

# Synthesis and Structural Study of Organoantimony(III) and Organobismuth(III) Triflates and Cations Containing O,C,O-Pincer Type Ligands<sup>†</sup>

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Received February 28, 2007

The reactions of intramolecularly coordinated organoantimony and organobismuth dihalides L<sup>1</sup>SbCl<sub>2</sub> and L<sup>2</sup>BiCl<sub>2</sub>, containing two types of O,C,O-pincer ligands 2,6-(ROCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub><sup>−</sup> (L<sup>1</sup>, R = Me; L<sup>2</sup>, R = <sup>t</sup>Bu), with silver salts of the weakly nucleophilic polar groups CF<sub>3</sub>SO<sub>3</sub><sup>−</sup> (OTf) and CB<sub>11</sub>H<sub>12</sub><sup>−</sup> (in 1:1 and 1:2 molar ratios) gave the following compounds: L<sup>1</sup>SbCl(OTf) (**1**), L<sup>2</sup>BiCl(OTf) (**2**), L<sup>1</sup>Sb(OTf)<sub>2</sub> (**3**), L<sup>2</sup>Bi(OTf)<sub>2</sub> (**4**), L<sup>1</sup>SbCl(CB<sub>11</sub>H<sub>12</sub>) (**5**), L<sup>2</sup>BiCl(CB<sub>11</sub>H<sub>12</sub>) (**6**). All compounds were characterized structurally by X-ray diffraction. In the solid state, compounds **1–3** have OTf groups covalently (although weakly) bound to the central metal atom. In compound **4**, one of the OTf groups is bound in a unidentate fashion and the other in a weakly chelating fashion. Compounds **5** and **6** exist as separated ion pairs consisting of a [L<sup>1</sup>SbCl(THF)]<sup>+</sup> or [L<sup>2</sup>BiCl]<sup>+</sup> cation and CB<sub>11</sub>H<sub>12</sub><sup>−</sup> anion. The donor oxygen atoms are coordinated to the metal atoms through strong intramolecular interactions in all compounds. The solution structures of all compounds were studied by the help of variable-temperature <sup>1</sup>H NMR measurements.

## Introduction

Various types of organometallic cations of both transition and main-group metals constitute an interesting class of compounds from both structural and chemical points of view: for example, the utilization of rare-earth-metal cations in many organic transformations,<sup>1</sup> the activity of Ti and Zr cations in the polymerization of alkenes,<sup>2</sup> and the use of Al cations as catalysts for polymerizations and ROP processes<sup>3</sup> and Sn cations for esterification, transesterification, and other organic reactions.<sup>4</sup>

Also, organobismuth cations or at least strong Lewis acids (such as Bi(OTf)<sub>3</sub>) are widely used in organic synthesis.<sup>5</sup>

In many cases, the successful formation of stable organometallic cations (as highly electrophilic species) requires the presence of Lewis bases as electron donors in their structure. The possibility of stabilizing metallic cations of the type [MX<sub>2</sub>]<sup>+</sup>·D<sub>n</sub> (M = Sb, Bi, X = halide, D = various neutral donors) was clearly demonstrated by several groups.<sup>6</sup> References dealing with organometallic (Sb, Bi) cations are somewhat scarce. Norman and co-workers reported several organoantimony and organobismuth monocations of the type [R<sub>2</sub>M]<sup>+</sup>·D<sub>2</sub> (M = Sb, Bi, D = OPPPh<sub>3</sub>, OP(NMe<sub>2</sub>)<sub>3</sub>).<sup>7</sup> The same group succeeded even in the synthesis of the unique dication [PhBi]<sup>2+</sup>·4OP(NMe<sub>2</sub>)<sub>3</sub>.<sup>7b</sup>

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<sup>†</sup> Dedicated to Dr. K. Mach on the occasion of his 70th birthday.

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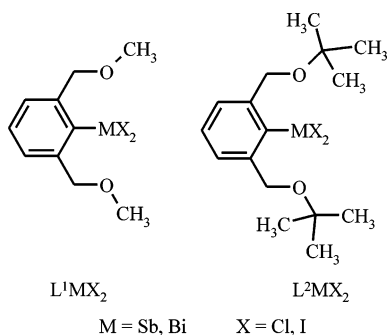
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Chart 1



A method of choice for stabilization of organometallic cations uses the so-called C,Y-chelating or even a special class of Y,C,Y-pincer ligands (Y = 2e donor atom, such as N, P, O, S, etc.).<sup>8</sup> The compounds [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>M<sup>+</sup> (M = Sb, Bi) represent rare examples of pnictogen cations stabilized by C,Y-chelating ligands.<sup>9</sup>

Recently, we have reported on the synthesis of organoantimony and organobismuth compounds containing the O,C,O-pincer ligands 2,6-(ROCH<sub>2</sub>)C<sub>6</sub>H<sub>3</sub><sup>-</sup> (L<sup>1</sup>, R = Me; L<sup>2</sup>, R = <sup>t</sup>Bu) (Chart 1).<sup>10</sup> We now turn our attention to stabilization of the corresponding organometallic cations. We have recently prepared a cationic organoantimony complex bearing two O,C,O-pincer ligands (L<sup>1</sup>)<sub>2</sub>Sb<sup>+</sup> as a chemical intermediate in the metathesis reaction between L<sup>1</sup>Li and SbCl<sub>3</sub>.<sup>11</sup> In the course of our continuing investigations of main-group-metal derivatives of O,C,O-pincer ligands we report here the synthesis of organoantimony and organobismuth compounds containing the weakly nucleophilic polar groups CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> (OTf) and CB<sub>11</sub>H<sub>12</sub><sup>-</sup>, L<sup>1</sup>SbCl(OTf) (**1**), L<sup>2</sup>BiCl(OTf) (**2**), L<sup>1</sup>Sb(OTf)<sub>2</sub> (**3**), L<sup>2</sup>Bi(OTf)<sub>2</sub> (**4**), L<sup>1</sup>SbCl(CB<sub>11</sub>H<sub>12</sub>) (**5**), and L<sup>2</sup>BiCl(CB<sub>11</sub>H<sub>12</sub>) (**6**), with the aim of obtaining and stabilizing the corresponding organometallic cations.

## Results and Discussion

**Synthetic Aspects.** Compounds **1–6** were prepared in good yields by reactions of the intramolecularly coordinated chlorides L<sup>1</sup>SbCl<sub>2</sub> and L<sup>2</sup>BiCl<sub>2</sub><sup>10</sup> with the appropriate silver salts of polar groups, according to Scheme 1. The utilization of two different ligands L<sup>1</sup> and L<sup>2</sup> for Sb and Bi compounds stems from the fact that the use of the precursor L<sup>2</sup>SbCl<sub>2</sub> in the reaction with AgOTf or AgCB<sub>11</sub>H<sub>12</sub> led to decomposition of the ligand via intramolecular ether bond cleavage.<sup>12</sup> All compounds had satisfactory elemental analyses, and their identities were established by ESI mass spectrometry.

