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Synthesis, structure, and reaction of tricoordinate stibine and tetracoordinate stiboranide

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ABSTRACT

Tricoordinate stibine **1** and tetracoordinate stiboranide **2a** were synthesized by utilizing $SbCl_3$. The structure of **2a** was confirmed by X-ray analysis. The interconversion between **1** and **2** could be achieved by $BrNEt_4$ and NaH or BuLi. The pentacoordinate apicophilic stiborane **6** was prepared from **1**. Due to steric repulsion between the TIP group and the aromatic ring, the C1–Sb–C2 angle of **6b** was narrowed by 4.4° compared to that of **6a** by X-ray analysis.

1. Introduction

Hypervalent compounds of the main group elements have been attractive subjects for both experimental and theoretical chemists for a long time [1]. Especially, hypervalent phosphorus chemistry [2–4], which is deeply related to the phosphoryl transfer reaction in biological systems [5–9], has elucidated the significant fundamental properties of pentacoordinated molecules. Pentacoordinate compounds are discovered to have two different structures, one is trigonal bipyramid (TBP) structure and the other is square pyramid (SP) structure, and the former is generally preferred (Fig. 1). The TBP structure includes two distinct bonds, apical bond and equatorial bond. The apical bond is described as a three-center-four-electron (hypervalent) bond, whereas the equatorial bond is described as an sp^2 bond. The apical bond comprising of the two sites positioned linearly with the center intersects the equatorial plane perpendicularly.

A very rapid nondissociative intramolecular exchange of sites, i.e., the exchange between the apical ligand and the equatorial ligand, is usually advocated by Berry pseudorotation (BPR) [10–12], which is presumed to be a very low energy process (calculated to be ≈ 2 kcal mol^{-1} for BPR of PH_5) [13]. Another alternative mechanism called turnstile rotation (TR) proposed by Ugi et al. [14,15] has been calculated to be higher in energy than BPR (calculated to be ≈ 10 kcal mol^{-1} for TR of PH_5) [16–18]. Therefore, usually TR is not taken into consideration in discussions on the isomerization of pentacoordinate molecules. The motion of BPR is illustrated in Fig. 2 where one of the equatorial ligands is taken as a pivot (3) and the originally apical bonds (1, 2) undergo an angular bending from 180° to 120°, and two equatorial ligands (4, 5) bend from 120° to 180° in equatorial plane including the pivot ligand. In this process, an SP structure is the transition state.

In the TBP structure, electronegative and sterically small groups generally prefer to occupy the apical sites, whereas electron-donating and bulky ligands prefer the equatorial sites. The relative preference of substituent occupying the apical site is particularly known as apicophilicity [19–36]. From many experimental systems and theoretical calculations, an oxygen atom is determined to be much more apicophilic than a carbon atom [19–36]. Anti-apicophilic compound, which violates relative apicophilicity of the elements, generally has high energy and is unstable, thus easily isomerizes into its stable apicophilic compound.

Using Martin ligand [37] and new bidentate ligand with two C_2F_5 groups [38], synthesis, structure, and reaction of pentacoordinate compounds in the central atom of phosphorus and arsenic had been reported [20,38–43]. Herein, we now report the synthesis of tricoordinate stibine **1** and a unique tetracoordinate stiboranide **2a** bearing new bidentate ligand. The reactivity of **1** and **2** are investigated. Synthesis and structure of the pentacoordinate stiborane are then discussed.

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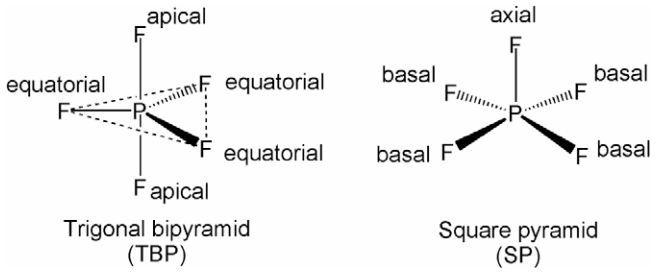
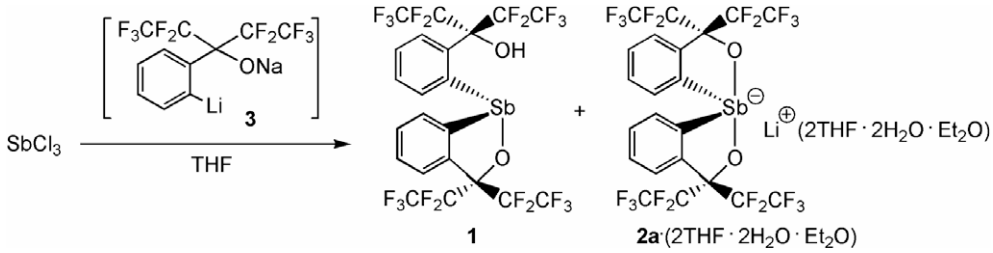


Fig. 1. Trigonal bipyramid and square pyramid.

2. Result and discussion

2.1. Synthesis and structure of *1* and *2a*

Dianion **3** [38] was added to a solution of $SbCl_3$ in THF to give tricoordinate stibine **1** (8%) and tetracoordinate stiboranide **2a** (7%) (Scheme 1). Compound **1** showed two sets of distinct hydrogen signals for two aromatic rings in the ^1H NMR spectrum (δ = 8.23 (dd, 2H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.7 Hz), 7.82 (td, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.7 Hz), and 7.79 (td, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.7 Hz) ppm; δ = 7.97–8.01 (m, 2H), and 7.80 (t, 2H, $^3J_{H-H}$ = 7.6 Hz) ppm), and the two aromatic rings were unequivalent. This showed that compound **1** was a tricoordinate stibine and compared with arsenic analogue similarly to our previous result [43]. In comparison with compound **2a** in the ^1H NMR spectrum (δ = 7.79 (d, 2H, $^3J_{H-H}$ = 8 Hz), 7.61 (br d, 2H, $^3J_{H-H}$ = 8 Hz), 7.42 (td, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 1.5 Hz), and 7.32 (td, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 1.5 Hz) ppm at 25 °C), two aromatic rings were equivalent. Furthermore, the ^{19}F NMR spectrum of CF_3 groups in **2a** showed sharp signal, in which all CF_3 groups were magnetically equivalent. The solid-state structure of stiboranide **2a** was confirmed by the X-ray crystallographic analysis (Fig. 3 and Table 1). The bond length of Sb1–O1 and Sb1–O2 was same, which was 2.188(6) Å. The molecule of compound **2a** was symmetrical by the central atom of antimony, therefore the ^1H NMR spectrum of two aromatic rings was same and in agreement with that described above. Compound **2a** was stable in air and water.



