Synthesis, Structure, and Reactivity of Intramolecularly Coordinated Organoantimony and Organobismuth Sulfides

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Organoantimony(III) and organobismuth(III) sulfides, containing O,C,O-chelating ligands (L^{1-3} = 2,6-$(ROCH_2)_2C_6H_3^-$, where R = Me (L^1), *t*-Bu (L^2), or mesityl (L^3)), $[L^{1-3}MS]_2$, where M = Sb (L^1 (**5**), L^2 (**6**), L^3 (**7**)) or M = Bi (L^2 (**8**)), were prepared by the reaction of parent organoantimony and organobismuth chlorides with $Na_2S \cdot 9H_2O$ in toluene/water. All sulfides **5**−**8** were characterized by elemental analysis, electrospray ionization mass spectrometry, ^1H and ^{13}C NMR spectroscopy, and X-ray diffraction techniques. Organoantimony sulfides **5**−**7** are stable both in solution and in the solid state in contrast to the organobismuth congener, which is stable at −30 °C but decomposes at ambient temperature. While the reaction of **5** and **7** with I_2 yielded the expected organoantimony iodides $L^{1,3}SbI_2$ (L^1 (**9**), L^3 (**10**)), compound **6** containing ligand L^2 gives the unexpected oxastibol **12** besides the intended diiodide L^2SbI_2 (**11**). The molecular structure of **12** in the solid state was determined by X-ray diffraction techniques and showed formation of an Sb−O covalent bond as a result of C−O ether bond cleavage.

Introduction

The so-called Y,C,Y-chelating, or pincer, ligands [2,6-$(YCH_2)_2C_6H_3]^-$ (Y = N, O, P, S, etc.) have been shown to be a very useful platform for the preparation of organometallic compounds with both transition[1] and main group[2] metals. These ligands often give special chemical and structural properties to the coordinated central metal due to their ability to form two more or less strong intramolecular M−Y dative bonds.

Among the heavier pnictogens (in particular Sb and Bi), such pincer ligands recently have found application. Organoantimony and organobismuth halides containing O,C,O- or N,C,N-chelated ligands display interesting structures depending both on the ligand and on the halide used.[3] These ligands allowed synthesis of the first examples of organoantimony difluorides,[4] highly Lewis acidic organoantimony and organobismuth cations,[5] and compounds containing a M−M bond or terminal Sb−Se(Te) bonds.[6]

As a part of our continuing investigation of main group metal complexes bearing Y,C,Y pincer ligands, we report here the synthesis and structures of organoantimony and organobismuth sulfides containing O,C,O pincer ligands. To date most of the reported organoantimony and organobismuth sulfides contain monodentate ligands.

Diorgano derivatives (type R_2MSMR_2, where R = carbon-bound ligand and M = Sb or Bi)[7] are monomeric, and monorganoantimony and bismuth compounds form dimers to tetramers (type $[RMS]_x$, x = 2 or 4) depending on the nature of the substituent R. They often display ring−ring equilibrium in solution.[8] Use of a sterically demanding ligand allowed the isolation of unusual Sb_2S_3, SbS_5, SbS_7, and Bi_2S_3 ring systems.[9]

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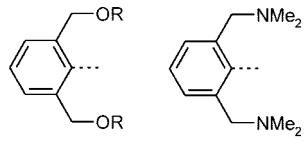
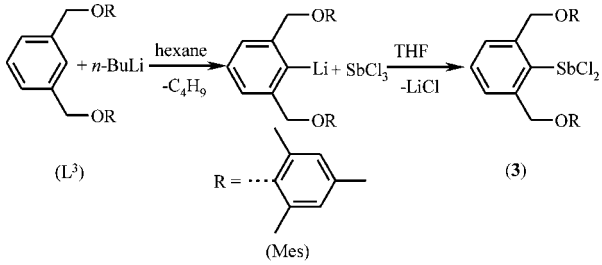
Chart 1



R = Me, L^1
R = *t*-Bu, L^2
R = Mes, L^3

L^4

Scheme 1. Preparation of Compound 3



Few examples of the use of chelating ligands for stabilization of organoantimony sulfides have been reported. The only examples of N,C-chelated organoantimony sulfides are $[2\text{-}(Me_2NCH_2)C_6H_3SbS]_2$, which is dimeric (forming a central Sb_2S_2 ring) both in solution and in the solid state without any ring−ring equilibrium, and a compound with a single μ-S bridge, $[2\text{-}(Me_2NCH_2)C_6H_4SbCl]_2S$.[10] In the case of analogous organobismuth compounds, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3BiS]_2$ and $[2\text{-}(Me_2NCH_2)C_6H_4BiS]_2$ are the only examples of intramolecularly coordinated sulfides.[11]