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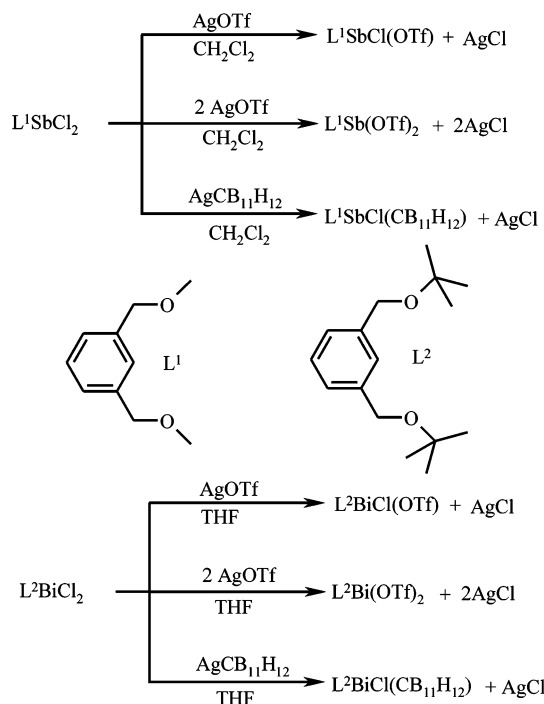
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Scheme 1. Synthesis of Studied Compounds

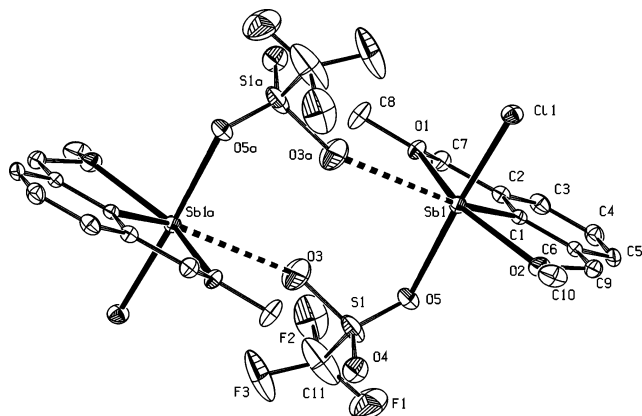


**Molecular Structures of 1–6.** The molecular structures of **1–6** were determined by single-crystal X-ray diffraction and are depicted in Figures 1–6. Selected bond lengths and bond angles are given in the corresponding figure captions.

The OTf group is coordinated to the central antimony atom of **1** (Figure 1), but the bond length Sb(1)–O(5) = 2.672(11) Å is considerably longer than the corresponding  $\Sigma_{\text{cov}}(\text{Sb},\text{O}) = 2.14 \text{ \AA}^{13}$  (sufficiently shorter than  $\Sigma_{\text{vdw}}(\text{Sb},\text{O}) = 3.78 \text{ \AA}^{13}$ ), indicating a rather weak interaction. Donor atoms O(1) and O(2) of L<sup>1</sup> are both strongly coordinated to the central metal atom (Sb(1)–O(1) = 2.226(7) Å, Sb(1)–O(2) = 2.324(8) Å). These intramolecular interactions are considerably stronger than those found in the parent L<sup>1</sup>SbCl<sub>2</sub> (Sb(1)–O(1) = 2.577(2) Å and Sb(1)–O(2) = 2.523(2) Å),<sup>10</sup> reflecting an increased Lewis acidity of the central antimony atom in **1**. Also, the bond angle O(1)–Sb(1)–O(2) = 148.0(2)<sup>o</sup> in **1** points to a different coordination mode of the ligand compared to that in L<sup>1</sup>SbCl<sub>2</sub>, with O(1)–Sb(1)–O(2) = 116.68(6)<sup>o</sup>.<sup>10</sup> Interestingly, both donor atoms of the ligand are bound to the antimony atom more tightly than the oxygen atom O(5) of the OTf group, as demonstrated by antimony–oxygen distances. This bonding situation may be interpreted in terms of a transition between a purely ionic compound and an ordinary covalent complex (where the bond distance Sb(1)–O(5) should be approximately 2.14 Å<sup>13</sup>). Similar weak bonds were found in organoantimony(V) sulfonates of the type Ph<sub>4</sub>Sb(ArSO<sub>3</sub>) (range of Sb–O bond lengths 2.463–2.699 Å).<sup>14</sup> The chlorine atom Cl(1) is bonded to the central antimony atom through the regular covalent bond Sb(1)–Cl(1) = 2.400(3) Å ( $\Sigma_{\text{cov}}(\text{Sb},\text{Cl}) = 2.37 \text{ \AA}^{13}$ ). The overall geometry around the central atom can be described as a distorted

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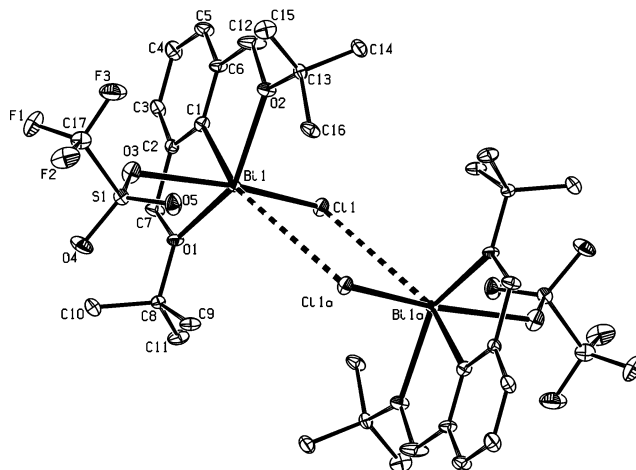
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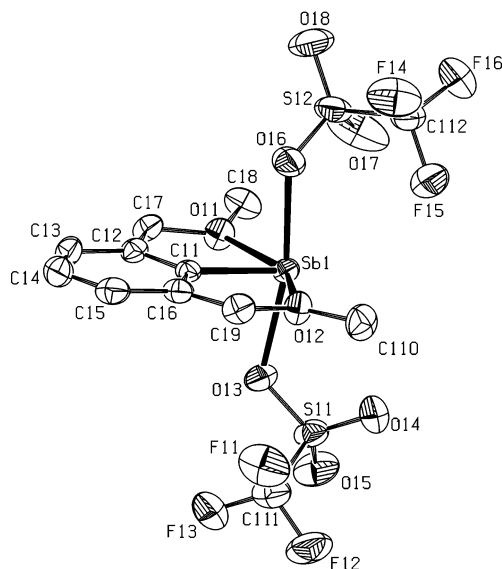
**Figure 1.** ORTEP plot of molecules of **1** showing 20% probability displacement ellipsoids and the atom-numbering scheme (symmetry code (a):  $-x, 1/2 + y, 1/2 - z$ ). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Sb(1)–O(1) = 2.226(7), Sb(1)–O(2) = 2.324(8), Sb(1)–C(1) = 2.093(8), Sb(1)–Cl(1) = 2.400(3), Sb(1)–O(5) = 2.672(11), Sb(1a)–O(3) = 3.398(14); O(1)–Sb(1)–O(2) = 148.0(2), O(5)–Sb(1)–Cl(1) = 168.1(2).