Scheme 1. Synthesis of **1** and **2a**.

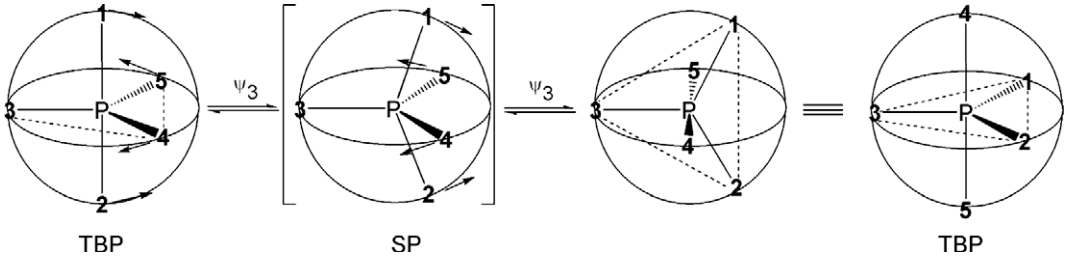


Fig. 2. The motion of BPR.

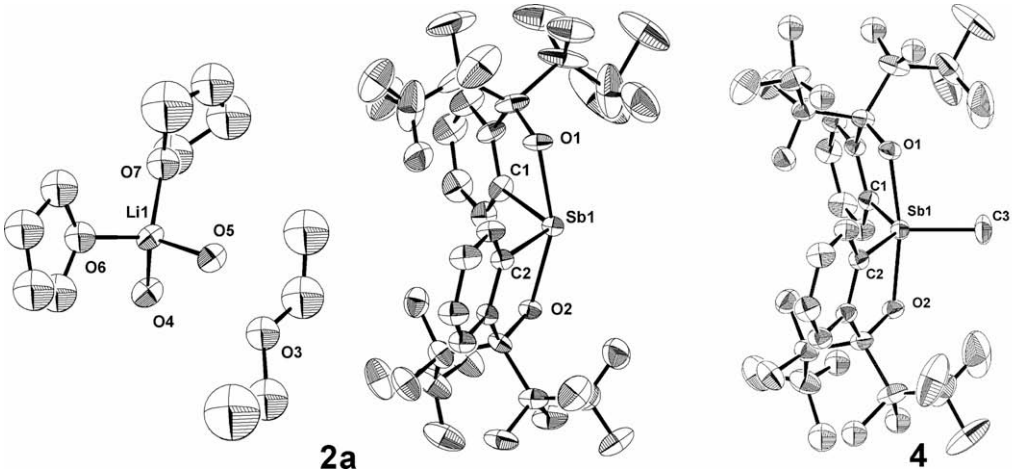


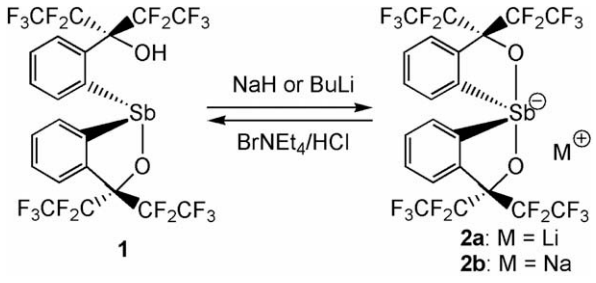
Fig. 3. The ORTEP drawings of **2a** and **4** showing the thermal ellipsoids at the 30% probability level. The hydrogen atoms are omitted for clarity.

2.2. Interconversion between **1** and **2**

The interconversion between **1** and **2** was investigated. Under air, after $BrNEt_4$ was added to a solution of **2a** in acetone and the reaction was quenched with 6 M HCl, **2a** was almost quantitatively converted into **1** (Scheme 2). When **2a** was only quenched with HCl, **1** was not obtained at all. **2a** may be stabilized by coordination of the lithium cation with the two oxygen atoms of the apical bond in solution. By using $BrNEt_4$, the reaction of **2a** gave LiBr and the lithium cation could be removed from **2a**. In contrast, **2** was easily prepared by the reaction of **1** in the presence of NaH or BuLi. To the best of our knowledge, the interconversion between tricoordinate stibine and tetracoordinate stiboranide was a first example.

Table 1
Selected bond lengths (Å) and angles (°) for the **2a** and **4**.

	2a	4
Bond lengths (Å)		
Sb1–O1	2.188(6)	2.069(4)
Sb1–O2	2.188(6)	2.069(4)
Sb1–C1	2.160(8)	2.097(4)
Sb1–C2	2.149(8)	2.097(4)
Sb1–C3		2.088(8)
Bond angles (°)		
O1–Sb1–O2	156.1(3)	168.1(2)
O1–Sb1–C1	76.5(4)	80.70(16)
O1–Sb1–C2	89.5(3)	94.08(17)
O1–Sb1–C3		95.97(10)
O2–Sb1–C1	90.4(4)	94.08(17)
O2–Sb1–C2	76.2(3)	80.70(16)
O2–Sb1–C3		95.97(10)
C1–Sb1–C2	110.3(4)	128.5(2)
C1–Sb1–C3		115.75(12)
C2–Sb1–C3		115.75(13)



Scheme 2. Interconversion between **1** and **2**.