To add to our knowledge about intramolecularly coordinated organopnictogen sulfides, we report here the reactions of intramolecularly coordinated organoantimony and organobismuth chlorides $L^{1-3}MCl_2$ (L^{1-3} = 2,6-$(ROCH_2)_2C_6H_3^-$, where R = Me (L^1), *t*-Bu (L^2), or mesityl (L^3); M = Sb (L^1 (**1**), L^2 (**2**), L^3 (**3**)) or M = Bi (L^2 (**4**))) with $Na_2S\cdot 9H_2O$, which yielded corresponding sulfides $[L^{1-3}MS]_2$, where M = Sb (L^1 (**5**), L^2 (**6**), L^3 (**7**)) or M = Bi (L^2 (**8**)) (Chart 1). The structures of all compounds were studied by ^1H and ^{13}C NMR spectroscopy and X-ray diffraction techniques. Investigation on the reactions of the organoantimony sulfides **5**−**7** with iodine is also included.

Results and Discussion

Synthesis. Organoantimony chloride L^3SbCl_2 (**3**) containing the novel bulky O,C,O pincer-type ligand L^3 was prepared (Scheme 1, Chart 1) with the aim to stabilize monomeric sulfide (vide infra). Compound **3** was isolated as a colorless air-stable crystalline solid.

The solid-state structure of **3** was determined by X-ray diffraction. The unit cell contains two independent molecules (atropoisomeric pair), and only the selected one is depicted in Figure 1 and is described here in detail. Both donor oxygen atoms are coordinated to the central antimony atom Sb1,

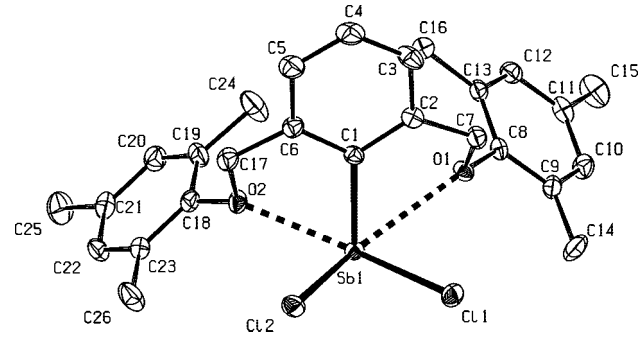


Figure 1. ORTEP drawing (50% probability atomic displacement ellipsoids, one of two independent molecules in the unit cell) of **3**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Sb1−O1, 2.818(4); Sb1−O2, 2.553(4); Sb1−Cl1, 2.4098(12); Sb1−Cl2, 2.3924(12); Sb1−C1, 2.147(4). Selected bond angles (deg): O1−Sb1−O2, 119.39(11); Cl1−Sb1−Cl2, 86.29(4); O1−Sb1−Cl1, 71.59(8); O2−Sb1−Cl2, 74.76(8); C1−Sb1−O1, 67.59(13); C1−Sb1−O2, 71.01(13); C1−Sb1−Cl1, 97.83(12); C1−Sb1−Cl2, 94.77(13).

Table 1. Comparison of Bonding Lengths Sb−Y (Y = O or N) (Å) in Various Organoantimony Halides Containing Y,C,Y-Chelating Ligands

	L^1SbX_2 (Sb−O)	L^2SbX_2 (Sb−O)	L^3SbX_2 (Sb−O)	L^4SbX_2 (Sb−N)
X = F	2.597(2)	2.640(2)	*a*	2.560(3)
	2.606(2)	2.678(2)	*a*	2.588(3)
X = Cl	2.523(2)	2.6294(14)	2.818(4)	2.491(9)
	2.577(2)	2.691(13)	2.544(4)	2.422(8)
X = I	2.293(2)	2.302(2)	2.620(2)	*a*
	2.279(2)	2.343(2)	5.004(2)	*a*

[a] Not determined by X-ray diffraction.

although one of these interactions is significantly stronger, Sb1−O1 = 2.554(4) Å and Sb1−O2 = 2.818(4) Å ($\sum_{cov}$(Sb,O) = 2.14 Å, $\sum_{vdW}$(Sb,O) = 3.78 Å).[12] This is in contrast to antimony dichlorides[3b] **1** and **2** containing $L^{1,2}$, where both Sb−O intramolecular interactions are nearly equivalent (Table 1), approaching the shorter Sb−O distance detected in **3**. This most probably reflects increasing steric demand of L^3 in **3**. Both oxygen atoms are placed mutually in *cis* fashion, O1−Sb1−O2 = 119.40(11)°, in **3**. The overall geometry around the central atom can be described in three alternative ways as a strongly distorted tetragonal pyramid, ψ-octahedron, or bicapped trigonal pyramid as previously discussed in detail for other O,C,O−chelated halides.[3b] There are no significant intermolecular contacts in the crystal structure of **3**.