square pyramid<sup>15</sup> with the carbon atom C(1) in the axial position and atoms Cl(1), O(1), O(2), and O(5) forming the basal plane (the sum of angles describing the SbO<sub>3</sub>Cl girdle is 354°). Both polar groups are placed in mutually trans positions in the basal plane with the angle O(5)–Sb(1)–Cl(1) = 168.1(2)°. Closer inspection of the structure of **1** revealed a weak intermolecular contact of O(3) of the OTf group with the antimony atom of the adjacent molecule (Sb(1a)–O(3) = 3.398(14)). This results in the formation of weakly bound dimeric units formed via unsymmetrical OTf bridges and the unusual eight-membered-ring system Sb<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (Figure 1). The OTf group in **1** seems to be a rare example of triflate bridging two antimony atoms.<sup>16</sup>

The bismuth congener **2** also forms a molecular complex (Figure 2) with the covalently bonded OTf group, although the Bi(1)–O(3) bond length of 2.609(8) Å again implies that the Bi–OTf bond is rather weak ( $\Sigma_{\text{cov}}(\text{Bi}, \text{O}) = 2.19$  Å;  $\Sigma_{\text{vdW}}(\text{Bi}, \text{O}) = 3.86$  Å<sup>13</sup>). Both oxygen donor atoms O(1) and O(2) of L<sup>2</sup> are strongly coordinated to the central atom with distances Bi(1)–O(1) = 2.363(7) Å and Bi(1)–O(2) = 2.406(6) Å. These values are comparable to those of the parent L<sup>2</sup>BiCl<sub>2</sub>.<sup>10</sup> Both donor atoms of the ligand are bound to the bismuth atom more tightly than oxygen O(3) of the OTf group, thus closely resembling the bonding situation in **1**. The overall geometry around the central atom can be described as a distorted square pyramid<sup>15</sup> with the carbon atom C(1) in the axial position and atoms Cl(1), O(1), O(2), and O(3) forming the basal plane (the sum of angles describing the BiO<sub>3</sub>Cl girdle is 356°). Both polar groups are coordinated in this plane in nearly ideal trans positions, with Cl(1)–Bi(1)–O(3) = 167.13(17)°. The molecular packing is further affected by a weak intermolecular contact of the chlorine atom with the bismuth atom from the second molecule, Cl(1)–Bi(1a) = 3.707(3) Å, resulting in dimeric units similar to those found in the parent L<sup>2</sup>BiCl<sub>2</sub> (Figure 2).<sup>10</sup> Interestingly, both **1** and **2** form weakly connected dimers in



**Figure 2.** ORTEP plot of molecules of **2** showing 50% probability displacement ellipsoids and the atom-numbering scheme (symmetry code (a):  $-x, -y, -z$ ). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi(1)–O(1) = 2.363(7), Bi(1)–O(2) = 2.406(6), Bi(1)–C(1) = 2.202(10), Bi(1)–Cl(1) = 2.546(2), Bi(1)–O(3) = 2.609(8), Bi(1a)–Cl(1) = 3.707(3); O(1)–Bi(1)–O(2) = 145.3(2), O(3)–Bi(1)–Cl(1) = 167.13(17).



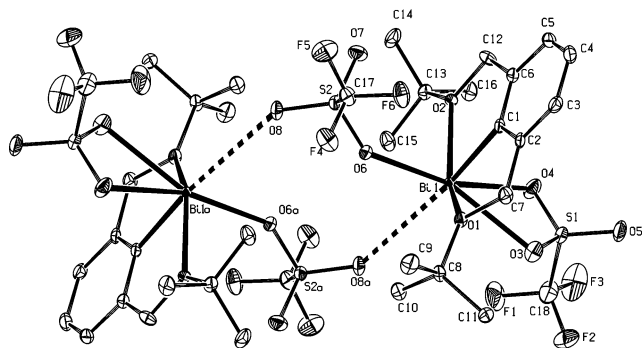
**Figure 3.** ORTEP plot of a molecule of **3** showing 50% probability displacement ellipsoids and the atom-numbering scheme. Hydrogen atoms were omitted for clarity. Two independent molecules are present in the crystal structure of **3**. Selected bond lengths (Å) and angles (deg) are as follows. Molecule A: Sb(1)–O(11) = 2.234(3), Sb(1)–O(12) = 2.246(4), Sb(1)–C(11) = 2.083(4), Sb(1)–O(13) = 2.277(4), Sb(1)–O(16) = 2.311(4); O(11)–Sb(1)–O(12) = 149.64(11), O(13)–Sb(1)–O(16) = 168.02(12). Molecule B: Sb(2)–O(21) = 2.297(3), Sb(2)–O(22) = 2.194(4), Sb(2)–C(21) = 2.091(4), Sb(2)–O(23) = 2.193(3), Sb(2)–O(26) = 2.368(4); O(21)–Sb(2)–O(22) = 149.48(11), O(23)–Sb(2)–O(26) = 165.72(14).

the solid state. In the case of **1** the OTf group is the bridge between two antimony atoms, but the chlorine atom can be found in a bridging position in **2**.

Two symmetrically independent molecules of **3** are present in the unit cell, differing mainly in the orientation of the OTf molecules toward the ligand due to the free rotation of OTf along the Sb–O bond. Only one of these molecules is shown in Figure 3. All OTf polar groups are bound covalently to the central antimony atom in compound **3** (Sb–O bond distances are within the range 2.193(3)–2.368(4) Å). As a result of the

(15) This structure also can be described as a  $\psi$ -octahedron, if the lone pair of the central metal is included in the overall geometry. This lone pair is then located in a position trans to the ipso carbon of the ligands L<sup>1,2</sup>.

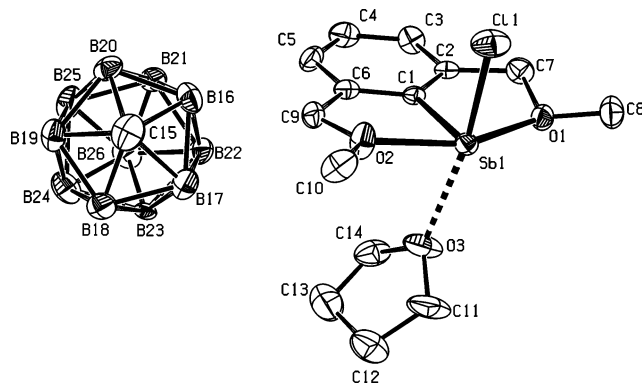
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**Figure 4.** ORTEP plot of molecules of **4** showing 50% probability displacement ellipsoids and the atom-numbering scheme (symmetry code (a):  $-x, -y, -z$ ). Hydrogen atoms and the solvent  $\text{CH}_2\text{Cl}_2$  molecule were omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi(1)–O(1) = 2.389(7), Bi(1)–O(2) = 2.393(6), Bi(1)–C(1) = 2.158(9), Bi(1)–O(3) = 2.628(7), Bi(1)–O(4) = 2.703(9), Bi(1)–O(6) = 2.377(7), Bi(1a)–O(8) = 3.295(8); O(1)–Bi(1)–O(2) = 141.3(2), O(3)–Bi(1)–O(6) = 149.6(2), O(4)–Bi(1)–O(6) = 157.8(2), O(3)–Bi(1)–O(4) = 56.2(2).