2.3. Reactivity of **1** and **2a** to MeI

The ability of ER_3 (E = As, Sb, Bi) to act as Lewis base has long been recognized. Such compounds arise from the donation of the lone pair of electrons on the E atom to an electrophile. Therefore, the reaction of **1** with MeI was carried out (Fig. 4). The expected result of methylstiborane **4** was not obtained. On the contrary, the reaction of **2a** with MeI gave stiborane **4** in 40% yield by S_N2 reaction (Fig. 4). The structure of **4** was confirmed by X-ray analysis (Fig. 3 and Table 1). The lone pair of electrons of **1** were sited in an sp^3 orbital; the structure of tetracoordinate stiboranide **2a** was a trigonal bipyramid structure, and the lone pair of electrons were sited in an sp^2 orbital. It is well known that the higher the energy of the lone pair is, the more reactive the compound is [44]. Therefore, the reactivity of the lone pair in sp^3 orbital of **1** should be higher than that in sp^2 orbital of **2a**, which was not in agreement with our experimental result. This could be explained in terms of the steric repulsion of the C_2F_5 group. The experimental result that compound **1** did not react with MeI showed that the steric bulk of the pentafluoroethyl group could prevent the lone pair from attacking MeI. This result was similar to the reported result [42,45]. On the other hand, for compound **2a**, the lone pair was sited in sp^2 orbital in the equatorial plane, and could react with MeI to give compound **4**.

2.4. Preparation of pentacoordinate apicophilic stiborane **6** from **1**

Using new bidentate ligand with two C_2F_5 groups, the pentacoordinate anti-apicophilic phosphoranes were successfully isolated by the reaction of P–H compound with RLi (R = alkyl, aryl) and I_2

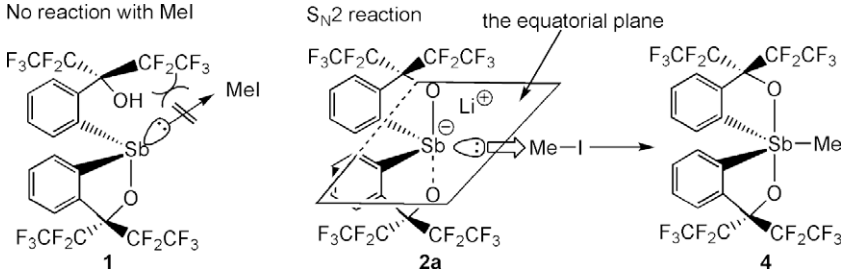
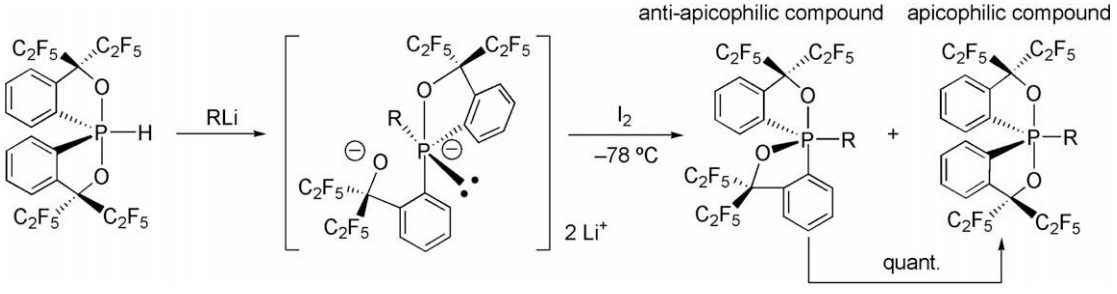
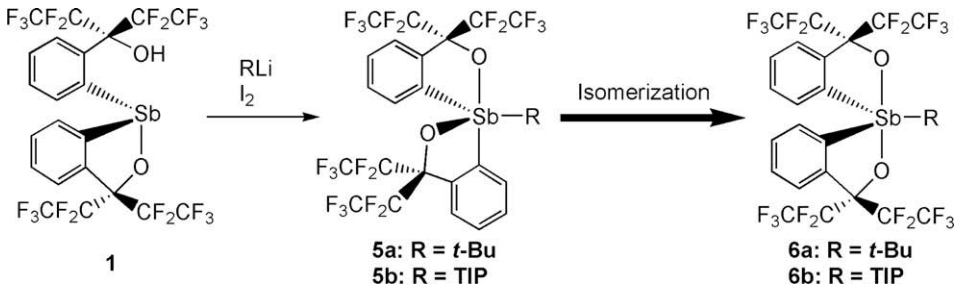


Fig. 4. The reaction of **1** and **2a** with MeI.



Scheme 3. Synthesis of pentacoordinate phosphoranes.



Scheme 4. Synthesis and isomerization of pencoordinate stiborane **6**.

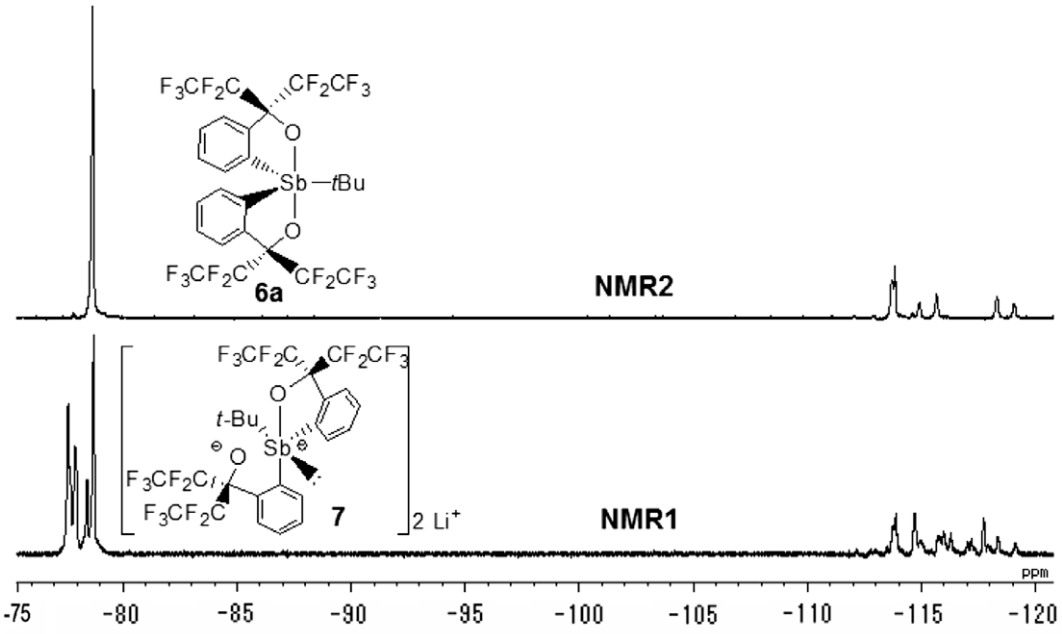


Fig. 5. ^{19}F NMR spectra of **6a** and **7** in THF.

