1/1) to give a mixture of diastereomers (20:1) of **39** (11 mg, 94%). Major isomer of **39**: ^1H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 9H), 4.38 (s, 1H), 6.59 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.98−7.12 (m, 8H), 7.15−7.18 (m, 2H), 7.42−7.44 (m, 2H), 7.51−7.61 (m, 7H), 7.69 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.88 (br d, $^3J_{HH}$ = 7.4 Hz, 1H), 8.53 (s, 1H, O*H*); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 31.3 (s), 34.5 (s), 65.4 (s), 78.1 (q, $^2J_{CF}$ = 27 Hz), 123.4 (q, $^1J_{CF}$ = 291 Hz), 123.6 (q, $^1J_{CF}$ = 289 Hz), 124.0 (q, $^1J_{CF}$ = 290 Hz), 126.4 (s), 127.4 (s), 127.5 (s), 127.6 (s), 127.8 (s), 128.1 (s), 130.0 (s), 130.1 (s), 130.3 (s), 130.8 (s), 131.5 (s), 131.7 (s), 133.6 (s), 133.7 (s), 134.3 (s), 134.5 (s), 134.6 (s), 134.8 (s), 136.1 (s), 136.6 (s), 137.4 (s), 153.3 (s). A quaternary carbon due to *C*$(CF_3)_2$ was not observed.; ^{19}F NMR (470 Hz, $CDCl_3$) δ −77.1 to −77.0 (m, 3F), −74.6 (q, $^4J_{FF}$ = 9.4 Hz, 3F), −73.6 to −73.5 (m, 3F); MS (FAB) *m*/*z* 839 ($M + H^+$, 3), 573 (100%); HRMS (FAB) *m*/*z* calcd for $C_{40}H_{35}F_9O_2Sb$ [$M + H^+$] 839.1532, found 839.1582. Minor isomer of **39**: ^1H NMR (500 MHz, $CDCl_3$) δ 1.16 (s, 9H), 4.34 (s, 1H), 6.50 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 6.98−7.12 (m, 8H), 7.15−7.18 (m, 2H), 7.51−7.61 (m, 7H), 7.65−7.68 (m, 3H), 7.68−7.70 (m, 1H), 7.86−7.88 (m, 1H), 8.46 (s, 1H, OH); ^{19}F NMR (470 MHz, $CDCl_3$) δ −77.0 to −76.9 (m, 3F), −74.3 to −74.5 (m, 3F), −73.6 to −73.5 (m, 3F).

Thermolysis of (2-Hydroxyalkyl)stiborane 7c in the Presence of LiH. To a solution of **7c** (89 mg, 0.10 mmol) in PhCN (1.0 mL) was added LiH (2.3 mg, 0.29 mmol) at room temperature and the reaction mixture was stirred at room temperature for 0.5 h. The mixture was stirred at 140 °C for 6 h. The solvent was removed under reduced pressure and the residue was separated by GPLC ($CHCl_3$) to give olefin **30** (56 mg, 87%) and a mixture (21 mg) of **34** (30%) and **35** (58%) as a white solid.[31] A 1:2 mixture of **34** and **35**: ^1H NMR (500 MHz, $CDCl_3$) δ 1.26 (s, 72H), 1.30 (s, 18H), 1.47 (s, 1H, OH), 7.23 (d, *J* = 8.4 Hz, 16H), 7.34−7.39 (m, 5H), 7.51 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 7.58 (t, $^3J_{HH}$ = 8.1 Hz, 4H), 7.62−7.66 (m, 18H), 7.88 (d, $^3J_{HH}$ = 7.7 Hz, 4H), 8.01 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 8.20 (d, $^3J_{HH}$ = 7.2 Hz, 4H), 8.31 (d, $^3J_{HH}$ = 7.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 31.1 (s), 34.5 (s), 34.9 (s), 79.5 (sept, $^2J_{CF}$ = 29 Hz), 123.9 (q, $^1J_{CF}$ = 290 Hz), 126.0 (s), 126.5 (s), 127.4 (s), 127.5 (s), 130.1 (s), 130.5 (s), 130.8 (s), 131.3 (s), 131.7 (s), 131.8 (s), 132.1 (s), 133.9 (s), 134.1 (s), 134.3 (s), 134.4 (s), 134.7 (s), 137.8 (s), 138.4 (s), 154.1 (s), 155.1 (s). An aliphatic carbon of the *t*-Bu group, two quaternary carbons of CF_3 group, and two aromatic carbons were not observed; ^{19}F NMR (254 Hz, $CDCl_3$) δ −75.0 (s, 24F), −74.9 (s, 6F); FAB-MS *m*/*z* 1275 (M + H^+ for **35**), 646 (M^+ for **34**).