increased Lewis acidity (electrophilicity) of the antimony atom, both OTf groups are coordinated more tightly in **3** in comparison to **1**. Also, the donor oxygen atoms of  $\text{L}^1$  are strongly coordinated to the central atom (range of Sb–O(ligand) bond lengths 2.194(3)–2.297 Å). The coordination polyhedron can be described as a distorted square pyramid<sup>15</sup> with the ligand ipso carbon atom C(11) in the axial position and the basal plane being formed by the central antimony atom and four oxygen atoms (two originating from OTf groups and two from  $\text{L}^1$ —the sum of angles describing the  $\text{SbO}_4$  girdle is 354°). Both donor atoms and OTf groups are placed in mutually trans positions with the bond angles O(11)–Sb(1)–O(12) = 149.64(11)° and O(13)–Sb(1)–O(16) = 168.02(12)° for the molecule A. There are weak C–H···O(OTf) intermolecular contacts stabilizing the OTf positions in the crystal.

Similar to some structural differences found in the solid-state structures of **1** and **2**, the organobismuth compound **4** also displayed a significantly different coordination mode of OTf groups in comparison to the case for **3** (Figure 4). One OTf moiety is coordinated to the central bismuth atom in a unidentate fashion through the relatively strong covalent bond Bi(1)–O(6) = 2.377(7) Å, while the second OTf group is bound to the Bi(1) atom only weakly, interestingly in a bidentate fashion with distances Bi(1)–O(3) = 2.628(7) Å and Bi(1)–O(4) = 2.703(9) Å. This bidentate OTf group represents a rare example of this bonding situation in bismuth chemistry; a similar situation was found only in  $\text{BiCl}(\text{OTf})_2$ .<sup>16c</sup> The coordination mode of this OTf group can be understood in the same manner as for **1** and **2** as an example of a transition between an ionic and a covalent complex. Both donor atoms of  $\text{L}^2$  are again strongly coordinated to the bismuth atom (Bi(1)–O(1) = 2.389(7) Å and Bi(1)–O(2) = 2.393(6) Å). The resulting geometry around the bismuth atom can be described as a pentagonal pyramid with the C(1) atom in an apical position and five oxygen atoms in the basal plane (the sum of angles describing  $\text{SbO}_5$  girdle is 363°). This coordination polyhedron is further affected by weak intermolecular contacts mediated by unsymmetrical bridges formed by OTf groups (Bi(1a)–O(8) = 3.295(8) Å), leading to dimeric units as in the case of **1**. The presence of even stronger sulfonate



**Figure 5.** ORTEP plot of a molecule of **5** showing 50% probability displacement ellipsoids and the atom-numbering scheme. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Sb(1)–O(1) = 2.305(3), Sb(1)–O(2) = 2.238(4), Sb(1)–C(1) = 2.091(5), Sb(1)–Cl(1) = 2.3945(15), Sb(1)–O(3) = 2.576(4); O(1)–Sb(1)–O(2) = 148.87(15), O(3)–Sb(1)–Cl(1) = 171.56(11).

bridges between two bismuth atoms has been discovered recently by other groups.<sup>17</sup>

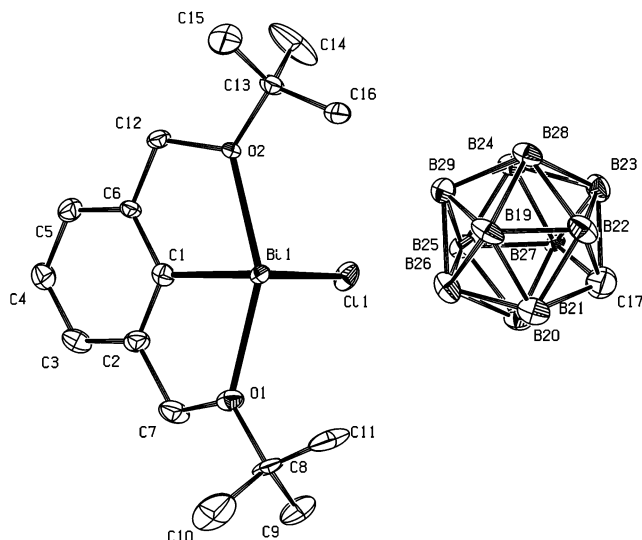
It is apparent that use of polar triflate groups in compounds **1**–**4** did not lead to an ionization of these complexes, although in these cases OTf groups are bound rather weakly. The even more weakly coordinating  $\text{CB}_{11}\text{H}_{12}^-$  cluster anion<sup>18</sup> was found to be effective for the stabilization of the corresponding organoantimony and organobismuth cations.

Compound **5** had only limited solubility in noncoordinating solvents. Thus, suitable single crystals of **5** could be grown only from THF and, as a result, a THF solvate was isolated (Figure 5). Compound **5** consists of the well-separated ion pair  $[\text{L}^1\text{SbCl}(\text{THF})]^+\text{CB}_{11}\text{H}_{12}^-$ . In the cation, both donor atoms of  $\text{L}^1$  are strongly coordinated to the central antimony atom with bond distances Sb(1)–O(1) = 2.305(3) Å and Sb(1)–O(2) = 2.238(4) Å. The chlorine atom Cl(1) is bound to the central Sb atom by a regular covalent bond: Sb(1)–Cl(1) = 2.3945(15) Å. The polyhedron of the central Sb atom is completed by the coordinated THF molecule with bond distance Sb(1)–O(1) = 2.576(4) Å. This value is comparable to those in other Sb–THF complexes.<sup>16c,19</sup> The THF molecule is coordinated in a position nearly ideally trans to Cl(1), with the angle O(3)–Sb(1)–Cl(1) = 171.56(11)°. The polyhedron around Sb(1) is a distorted square pyramid with C(1) of  $\text{L}^1$  in the apical position (the sum of angles describing  $\text{SbO}_3\text{Cl}$  girdle is 357°).

(17) For other bridging OTf groups at Bi see: (a) Sharutin, V. V.; Sharutina, O. K.; Zhitkevich, M. V.; Kharsika, A. N.; Bliznyuk, T. N.; Pakusina, A. P.; Bel'sky, V. K. *Russ. J. Gen. Chem.* **2000**, *70*, 923. (b) Sharutin, V. V.; Sharutina, O. K.; Pavlushkina, I. I.; Egorova, I. V.; Krivolapov, D. V.; Gubaidullin, A. T.; Litvinov, I. A. *Russ. J. Gen. Chem.* **2001**, *71*, 87. (c) Sharutin, V. V.; Egorova, I. V.; Sharutina, O. K.; Dorofeeva, O. A.; Ivanenko, T. K.; Gerasimenko, A. V.; Pushilin, M. A. *Coord. Chem.* **2004**, *30*, 925.