which acted as oxidative cyclization (Scheme 3) [38,42]. The anti-apicophilic compounds could quantitatively convert into the corresponding apicophilic compounds by heat in solution [38,42]. Furthermore, the kinetic study revealed that the steric hindrance of the C_2F_5 group was more effective for freezing pseudorotation [38,42]. This enables us to investigate synthesis and isolation of anti-apicophilic stiborane **5a**. Using our method for the synthesis of the pentacoordinate compounds [40], only the corresponding apicophilic stiborane **6a** was obtained in 50% yield, though the monodentate ligand was the *t*-butyl group which was effective for slowing the isomerization (Scheme 4). In order to trace the isomerization of **5a** to **6a**, the samples of two NMR tubes were prepared: after *t*-BuLi was added to compound **1** in THF, the supernatant was transferred to an NMR tube under N_2 (NMR1); after I_2 was added to the mixture, another NMR tube (NMR2) was prepared in the same condition. The reaction was monitored by ^{19}F NMR (Fig. 5). In NMR1 spectrum, the dianion **7** which have four distinct fluorine singles corresponding to CF_3 groups ($\delta = -77.5$, -77.9, -78.4, and -78.7 ppm at 25 °C) was observed. The NMR2 spectrum showed that the anti-apicophilic compound **5a** would be generated by dianion **7** just after the addition of I_2 and rapidly isomerized into its corresponding stable stiborane **6a** by BPR, and compound **5a** was not observed at all. Therefore, the activation free energy for the isomerization of **5a** to **6a** was not enough higher to achieve the isolation of **5a**. By the steric hindrance of the monodentate ligand, TIP (triisopropylphenyl) was employed [46]. The same result of the apicophilic stiborane **6b** was given in 61% yield. The structures of **6a** and **6b** were confirmed by X-ray analysis (Fig. 6 and Table 2), which show that all the structures have TBP geometry. The C1–Sb–C2 angle of **6b** (123.63°) was narrowed by 4.4°

Table 2
Selected bond lengths (Å) and angles (°) for the **6a** and **6b**.

	6a	6b
Bond lengths (Å)		
Sb1–O1	2.070(3)	2.0630(19)
Sb1–O2	2.073(3)	2.0666(19)
Sb1–C1	2.101(4)	2.107(3)
Sb1–C2	2.099(4)	2.108(3)
Sb1–C3	2.182(4)	2.122(3)
Bond angles (°)		
O1–Sb1–O2	161.53(12)	167.62(8)
O1–Sb1–C1	79.69(12)	80.65(10)
O1–Sb1–C2	91.44(14)	93.99(10)
O1–Sb1–C3	98.96(15)	95.16(9)
O2–Sb1–C1	92.63(13)	93.13(10)
O2–Sb1–C2	80.04(14)	80.49(10)
O2–Sb1–C3	99.96(15)	97.20(9)
C1–Sb1–C2	128.07(14)	123.63(10)
C1–Sb1–C3	117.19(18)	116.61(11)
C2–Sb1–C3	114.72(18)	119.76(10)

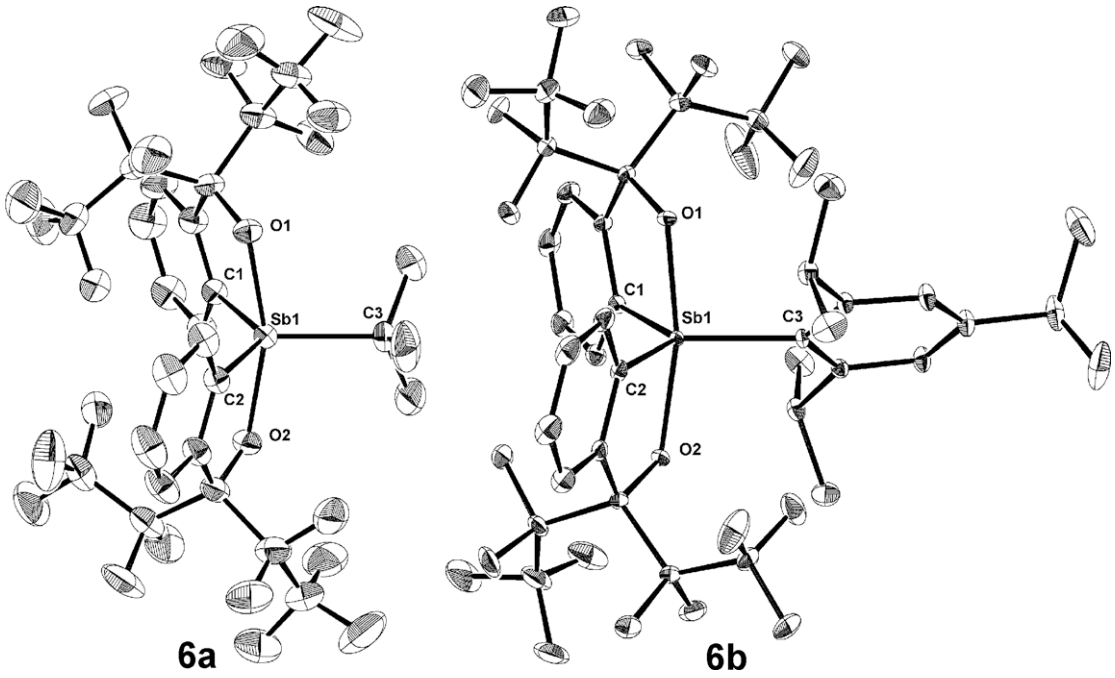


Fig. 6. The ORTEP drawings of stiboranes (**6a** and **6b**) showing the thermal ellipsoids at the 30% probability level. The hydrogen atoms are omitted for clarity.

compared to that of **6a** (128.07°). This was due to steric repulsion between the TIP group and the aromatic ring. To isolate anti-apicophilic stiborane, a bulky bidentate ligand or a bulky monodentate ligand should be necessary.