The Flash Vacuum Pyrolyses (FVP) of 3 and 14a. A quartz tube containing the starting materials (16 mg of **3** or **14a**) was evacuated and the pressure was kept in 1 × 10^{-1} Torr under a gentle and constant stream of nitrogen gas throughout the pyrolysis. To assist sublimation of the starting materials, **3** and **14a**, the head of the quartz tube was preheated with a ribbon heater at 47−50 and 105−107 °C, respectively, and the sublimed starting materials were pyrolyzed by passing through the quartz tube filled with quartz fillings heated at 500 °C in the oven. The decomposed products were accumulated in a trap cooled with liquid nitrogen. Heating was continued for 6 h and the products in a trap were analyzed by GC-MS and ^{19}F NMR spectroscopy. The yields of the products were summarized in Table 3.

A Typical Procedure of the Thermolysis of 3-Phenyl-1,2-oxastibetane (14c). In an NMR tube was placed an *o*-xylene-d_{10} (0.55 mL) solution of 1,2-oxastibetane **14c** (10 mg, 0.013 mmol). After several freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 220 °C for 17 h while being monitored by ^1H and ^{19}F NMR spectroscopy. The reaction conditions and the yields are summarized in Table 4. The products of the thermolysis, oxirane **28** with retention of configuration,[28] 1,3-dihydro-3,3-bis(trifluoromethyl)-1-(4-*tert*-butylphenyl)-1,2-benzoxastibole **25**, olefin **30**,[29] and oxirane **29** with inversion of relative configuration,[30] were identified with authentic samples. **25**: colorless solid (hexane/$CHCl_3$ = 1/1), mp 138−139 °C dec; ^1H NMR (270 MHz, $CDCl_3$) δ 1.27 (s, 9H), 7.39 (s, 4H), 7.52−7.64 (m, 3H), 7.80 (d, $^3J_{HH}$ = 7.3 Hz, 1H); ^{19}F NMR (254 Hz, $CDCl_3$) δ −77.2 (q, $^2J_{FF}$ = 8.9 Hz, 3F), −74.9 (q, $^2J_{FF}$ = 8.9 Hz, 3F); MS (FAB) *m*/*z* 496 (M^+). Anal. Calcd for $C_{19}H_{17}F_6OSb$: C, 45.91; H, 3.45. Found: C, 45.78; H, 3.55.

Thermolysis of 1,2-Oxastibetane 14c in the Presence of PhLi. To a solution of **14c** (11 mg, 0.014 mmol) in THF (0.5 mL) was

(28) Shanklin, J. R.; Johnson, C. R.; Ollinger, J.; Coates, R. M. *J. Am. Chem. Soc*. **1973**, *95*, 3429.

(29) Nader, B. S.; Cordova, J. A.; Reese, K. E.; Powell, C. L. *J. Org. Chem*. **1994**, *59*, 2898.

(30) House, H. O. *J. Am. Chem. Soc*. **1955**, *77*, 3070.

(31) The yields of **30**, **34**, and **35** were calculated assuming that 1 mol of **7c** gives 1 mol of **30** and **34**, and 0.5 mol of **35**, respectively.

added PhLi (2.28 M, 7.0 μL, 0.016 mmol) at room temperature and the mixture was stirred for 1 h. After the solvent was exchanged from THF to PhCN (0.5 mL), the reaction mixture was heated at 140 °C for 6 h to give olefin **30** (72%) and bis(stiboranyl)oxide **38**, which was assigned by FAB-MS spectra.

X-ray Crystallographic Analyses of 3, 14a, and 14c. Single crystals of **3**, **14a**, and **14c** were grown by the slow evaporation of the saturated hexane solution at room temperature. A colorless block crystal of **3**, **14a**, and **14c** having approximate dimensions of 0.60 $\times$ 0.40 $\times$ 0.25 mm^3, 0.20 $\times$ 0.20 $\times$ 0.15 mm^3, and 0.15 $\times$ 0.10 $\times$ 0.05 mm^3, respectively, was mounted on a glass fiber. All measurements were made on a Rigaku Mercury-CCD with graphite monochromated Mo Kα radiation (λ = 0.71070 Å). The structure was solved by direct methods and expanded by using Fourier techniques. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. There are four and two independent molecules of **3** and **14a**, which have slightly different structures in the unit cell, respectively. Crystallographic data and selected bond lengths and angles for **3**, **14a**, and **14c** are summarized in Tables 1 and 2.

Acknowledgment. This work was supported by Grants-in-Aid for The 21st Century COE Program for Frontiers in Fundamental Chemistry (T.K.) and for Scientific Research (T.K.) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We thank Central Glass and Tosoh Finechem Corporation for the gifts of organofluorine compounds and organolithium reagents, respectively.

Supporting Information Available: Experimental procedures of **6**, **7b**, **13b**−**d**, **14b**−**d**, **15b**, and **15d**, physical and spectral data of **6**, **8**, and **9**, and data for the X-ray crystallographic analyses of **3**, **14a**, and **14c** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0520700