(18) For example see: (a) Körbe, S.; Schreiber, P. J.; Michl, J. *Chem. Rev.* **2006**, *106*, 5208. (b) Kato, T.; Stoyanov, E.; Geier, J.; Grützmacher, H.; Reed, C. A. *J. Am. Chem. Soc.* **2004**, *126*, 12451. (c) Kato, T.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2908. (d) Xie, Z.; Manning, J.; Reed, R. W.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 2922. (e) Zharov, I.; King, B. T.; Havlas, Z.; Pardi, A.; Michl, J. *J. Am. Chem. Soc.* **2000**, *122*, 10253. (f) Zharov, I.; Weng, T. C.; Orendt, A. M.; Barich, D. H.; Penner-Hahn, J.; Havlas, Z.; Michl, J. *J. Am. Chem. Soc.* **2004**, *126*, 12033. (g) Ingleson, M. J.; Clarke, A.; Mahon, M. F.; Rourke, J. P.; Weller, A. S. *Chem. Commun.* **2003**, 1930.

(19) (a) Schiffer, M.; Johnson, B. P.; Scheer, M. Z. *Anorg. Allg. Chem.* **2000**, *626*, 2498. (b) Liu, L.; Zakharov, N. L.; Rheingold, A. L.; Hanna, T. A. *Chem. Commun.* **2004**, 1472. (c) Tanski, J. M.; Kelly, B. V.; Parkin, G. *Dalton Trans.* **2005**, 2442.



**Figure 6.** ORTEP plot of a molecule of **6** showing 50% probability displacement ellipsoids and the atom-numbering scheme. Hydrogen atoms and the solvent  $\text{CH}_2\text{Cl}_2$  molecule were omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi(1)–O(1) = 2.410(5), Bi(1)–O(2) = 2.393(5), Bi(1)–C(1) = 2.175(7), Bi(1)–Cl(1) = 2.4931(18); O(1)–Bi(1)–O(2) = 145.24(16), C(1)–Bi(1)–Cl(1) = 94.1(2).

The organobismuth compound **6** also is ionic in the solid state (Figure 6). In contrast to the case for **5**, the cation  $[\text{L}^2\text{BiCl}]^+$  of **6** is solvent free (single crystals were obtained from  $\text{CHCl}_3$  solution). The oxygen donor atoms are strongly coordinated to the bismuth atom with bond lengths Bi(1)–O(1) = 2.410(5) Å and Bi(1)–O(2) = 2.393(5) Å. The overall geometry is distorted  $\psi$ -trigonal bipyramidal with both oxygen donor atoms in axial positions (bond angle O(1)–Bi(1)–O(2) = 145.24(16)°), similar to the organobismuth cation  $[\text{2}-(\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{Bi}]^+$ , containing two N,C-chelating ligands.<sup>9</sup> The significant deviation from an ideal  $\psi$ -trigonal-bipyramidal environment is the value of the angle formed by oxygen donor atoms in axial positions, which can be ascribed to ligand rigidity.

**Solution Structures of 1–6.** The structures of all compounds in solution were studied with the help of variable-temperature (VT)  $^1\text{H}$  NMR measurements.

$^1\text{H}$  NMR spectra revealed one set of sharp signals for both  $\text{CH}_2\text{O}$  and  $\text{OCH}_3$  (**1**) or  $\text{OC}(\text{CH}_3)_3$  (**2**) groups for compounds **1** and **2** at 300 K. The signal appropriate to  $\text{CH}_2\text{O}$  groups is split into an AB pattern at 5.26 and 5.21 ppm below 230 K ( $\text{CDCl}_3$ ), reflecting unsymmetrical substitution at the antimony atom in **1** (resembling that found in the solid state). On the other hand, all signals in the  $^1\text{H}$  NMR spectrum of **2** remained unchanged in the whole temperature range studied (300–170 K,  $\text{THF}-d_8$ ; **2** was almost insoluble in  $\text{CDCl}_3$ ), although considerable  $\text{CH}_2\text{O}$  signal line broadening was observed below 190 K, most probably indicating fluxional behavior of **2** in THF solution similar to the case for **5** (vide infra).

The  $^1\text{H}$  NMR spectra of compound **3** revealed only one set of sharp signals for  $\text{CH}_2\text{O}$  and  $\text{OCH}_3$  in the whole temperature range studied (300–215 K,  $\text{CDCl}_3$ ), indicating a rigid and symmetrical structure of **3**, similar to that found for this derivative in the solid state (square pyramidal, with trans unidentate OTf groups). Its bismuth congener **4** displayed one set of sharp signals for  $\text{CH}_2\text{O}$  and  $\text{OC}(\text{CH}_3)_3$  groups in  $^1\text{H}$  NMR at 300 K ( $\text{CDCl}_3$ ), which in the case of the  $\text{CH}_2\text{O}$  groups split into an AX pattern at 5.60 and 5.40 ppm at 215 K. This finding proves nonequivalently bound OTf groups (unidentate and bidentate) as established for **4** in the solid state (see Figure 4).

It means that at ambient temperature (300 K) both OTf groups most probably undergo fast unidentate–bidentate conversion, which is slowed down with a decrease in temperature.

Compound **5** is nearly insoluble in aromatic and chlorinated solvents; thus, VT  $^1\text{H}$  NMR spectra were recorded in  $\text{THF}-d_8$ . Interestingly,  $^1\text{H}$  NMR spectra revealed only one set of relatively sharp signals for  $\text{CH}_2\text{O}$  and  $\text{OCH}_3$  in the whole temperature range studied (300–170 K). This situation does not correspond to an unsymmetrically substituted metal center, which should result in observation of an AX pattern for the protons of the  $\text{CH}_2\text{O}$  group. A plausible explanation can be found in the solvent used. The THF molecule can easily coordinate to the central antimony atom (as was shown in the solid state; Figure 5). The sufficiently fast dynamic process of coordination–decoordination of THF can hamper observation of any splitting of signals of the  $\text{CH}_2\text{O}$  group, which was readily observed in the bismuth analogue (vide infra).