3. Conclusion

Tricoordinate stibine **1** and tetracoordinate stiboranide **2a** were synthesized by the reaction of dianion **3** with $SbCl_3$. The structure of tetracoordinate stiboranide **2a** was confirmed by X-ray analysis. The interconversion between **1** and **2** was achieved by $BrNEt_4$ and NaH or BuLi. No reaction of **1** with MeI gave an example of the steric bulk of the pentafluoroethyl group to prevent the lone pair from attacking an electrophile. The pentacoordinate anti-apicophilic stiborane **5** was not successfully isolated and the corresponding apicophilic stiborane **6** was obtained from **1**. Due to steric repulsion between the TIP group and the aromatic ring, the C1–Sb–C2 angle of **6b** was narrowed by 4.4° compared to that of **6a** by X-ray analysis. Those researches of isolating anti-apicophilic stiborane are now ongoing.

4. Experimental

4.1. General procedures

Melting points were measured using a Yanaco micro melting point apparatus. ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz), ^{31}P NMR (162 MHz) were recorded using JEOL EX-400 or JEOL AL-400 spectrometers. ^{1}H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by residual chloroform (δ = 7.26 ppm). ^{19}F NMR chemical shifts are given in ppm downfield from external $CFCl_3$. ^{31}P NMR chemical shifts are given in ppm downfield from external 85% H_3PO_4. Elemental analyses were performed using a Perkin–Elmer 2400 CHN elemental analyzer. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from Na/benzophenone, *n*-hexane was distilled from Na, and other solvents were distilled from CaH_2. Merck silica gel 60 was used for the column chromatography.

4.2. Preparation of *1* and *2a*

Under N_2, dianion **3** [38] (1.23 mmol) which was prepared from the reaction of 1,1,1,3,3,3-hexafluro-2-(2-bromophenyl)-2-propanol (532 mg, 1.23 mmol) with *t*-BuLi (in 1.57 M pentane, 1.6 mL, 2.51 mmol) in the presence of excess NaH was added to a solution of $SbCl_3$ (143 mg, 0.614 mmol) in THF (3 mL) at −78 °C and stirred for 0.5 h. The mixture was warmed to room temperature and stirred for 3 h. The reaction was quenched with distilled water (50 mL × 2). The mixture was extracted with ether (80 mL × 2), and dried over anhydrous $MgSO_4$. After solvent removal by evaporation, the resulting crude product was separated by column chromatography ($CH_3COOC_2H_5$), followed by reversed-phase HPLC (CH_3CN) to afford **1** (RT = 14.4 min, 38.5 mg, 0.048 mmol, 8%) and **2a** (RT = 13.6 min, 33.3 mg, 0.041 mmol, 7%) as white solids. Colorless crystals of **2a** suitable for X-ray analysis were obtained by recrystallization from THF/Et_2O. **1**: ^{1}H NMR ($CDCl_3$) δ 8.23 (dd, 2H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.7 Hz), 7.97–8.01 (m, 2H), 7.82 (td, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.7 Hz), 7.80 (t, 2H, $^3J_{H-H}$ = 7.6 Hz), 7.79 (td, 1H, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.7 Hz); ^{19}F NMR ($CDCl_3$) δ −78.17 (t, 6F, $^5J_{F-F}$ = 4.9 Hz), −78.24 (d, 6F, $^3J_{F-F}$ = 12.3 Hz), −115.9 (dq, 2F, $^2J_{F-F}$ = 283 Hz, $^3J_{F-F}$ = 12.3 Hz), −116.8 (s, 4F), −119.8 (dq, 2F, $^2J_{F-F}$ = 283 Hz, $^5J_{F-F}$ = 4.9 Hz). **2a**: ^{1}H NMR ($CDCl_3$) δ 7.79 (d, 2H, $^3J_{H-H}$ = 8 Hz), 7.61 (br d, 2H, $^3J_{H-H}$ = 8 Hz), 7.42 (td, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 1.5 Hz), 7.32 (td, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 1.5 Hz); ^{19}F NMR ($CDCl_3$) δ −78.2 (s, 12F), −114.8 (d, 2F, $^2J_{F-F}$ = 290 Hz), −116.7 (d, 2F, $^2J_{F-F}$ = 290 Hz), −119.2 (s, 4F).

4.3. Interconversion of *2a* to *1*

Under air, $BrNEt_4$ (26 mg, 0.124 mmol) was added to a solution of **2a** (33.3 mg, 0.0413 mmol) in acetone (10 mL) at room temperature. The mixture was stirred for 16 h at room temperature. The reaction was quenched with 6 M HCl (50 mL). The mixture was extracted with ether (60 mL × 2), and dried over anhydrous $MgSO_4$. After solvent removal by evaporation, the resulting crude was separated by preparative TLC (*n*-hexane/CH_2Cl_2 = 4:1) to afford **1**

Table 3
Crystallographic data for **2a**, **4**, **6a** and **6b**.