VT  $^1\text{H}$  NMR spectra of **6** recorded in  $\text{CDCl}_3$  revealed already at 300 K an AX pattern (5.60 and 5.44 ppm) for the  $\text{CHO}_2$  group, which is invariable to 215 K, reflecting the presence of the  $[\text{L}^2\text{BiCl}]^+$  cation similar in structure to that found in the solid state (Figure 6). To demonstrate the ability of this cation to coordinate a THF molecule and to obtain proof for coordination of THF by compound **5**, a  $^1\text{H}$  NMR experiment involving addition of THF to a  $\text{CDCl}_3$  solution of **6** was performed.  $^1\text{H}$  NMR spectra of **6** revealed only one signal for the  $\text{CH}_2\text{O}$  group upon addition of THF at 300 K, which is in direct contrast to the experiment carried out in pure  $\text{CDCl}_3$ . This means that THF molecules start to coordinate to the bismuth center at this temperature, similar to the case for compound **5**. Below 230 K, the signal of the  $\text{CH}_2\text{O}$  group is again observed as an AX pattern (5.54 and 5.39 ppm), indicating that THF coordination is sufficiently slowed down to resolve the presence of the unsymmetric cation. All these findings prove the predicted solution structure of **5** and also show a significant tendency of **5** and **6** to act as strong Lewis acids. The ionic nature of both **5** and **6** in solution was also corroborated by  $^{11}\text{B}$  NMR spectra, where three well-resolved resonances in a 1:5:5 ratio (at –5.10, –11.39, and –14.26 ppm for **5** and –12.03, –17.16, and –18.98 ppm for **6**) were observed, the typical pattern for the free  $\text{CB}_{11}\text{H}_{12}^-$  anion.<sup>20</sup>

## Experimental Section

**General Procedures.** All air- and moisture-sensitive manipulations were carried out under an argon atmosphere using standard Schlenk tube techniques. All solvents were dried by standard procedures and distilled prior to use. The reaction flasks were protected against daylight by an aluminum foil covering.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  NMR spectra were recorded on Bruker AMX360 and Bruker500 Avance spectrometers, respectively, using 5 mm tunable broad-band probes. Appropriate chemical shifts in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were calibrated on the residual signals of the solvents ( $\text{CDCl}_3$ ,  $\delta(^1\text{H})$  7.27 ppm and  $\delta(^{13}\text{C})$  77.23 ppm;  $\text{THF}-d_8$ ,  $\delta(^1\text{H})$  3.58, 1.73 ppm and  $\delta(^{13}\text{C})$  67.57, 25.37 ppm).  $^{11}\text{B}$  NMR spectra are related to the external standard  $\text{BF}_3\cdot\text{OEt}_2$  (0.00 ppm). The positive-ion and negative-ion electrospray ionization (ESI) mass spectra were measured on an Esquire 3000 ion trap analyzer (Bruker Daltonics, Bremen, Germany) in the range  $m/z$  50–1000. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 5  $\mu\text{L}/\text{min}$ . The ion source temperature was 300 °C, the tuning parameter compound stability was 100%,

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Table 1. Crystallographic Data for 1–6

	1	2	3	4	5	6
empirical formula	C <sub>11</sub> H <sub>13</sub> ClO <sub>5</sub> -F <sub>3</sub> SSb	C <sub>17</sub> H <sub>25</sub> ClO <sub>5</sub> -F <sub>3</sub> Sb	C <sub>12</sub> H <sub>13</sub> O <sub>8</sub> -F <sub>6</sub> S <sub>2</sub> Sb	C <sub>18</sub> H <sub>25</sub> O <sub>8</sub> F <sub>6</sub> SBi·CH <sub>2</sub> Cl <sub>2</sub>	C <sub>15</sub> H <sub>33</sub> Bi <sub>11</sub> -O <sub>3</sub> Sb	C <sub>34</sub> H <sub>74</sub> B <sub>22</sub> Bi <sub>2</sub> -Cl <sub>2</sub> O <sub>4</sub> ·CH <sub>2</sub> Cl <sub>2</sub>
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	11.7660(8)	12.7860(12)	12.2330(6)	10.3090(4)	15.2900(13)	19.8923(10)
<i>b</i> (Å)	7.9810(6)	15.0940(14)	12.2920(6)	12.5560(9)	11.3730(8)	12.9688(17)
<i>c</i> (Å)	17.7740(9)	11.5140(11)	13.9810(5)	13.5140(8)	16.1530(9)	22.106(3)
α (deg)	90	90	68.775(3)	97.763(5)	90	90
β (deg)	90.837(5)	101.349(6)	81.296(3)	111.887(4)	117.880(6)	100.261(8)
γ (deg)	90	90	87.817(2)	114.022(5)	90	90
<i>Z</i>	4	4	4	2	4	4
μ (mm <sup>-1</sup> )	1.985	8.361	1.735	6.595	1.235	7.168
<i>D</i> <sub>exptl</sub> (Mg m <sup>-3</sup> )	1.876	1.960	2.007	1.860	1.451	1.725
cryst size (mm)	0.44 × 0.24 × 0.11	0.36 × 0.23 × 0.1	0.25 × 0.2 × 0.18	0.32 × 0.24 × 0.1	0.26 × 0.26 × 0.04	0.25 × 0.25 × 0.19
θ range (deg)	1–27.5	1–27.5	1–27.5	1–27.5	1–27.5	1–27.5
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.597, 0.814	0.287, 0.644	0.770, 0.816	0.289, 0.596	<i>e</i>	0.086, 0.274
no. of rflns measd	22 399	38 676	26 232	21 490	39 085	36 169
no. of unique rflns, <i>R</i> <sub>int</sub> <sup>a</sup>	3783, 0.031	5004, 0.074	8712, 0.043	6393, 0.074	5699, 0.071	6274, 0.031
no. of obsd rflns ( <i>I</i> > 2σ( <i>I</i> ))	2813	3709	6569	5081	3478	5249
no. of params	200	253	527	343	280	303
<i>w</i> <sub>1</sub> / <i>w</i> <sub>2</sub> <sup>b</sup>	0.1060/9.0627	0.0175/30.7613	0.0483/1.8792	0.0868/0	0.0344/11.9694	0.0722/71.0868
<i>S</i> <sup>c</sup> (all data)	1.099	1.135	1.051	1.094	1.047	1.125
final <i>R</i> <sup>d</sup> indices ( <i>I</i> > 2σ( <i>I</i> ))	0.068	0.054	0.042	0.051	0.054	0.049
w <i>R</i> <sup>d</sup> indices (all data)	0.209	0.115	0.105	0.141	0.102	0.144
max, min Δρ (e Å <sup>-3</sup> )	2.085, -2.315	2.352, -1.718	0.989, -0.875	4.553, -4.312	0.714, -0.807	3.871, -2.533

<sup>a</sup>  $R_{\text{int}} = \sum |F_o^2 - F_{o,\text{mean}}^2| / \sum F_o^2$ . <sup>b</sup> Weighting scheme:  $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$ , where  $P = [\max(F_o^2) + 2F_c^2]$ . <sup>c</sup>  $S = [\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{diffs}} - N_{\text{params}})]^{1/2}$ . <sup>d</sup>  $R(F) = \sum |F_o| - |F_c| / \sum |F_o|$ ;  $wR(F^2) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$ . <sup>e</sup> Corrected by SADABS ( $T_{\text{min}}/T_{\text{max}} = 0.7898$ ).

and the flow rate and the pressure of nitrogen were 4 L/min and 10 psi, respectively.

The basic mechanism of the ion formation is the cleavage of the most labile bond in the molecules, yielding two complementary ions, where the cationic part (for example, [M - OTf]<sup>+</sup>) of the molecule is measured in the positive-ion mode and the anionic part (for example, [OTf]<sup>-</sup>) is measured in the negative-ion mode of electrospray. Further, the typical neutral losses of hydrogen chloride, butene, formaldehyde, and methanol confirming the presence of substituents in the molecule are observed in the spectra.

The starting compounds AgSO<sub>3</sub>CF<sub>3</sub> (99%) and [Me<sub>3</sub>NH]<sup>+</sup>[CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> were obtained from commercial suppliers and used as delivered. The compounds Ag<sup>+</sup>[CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup><sup>21</sup> and 2,6-(MeOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SbCl<sub>2</sub> and 2,6-(<sup>t</sup>BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>BiCl<sub>2</sub><sup>10</sup> were prepared according to literature procedures.

**Synthesis of 2,6-(MeOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SbCl(CF<sub>3</sub>SO<sub>3</sub>) (1).** CF<sub>3</sub>SO<sub>3</sub>-Ag (72 mg, 0.28 mmol) was added to a solution of 2,6-(MeOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SbCl<sub>2</sub> (100 mg, 0.28 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) in a Schlenk flask protected against light by aluminum foil. The reaction mixture was stirred overnight, and then AgCl was filtered and the filtrate was evaporated in vacuo to dryness, providing white crystals of the product. The crude product was washed twice with hexane (5 mL) and dried in vacuo. Yield: 117 mg (89%). Mp: 135–138 °C. Anal. Calcd for C<sub>11</sub>H<sub>13</sub>SbClF<sub>3</sub>O<sub>5</sub>S (mol wt 471.49): C, 28.02; H, 2.78. Found: C, 27.88; H, 2.67. Positive-ion MS: *m/z* 473 [M + H]<sup>+</sup>; *m/z* 321 [M - OTf]<sup>+</sup>, 100%; *m/z* 291 [M - OTf - HCOH]<sup>+</sup>; *m/z* 261 [M - OTf - 2\*HCOH]<sup>+</sup>. Negative-ion MS: *m/z* 149 [OTf]<sup>-</sup>, 100%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 4.06 (6H, s, CH<sub>3</sub>O), 5.22 (4H, s, OCH<sub>2</sub>), 7.32 (2H, d, Ar H3,5), 7.51 (1H, t, Ar H4). <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>): δ 61.9 (s, CH<sub>3</sub>O), 78.4 (s, OCH<sub>2</sub>), 119.4 (q, CF<sub>3</sub>, <sup>1</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 318 Hz), 123.0 (s, Ar C3,5), 131.5 (s, Ar C4), 142.2 (s, Ar C2,6), 150.3 (Ar C1).

**Synthesis of 2,6-(<sup>t</sup>BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>BiCl(CF<sub>3</sub>SO<sub>3</sub>) (2).** The procedure was analogous to that used for 1: CF<sub>3</sub>SO<sub>3</sub>Ag (51 mg, 0.20 mmol); 2,6-(<sup>t</sup>BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>BiCl<sub>2</sub> (105 mg, 0.20 mmol) in THF (30 mL). Yield: 99 mg (94%). Mp 145–148 °C. Anal. Calcd for C<sub>17</sub>H<sub>25</sub>BiClF<sub>3</sub>O<sub>5</sub>S (mol wt 642.88): C, 31.76; H, 3.92. Found: C,

31.85; H, 4.01. Positive-ion MS: *m/z* 493 [M - CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>, 100%; *m/z* 437 [M - CF<sub>3</sub>SO<sub>3</sub> - butene]<sup>+</sup>; *m/z* 401 [M - CF<sub>3</sub>SO<sub>3</sub> - butene - HCl]<sup>+</sup>; *m/z* 381 [M - CF<sub>3</sub>SO<sub>3</sub> - 2\*butene]<sup>+</sup>; *m/z* 345 [M - CF<sub>3</sub>SO<sub>3</sub> - 2\*butene - HCl]<sup>+</sup>. Negative-ion MS: *m/z* 149 [CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup>, 100%. <sup>1</sup>H NMR (500 MHz, THF-*d*<sub>8</sub>): δ 1.53 (18H, s, (CH<sub>3</sub>)<sub>3</sub>CO), 5.29 (4H, s, OCH<sub>2</sub>), 7.44 (1H, t, Ar H4), 7.85 (2H, d, Ar H3,5). <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>): δ 28.7 (s, (CH<sub>3</sub>)<sub>3</sub>CO), 72.5 (s, OCH<sub>2</sub>), 83.9 (s, CO), 121.5 (q, CF<sub>3</sub>, <sup>1</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 319 Hz), 127.4 (s, Ar C3,5), 129.6 (s, Ar C4), 152.6 (s, Ar C2,6), Ar C1 not found.

**Synthesis of 2,6-(MeOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Sb(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (3).** The procedure was analogous to that used for 1: CF<sub>3</sub>SO<sub>3</sub>Ag (157 mg, 0.62 mmol); 2,6-(MeOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SbCl<sub>2</sub> (109 mg, 0.31 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL). Yield: 157 mg (88%). Mp: 204–206 °C dec. Anal. Calcd for C<sub>12</sub>H<sub>13</sub>SbF<sub>6</sub>O<sub>8</sub>S<sub>2</sub> (mol wt 585.10): C, 24.63; H, 2.24. Found: C, 24.49; H, 2.38. Positive-ion MS: *m/z* 453 [M - CF<sub>3</sub>SO<sub>3</sub> + H<sub>2</sub>O]<sup>+</sup>, 100%; *m/z* 435 [M - CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>; *m/z* 421 [M - CF<sub>3</sub>SO<sub>3</sub> + H<sub>2</sub>O - CH<sub>3</sub>OH]<sup>+</sup>; *m/z* 321 [LSBoH + H<sub>2</sub>O]<sup>+</sup>. Negative-ion MS: *m/z* 149 [CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup>, 100%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 4.19 (6H, s, CH<sub>3</sub>O), 5.30 (4H, s, OCH<sub>2</sub>), 7.37 (2H, d, Ar H3,5), 7.57 (1H, t, Ar H4). <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>): δ 62.6 (s, CH<sub>3</sub>O), 78.8 (s, OCH<sub>2</sub>), 119.4 (q, CF<sub>3</sub>, <sup>1</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 317 Hz), 123.1 (s, Ar C3,5), 132.2 (s, Ar C4), 142.6 (s, Ar C2,6), 150.5 (Ar C1).

**Synthesis of 2,6-(<sup>t</sup>BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Bi(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (4).** The procedure was analogous to that used for 1: CF<sub>3</sub>SO<sub>3</sub>Ag (90 mg, 0.35 mmol); 2,6-(<sup>t</sup>BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>BiCl<sub>2</sub> (93 mg, 0.175 mmol) in THF (30 mL). Yield: 119 mg (90%). Mp > 290 °C dec. Anal. Calcd for C<sub>18</sub>H<sub>25</sub>BiF<sub>6</sub>O<sub>8</sub>S<sub>2</sub> (mol wt 756.49): C, 28.58; H, 3.33. Found: C, 28.70; H, 3.46. Positive-ion MS: *m/z* 607 [M - CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>; *m/z* 551 [M - CF<sub>3</sub>SO<sub>3</sub> - butene]<sup>+</sup>; *m/z* 401 [M - CF<sub>3</sub>SO<sub>3</sub> - CF<sub>3</sub>SO<sub>3</sub>H - butene]<sup>+</sup>; *m/z* 345 [M - CF<sub>3</sub>SO<sub>3</sub> - CF<sub>3</sub>SO<sub>3</sub>H - 2\*butene]<sup>+</sup>. Negative-ion MS: *m/z* 149 [CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup>, 100%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.69 (18H, s, (CH<sub>3</sub>)<sub>3</sub>CO), 5.49 (4H, s, OCH<sub>2</sub>), 7.61 (1H, t, Ar H4), 7.99 (2H, d, Ar H3,5). <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>): δ 28.6 (s, (CH<sub>3</sub>)<sub>3</sub>CO), 73.2 (s, OCH<sub>2</sub>), 84.7 (s, CO), 119.6 (q, CF<sub>3</sub>, <sup>1</sup>J(<sup>19</sup>F, <sup>13</sup>C) = 319 Hz), 126.5 (s, Ar C3,5), 130.5 (s, Ar C4), 152.3 (s, Ar C2,6), Ar C1 not found.