Compound	**2a**·(2THF·2H_2O·Et_2O)	**4**	**6a**	**6b**
Formula	$C_{34}H_{38}F_{20}LiO_7Sb$	$C_{23}H_{11}F_{20}O_2Sb$	$C_{26}H_{17}F_{20}O_2Sb$	$C_{37}H_{31}F_{20}O_2Sb$
Molecular weight	1067.33	821.07	863.15	1009.37
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	*Pbca*	*P2/c*	*Pbca*	$P2_1/c$
Color	Colorless	Colorless	Colorless	Colorless
Habit	Plate	Plate	Plate	Plate
Crystal dimensions (mm)	0.30, 0.20, 0.10	0.25, 0.20, 0.15	0.40, 0.40, 0.30	0.60, 0.50, 0.40
a (Å)	18.6260(5)	22.3180(6)	11.9550(2)	14.9670(2)
b (Å)	21.6460(7)	11.8360(3)	28.0850(5)	10.39900(10)
c (Å)	22.2110(6)	10.4360(3)	18.1130(2)	26.0680(3)
α (°)	90	90	90	90
β (°)	90	98.3080(10)	90	102.6910(10)
γ (°)	90	90	90	90
V (Å^3)	8955.0(4)	2727.80(13)	6081.55(16)	3958.15(8)
Z	8	4	8	4
D_{calc} (g cm^{-3})	1.583	1.999	1.885	1.694
Absolute coefficient (mm^{-1})	0.741	1.171	1.056	0.825
F(0 0 0)	4256	1584	3360	2000
Radiation: λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
Temperature (°C)	25	20	20	−100
Data collected	+*h*, ±*k*, ±*l*	+*h*, +*k*, ±*l*	+*h*, +*k*, ±*l*	+*h*, +*k*, ±*l*
Data/restrains/parameters	10379/0/493	3283/0/207	6200/0/446	7447/0/547
R_1 ($I > 2\sigma(I)$)	0.1120	0.0640	0.0474	0.0393
wR_2 (all data)	0.3543	0.1900	0.1534	0.1405
Goodness-of-fit	1.092	1.092	1.123	1.208
Largest difference in peak, hole (e Å^{-3})	0.982, −2.156	0.745, −2.255	0.951, −2.116	0.982, −2.156

(32.5 mg, 0.0402 mmol, 97%). The spectral data of **1** were consistent with those of the same product described above.

4.4. Interconversion of *1* to *2*

Method 1: under N_2, a solution of **1** (22.5 mg, 0.027 mmol) in THF (3 mL) was added to a suspension of NaH (40 mg, 1.0 mmol) in THF (2 mL) at 0 °C. The mixture was stirred for 1 h at room temperature. The reaction was quenched with distilled water (50 mL × 2). The mixture was extracted with ether (70 mL × 2), and dried over anhydrous $MgSO_4$. After solvent removal by evaporation, the mixture of **1** and **2b** (24 mg) was obtained. The ^{1}H NMR ($CDCl_3$) showed the signals for **1** and **2b** with the ratio of **1**/**2b** = 21:79. The spectral data of **2b** were consistent with those of the product **2a** described above.

Method 2: under N_2, *n*-BuLi (in 1.59 M *n*-hexane, 0.02 mL, 0.031 mmol) was added to a solution of **1** (24.2 mg, 0.03 mmol) in Et_2O (1.5 mL) at 0 °C and stirred for 0.5 h at the same temperature. The mixture was warmed to room temperature and stirred for 3 h. The reaction was quenched with distilled water (60 mL × 2). The mixture was extracted with ether (50 mL × 2), and dried over anhydrous $MgSO_4$. After solvent removal by evaporation, the mixture of **1** and **2a** (20 mg) was obtained. The ^{1}H NMR ($CDCl_3$) showed the signals for **1** and **2a** with the ratio of **1**/**2a** = 40:60. The spectral data of **2a** were consistent with those of the same product described above.

4.5. Preparation of [TBPY-5-11]-methyl-3,3,3′,3′-tetrakis(pentafluoroethyl)-1,1′-spirobi [3H,2,1,^{5}-benzoxastibole] (*4*)

Under N_2, MeI (0.01 mL, 0.16 mmol) was added to a solution of **2a** (37.3 mg, 0.035 mmol) at 0 °C. The mixture was stirred for 6 h at room temperature. The mixture was extracted with ether (80 mL × 2), and the organic layer was washed with brine (60 mL × 2) and dried over anhydrous $MgSO_4$. After solvent removal by evaporation, the resulting crude was separated by TLC (*n*-hexane/CH_2Cl_2 = 4:1) to afford **4** (11.2 mg, 0.0136 mmol, 40%). Colorless crystals of **4** suitable for X-ray analysis were obtained by recrystallization from *n*-hexane/CH_2Cl_2. ^{1}H NMR ($CDCl_3$) δ 8.14 (d, 2H, $^3J_{H-H}$ = 8 Hz), 7.86 (br d, 2H, $^3J_{H-H}$ = 8 Hz), 7.72 (td, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.68 (td, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 1.2 Hz), 1.72 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −78.2 (s, 6F), −78.4 (dd, 6F, $^3J_{F-F}$ = 14.8 Hz, $^5J_{F-F}$ = 6.1 Hz), −115.8 (dq, 2F, $^2J_{F-F}$ = 283 Hz, $^3J_{F-F}$ = 14.8 Hz), −116.1 (d, 2F, $^2J_{F-F}$ = 283 Hz), −117.2 (br d, 2F, $^2J_{F-F}$ = 283 Hz), −119.9 (dq, 2F, $^2J_{F-F}$ = 283 Hz, $^5J_{F-F}$ = 6.1 Hz). MS (EI(+)): *m*/*z* = 806[M]$^+$, 687[M−C_2F_5]$^+$.

4.6. Preparation of [TBPY-5-11]-1-t-butyl-3,3,3′,3′-tetrakis(pentafluoroethyl)-1,1′-spirobi [3H,2,1,^{5}-benzoxastibole] (*6a*)