**Synthesis of 2,6-(MeOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SbCl(CB<sub>11</sub>H<sub>12</sub>) (5).** The procedure was analogous to that used for 1: CB<sub>11</sub>H<sub>12</sub>Ag (73 mg,

0.29 mmol); 2,6-(MeCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SbCl<sub>2</sub> (105 mg, 0.29 mmol) in CH<sub>2</sub>-Cl<sub>2</sub> (30 mL). Yield: 122 mg (89%). Mp: 180–184 °C. Anal. Calcd for C<sub>11</sub>H<sub>25</sub>SbB<sub>11</sub>O<sub>2</sub>Cl (mol wt 465.44): C, 28.39; H, 5.41. Found: C, 28.09; H, 5.32. Positive-ion MS: *m/z* 321 [M – CB<sub>11</sub>H<sub>12</sub>]<sup>+</sup>, 100%. Negative-ion MS: *m/z* 145 [CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup>, 100%. <sup>1</sup>H NMR (500 MHz, THF-*d*<sub>8</sub>): δ 4.07 (6H, s, CH<sub>3</sub>O), 5.38 (4H, s, OCH<sub>2</sub>), 7.42 (2H, d, Ar H<sub>3,5</sub>), 7.55 (1H, t, Ar H<sub>4</sub>). <sup>13</sup>C NMR (125.76 MHz, THF-*d*<sub>8</sub>): δ 51.8 (bs, CB), 62.1 (s, CH<sub>3</sub>O), 78.6 (s, OCH<sub>2</sub>), 124.4 (s, Ar C<sub>3,5</sub>), 132.2 (s, Ar C<sub>4</sub>), 144.1 (s, Ar C<sub>2,6</sub>), 150.9 (Ar C<sub>1</sub>). <sup>11</sup>B NMR (115.54 MHz, THF-*d*<sub>8</sub>): δ -5.10 (bs), -11.39 (bs), -14.26 (bs). IR (CHCl<sub>3</sub>): ν(B–H) 2557 cm<sup>-1</sup>. IR (Nujol): ν(B–H) 2542 cm<sup>-1</sup>.

**Synthesis of 2,6-(<sup>t</sup>BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>BiCl(CB<sub>11</sub>H<sub>12</sub>) (6).** The procedure was analogous to that used for **1**: CB<sub>11</sub>H<sub>12</sub>Ag (41 mg, 0.17 mmol); 2,6-(<sup>t</sup>BuOCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>BiCl<sub>2</sub> (87 mg, 0.17 mmol) in THF (30 mL). Yield: 97 mg (92%). Mp: 130 °C dec. Anal. Calcd for C<sub>17</sub>H<sub>37</sub>BiB<sub>11</sub>ClO<sub>2</sub> (mol wt 636.84): C, 32.06; H, 5.86. Found: C, 32.20; H, 5.99. Positive-ion MS: *m/z* 493 [M – CB<sub>11</sub>H<sub>12</sub>]<sup>+</sup>, 100%; *m/z* 437 [M – CB<sub>11</sub>H<sub>12</sub> – butene]<sup>+</sup>; *m/z* 381 [M – CB<sub>11</sub>H<sub>12</sub> – 2\*butene]<sup>+</sup>; *m/z* 345 [M – CB<sub>11</sub>H<sub>12</sub> – 2\*butene – HCl]<sup>+</sup>. Negative-ion MS: *m/z* 145 [CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup>, 100%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 1.69 (18H, s, (CH<sub>3</sub>)<sub>3</sub>CO), 5.60 and 5.44 (4H, AX pattern, OCH<sub>2</sub>), 7.65 (1H, t, Ar H<sub>4</sub>), 8.00 (2H, d, Ar H<sub>3,5</sub>). <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>): δ 28.8 (s, (CH<sub>3</sub>)<sub>3</sub>CO), 53.1 (s br, CB), 72.7 (s, OCH<sub>2</sub>), 86.3 (s, CO), 127.0 (s, Ar C<sub>3,5</sub>), 130.8 (s, Ar C<sub>4</sub>), 151.9 (s, Ar C<sub>2,6</sub>), Ar C<sub>1</sub> not found. <sup>11</sup>B NMR (115.54 MHz, CDCl<sub>3</sub>): δ -12.03 (s br), -17.16 (s br), -18.98 (s br). IR (CHCl<sub>3</sub>): ν(B–H) 2555 cm<sup>-1</sup>. IR (Nujol): ν(B–H) 2550 cm<sup>-1</sup>.

**X-ray Crystallographic Study.** The details of the crystal structure determination and refinement for compounds **1–6** are given in Table 1. Suitable single crystals of **1–6** were mounted on glass fibers with oil and measured on a KappaCCD four-circle diffractometer with CCD area detector by monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 150(1) K. Numerical<sup>22</sup> absorption corrections from crystal shape were applied for crystals of **2** and **6**, multiscan<sup>23</sup> absorption corrections were applied for **1**, **3**, and **4**,

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and SADABS<sup>24</sup> correction was applied for **5**. The structures were solved by direct methods (SIR92<sup>25</sup>) and refined by full-matrix least-squares procedures based on *F*<sup>2</sup> (SHELXL97<sup>26</sup>). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors  $U_{\text{iso}}(\text{H}) = 1.2[U_{\text{eq}}(\text{pivot atom})]$ ; for the methyl moiety a multiple of 1.5 was chosen. The final difference maps displayed no peaks of chemical significance, as the highest peaks and holes are in close vicinity ( $\sim 1$  Å) of heavy atoms.

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre: CCDC Nos. 632153–632157 for **1**, **2**, and **4–6** and CCDC No. 636272 for **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, <http://www.ccdc.cam.ac.uk>).

**Acknowledgment.** We thank the Grant Agency of the Czech Republic (Project No. 203/07/P094) and the Ministry of Education of the Czech Republic (Project Nos. MSM0021627501 and LC523) for financial support. R.Jirásko acknowledges the support of Grant Project No. MSM0021627502 sponsored by The Ministry of Education, Youth and Sports of the Czech Republic.

**Supporting Information Available:** CIF files giving crystal data for compounds **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM070186B

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