Under N_2, a solution of **1** (31.3 mg, 0.038 mmol) in THF (1 mL) was added to a suspension of NaH (41.6 mg, 1.04 mmol) in THF (1 mL) at 0 °C and the mixture was stirred for 10 min at room temperature. The mixture was then cooled at −78 °C, and *t*-BuLi (in 1.57 M *n*-pentane, 0.030 mL, 0.047 mmol) was added. The mixture was then stirred for 15 min at room temperature. I_2 (12 mg, 0.047 mmol) was added to the mixture at −78 °C and stirred for 1 h at 0 °C. The reaction was quenched with aqueous $Na_2S_2O_3$ (30 mL × 2). The mixture was extracted with Et_2O (30 mL × 2), and the organic layer was washed with brine (20 mL × 2) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the resulting crude was separated by TLC (*n*-hexane/CH_2Cl_2 = 4:1) to afford **6a** (16.8 mg, 0.019 mmol, 50%) as a white solid. Colorless crystals of **6a** suitable for X-ray analysis were obtained by recrystallization from *n*-hexane/CH_2Cl_2. ^{1}H NMR ($CDCl_3$) δ 8.08 (d, 2H, $^3J_{H-H}$ = 8 Hz), 7.83 (br d, 2H, $^3J_{H-H}$ = 8 Hz), 7.68 (td, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 1.2 Hz), 7.63 (td, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 1.2 Hz), 1.39 (s, 9H); ^{19}F NMR ($CDCl_3$) δ −78.3 (dd, 6F, $^3J_{F-F}$ = 14.8 Hz, $^5J_{F-F}$ = 4.9 Hz), −78.4 (br s, 6F), −113.2 (dq, 2F, $^2J_{F-F}$ = 285 Hz, $^3J_{F-F}$ = 14.8 Hz), −114.1 (br d, 2F, $^2J_{F-F}$ = 285 Hz), −115.3 (d, 2F, $^2J_{F-F}$ = 285 Hz), −118.6 (dq, 2F, $^2J_{F-F}$ = 285 Hz, $^5J_{F-F}$ = 4.9 Hz). Anal. Calc. for $C_{26}H_{17}F_{20}O_2Sb$: C, 36.18; H, 1.90. Found: C, 36.45; H, 1.80%.

4.7. Preparation of [TBPY-5-11]-1-TIP-3,3,3′,3′-tetrakis(pentafluoroethyl)-1,1′-spirobi [3H,2,1,^{5}-benzoxastibole] (*6b*)

Under N_2, triisopropylphenyllithium (0.689 mmol) which was prepared from the reaction of 1-bromo-2,4,6-triisopropylbenzene (195.3 mg, 0.689 mmol) with *n*-BuLi (in 1.58 M *n*-hexane, 0.43 mL,

0.679 mmol) was added to a solution of **1** (88.5 mg, 0.109 mmol) in Et_2O (3 mL) at −78 °C. The mixture was then stirred for 1 h at room temperature. I_2 (110 mg, 0.433 mmol) was added to the mixture at −78 °C and stirred for 1 h at 0 °C. The reaction was quenched with aqueous $Na_2S_2O_3$ (50 mL × 2). The mixture was extracted with Et_2O (60 mL × 2), and the organic layer was washed with brine (50 mL × 2) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the resulting crude was separated by TLC (*n*-hexane/CH_2Cl_2 = 4:1) to afford **6b** (67.4 mg, 0.0667 mmol, 61%) as a white solid. Colorless crystals of **6b** suitable for X-ray analysis were obtained by recrystallization from *n*-hexane/CH_2Cl_2. M.p.: 160.5–161.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.27 (d, 2H, $^3J_{H-H}$ = 8 Hz), 7.81 (br d, 2H, $^3J_{H-H}$ = 8 Hz), 7.74 (t, 2H, $^3J_{H-H}$ = 8 Hz), 7.64 (t, 2H, $^3J_{H-H}$ = 8 Hz), 6.99 (s, 2H), 3.39 (sept, 2H, $^3J_{H-H}$ = 6.6 Hz), 2.83 (sept, 1H, $^3J_{H-H}$ = 6.6 H z), 1.34 (d, 6H, $^3J_{H-H}$ = 6.6 Hz), 1.21 (d, 6H, $^3J_{H-H}$ = 6.6 Hz), 0.66 (d, 6H, $^3J_{H-H}$ = 6.6 Hz); ^{19}F NMR ($CDCl_3$) δ −78.3 (s, 6F), −78.5 (dd, 6F, $^3J_{F-F}$ = 18.5 Hz, $^5J_{F-F}$ = 4.9 Hz), −114.1 (d, 2F, $^2J_{F-F}$ = 286 Hz), −116.0 (dq, 2F, $^2J_{F-F}$ = 286 Hz, $^3J_{F-F}$ = 18.5 Hz), −117.9 (d, 2F, $^2J_{F-F}$ = 286 Hz), −119.3 (dq, 2F, $^2J_{F-F}$ = 286 Hz, $^5J_{F-F}$ = 4.9 Hz). Anal. Calc. for $C_{37}H_{31}F_{20}O_2Sb$: C, 44.03; H, 3.10. Found: C, 44.02; H, 2.83%.

4.8. Single crystal X-ray analysis of *2a*, *4*, *6a*, and *6b*

Crystals suitable for the X-ray structural determination were mounted on a Mac Science DIP2030 imaging plate diffractometer and irradiated with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) for the data collection. The unit cell parameters were determined by separately autoindexing several images in each data set using the DENZO program (MAC Science) [47]. For each data set, the rotation images were collected in 3° increments with a total rotation of 180° about the φ axis. The data were processed using SCALEPACK. The structure was solved by a direct method with the SHELX-97 program [48]. Refinement on F^2 was carried out using the full-matrix leat-squares by the SHELX-97 program [48]. All non-hydrogen atoms were refined using the anisotropic thermal parameters. The hydrogen atoms were included in the refinement along with the isotropic thermal parameters. The crystallographic data are summarized in Table 3.

Supplementary material

CCDC 752614, 752615, 752616, and 752617 contain the supplementary crystallographic data for **2a**, **4**, **6a**, and **6b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] K.-Y. Akiba, Chemistry of Hypervalent Compounds, Wiley-VCH, New York, 1999.
[2] R.R. Homes, Pentacoordinated Phosphorus-Structure and Spectroscopy ACS Monograph 175 and 176, vol. I and II, American Chemical Society, Washington, DC, 1980.
[3] D.E.C. Corbridge, Phosphorus: An Outline of its Chemistry, Biochemistry and Technology, fourth ed., Elsevier, Amsterdam, 1990 (Chapter 14).
[4] R. Burgada, R. Setton, in: F.R. Hartley (Ed.), The Chemistry of Organophosphorus Compounds, vol. 3, Wiley-Interscience, Chichester, 1994, pp. 185–277.
[5] A.C. Hengge, Acc. Chem. Res. 35 (2002) 105–112.
[6] S.D. Lahiri, G. Zhang, D. Dunaway-Mariano, K.N. Allen, Science 299 (2003) 2067–2071.
[7] R.R. Holmes, Acc. Chem. Res. 37 (2004) 746–753.
[8] F.H. Westheimer, Acc. Chem. Res. 1 (1968) 70–78.
[9] G.R.J. Thatcher, R. Kluger, Adv. Phys. Org. Chem. 25 (1989) 99–265.
[10] R.S. Berry, J. Chem. Phys. 32 (1960) 933–938.
[11] K. Mislow, Acc. Chem. Res. 3 (1970) 321–331.
[12] E.L. Muetterties, Acc. Chem. Res. 3 (1970) 266–273.
[13] J. Moc, K. Morokuma, J. Am. Chem. Soc. 117 (1995) 11790–11797.
[14] I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, F. Ramirez, Acc. Chem. Res. 4 (1971) 288–296.
[15] P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E.A. Tsolis, I. Ugi, Angew. Chem., Int. Ed. 10 (1971) 687–715.
[16] J.A. Altmann, K. Yates, I.G. Csizmadia, J. Am. Chem. Soc. 98 (1976) 1450–1454.
[17] A. Strich, A. Veillard, J. Am. Chem. Soc. 95 (1973) 5574–5581.
[18] S.-K. Shih, S.D. Peyerimhoff, J. Chem. Soc., Faraday Trans. II 75 (1979) 379–389.
[19] M. Nakamoto, S. Kojima, S. Matsukawa, Y. Yamamoto, K.-Y. Akiba, J. Organomet. Chem. 643–644 (2002) 441–452.
[20] S. Matsukawa, K. Kajiyama, S. Kojima, S.-Y. Furuta, Y. Yamamoto, K.-Y. Akiba, Angew. Chem., Int. Ed. 41 (2002) 4718–4722.
[21] S. Trippett, Phosphorus Sulfur 1 (1976) 89–98.
[22] S. Trippett, Pure Appl. Chem. 40 (1974) 595–604.
[23] G. Buono, J.R. Llinas, J. Am. Chem. Soc. 103 (1981) 4532–4540.
[24] M. Eisenhut, H.L. Mitchell, D.D. Traficante, R.J. Kaufman, J.M. Deutsch, G.M. Whitesides, J. Am. Chem. Soc. 96 (1974) 5385–5397.
[25] L.V. Griend, R.G. Cavell, Inorg. Chem. 22 (1983) 1817–1820.
[26] S. Kumaraswamy, C. Muthiah, K.C. Kumara Swamy, J. Am. Chem. Soc. 122 (2000) 964–965.
[27] P. Kommana, S. Kumaraswamy, J.J. Vittal, K.C. Kumara Swamy, Inorg. Chem. 41 (2002) 2356–2363.
[28] P. Kommana, N.S. Kumar, J.J. Vittal, E.G. Jayasree, E.D. Jemmis, K.C. Kumara Swamy, Org. Lett. 6 (2004) 145–148.
[29] R. Hoffmann, J.M. Howell, E.L. Muetterties, J. Am. Chem. Soc. 94 (1972) 3047–3058.
[30] R.S. McDowell, A. Streitwieser Jr., J. Am. Chem. Soc. 107 (1985) 5849–5855.
[31] J.A. Deiters, R.R. Holmes, J.M. Holmes, J. Am. Chem. Soc. 110 (1988) 7672–7681.
[32] P. Wang, Y. Zhang, R. Glaser, A.E. Reed, P.V.R. Schleyer, A. Streitwieser Jr., J. Am. Chem. Soc. 113 (1991) 55–64.
[33] H. Wasada, K. Hirao, J. Am. Chem. Soc. 114 (1992) 16–27.
[34] G.R.J. Thatcher, A.S. Campbell, J. Org. Chem. 58 (1993) 2272–2281.
[35] P. Wang, Y. Zhang, R. Glaser, A. Streitwieser, P.V.R. Schleyer, J. Comput. Chem. 14 (1993) 522–529.
[36] B.D. Wladkowski, M. Krauss, W.J. Stevens, J. Phys. Chem. 99 (1995) 4490–4500.
[37] J.C. Martin, Science 221 (1983) 509–514.
[38] X.-D. Jiang, K.-I. Kakuda, S. Matsukawa, H. Yamamichi, S. Kojima, Y. Yamamoto, Chem. Asian J. 2 (2007) 314–323.
[39] S. Kojima, K. Kajiyama, M. Nakamoto, K.-Y. Akiba, J. Am. Chem. Soc. 118 (1996) 12866–12867.
[40] K. Kajiyama, M. Yoshimune, M. Nakamoto, S. Matsukawa, S. Kojima, K.-Y. Akiba, Org. Lett. 3 (2001) 1873–1875.
[41] X.-D. Jiang, S. Matsukawa, H. Yamamichi, Y. Yamamoto, Heterocycles 73 (2007) 805–824.
[42] X.-D. Jiang, S. Matsukawa, Y. Yamamoto, Dalton Trans. 28 (2008) 3678–3687.
[43] X.-D. Jiang, S. Matsukawa, H. Yamamichi, Y. Yamamoto, Inorg. Chem. 46 (2007) 5480–5482.
[44] V.G.S. Box, J. Mol. Struct. 569 (2001) 167–178.
[45] X.-D. Jiang, S. Matsukawa, H. Yamamichi, K.-I. Kakuda, S. Kojima, Y. Yamamoto, Eur. J. Org. Chem. (2008) 1392–1405.
[46] When TTP (2,4,6-tri-tert-butylphenyl) was employed, the anti-apicophilic stiborane and its corresponding apicophilic stiborane were not obtained. It was due to steric hindrance of the bulky monodentate ligand of TTP.
[47] Z. Otwinowski, W. Minor, Methods in enzymology, in: C.W. Carter Jr., R.M. Sweet (Eds.), Macromolecular Crystallography, Part A, vol. 276, Academic Press, 1997, pp. 307–326.
[48] G.M. Sheldrick, SHELX-97, University of Göttingen, Göttingen, Germany, 1997.