The reactions of starting chlorides **1**−**4** with $Na_2S\cdot 9H_2O$ in toluene/water gave the expected organoantimony and organobismuth sulfides $[L^{1-3}MS]_2$ (**5**−**8**) in moderate yield (Scheme 2). All compounds were isolated as slightly yellow powders, which are soluble in chlorinated and aromatic solvents, but nearly insoluble in aliphatic hydrocarbons. The proposed dimeric nature of **5**−**8** was confirmed by mass spectra, where the molecular adducts with alkali-metal ions, such as sodium, $[M + Na]^+$, and potassium, $[M + K]^+$, were detected in all cases.

Organoantimony sulfides **5**−**7** are stable at room temperature both in solution and in the solid state for a long time (even when heated to 50 °C for one week, no significant decomposition was observed by ^1H NMR spectroscopy). In contrast,

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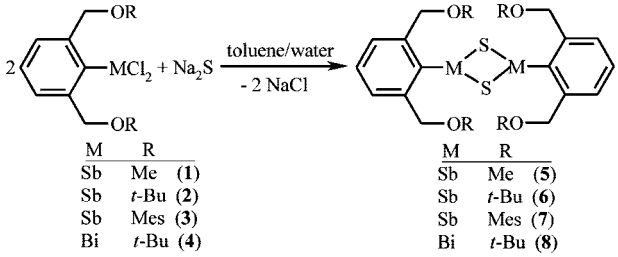
Scheme 2. Preparation of Studied Sulfides 5−8



M	R		M	R	
Sb	Me	(1)	Sb	Me	(5)
Sb	*t*-Bu	(2)	Sb	*t*-Bu	(6)
Sb	Mes	(3)	Sb	Mes	(7)
Bi	*t*-Bu	(4)	Bi	*t*-Bu	(8)

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Compounds 5−8

	5 (M = Sb)	**6** (M = Sb)	**7** (M = Sb)	**8** (M = Bi)[a]	
M1−S1	2.4666(7)	2.460(3)	2.4536(12)	2.560(3)	2.549(3)
M1−S1a	2.4834(7)	2.463(3)	2.4619(12)	2.555(3)	2.547(3)
M1−C1	2.169(3)	2.179(10)	2.178(4)	2.269(10)	2.268(10)
M1−O1	2.8362(18)	2.792(8)	2.717(3)	2.825(6)	2.777(7)
M1−O2	2.6323(17)	2.775(8)	2.894(3)	2.809(7)	2.815(7)
S1−M1−S1a	85.75(2)	84.89(9)	86.22(4)	86.17(10)	85.81(10)
M1−S1−M1a	94.26(2)	91.30(10)	93.78(2)	93.83(11)	94.19(11)
O1−M1−O2	116.20(5)	114.7(2)	118.58(8)	113.44(19)	115.5(2)
C1−M1−S1	96.62(6)	97.6(3)	98.31(12)	96.5(2)	98.6(3)
C1−M1−S1a	99.97(6)	98.3(2)	99.08(12)	99.6(2)	98.3(3)

[a] Two independent molecules in the unit cell.

organobismuth sulfide **8** is stable for weeks in solution and in the solid state only below −30 °C. However, when kept at room temperature for a longer time in chloroform solution, gradual decomposition (within a few days) occurred and a completely insoluble brown-black precipitate formed. Similar decomposition had also been detected in the case of other organobismuth sulfides.[7c]

Structure of Studied Sulfides. The molecular structures of all sulfides **5**−**8** were determined in the solid state using the single-crystal X-ray diffraction technique. Selected structural parameters are collected in Table 2, and for crystallographic data see Table 3. The single crystals were always grown from solution containing both possible (*cis*, *trans*) isomers, but in all cases in the crystal structures only one of these isomers was present (*trans* for **5**, **7**, and **8** and *cis* for **6**). Moreover, when collected single crystals are dissolved, both isomers are present in $CDCl_3$ solution in a molar ratio (based on ^1H NMR) almost identical to that detected after isolation of products from the reaction mixtures, indicating fast formation of both isomers upon dissolution.

The molecular structure of organoantimony sulfides *trans*-**5** and *trans*-**7** are depicted together in Figure 2. Both structures are very similar. Both compounds are centrosymmetric dimers with a planar central Sb_2S_2 ring, and both ligands L are located in *trans* positions. The Sb1−S1 and Sb1−S1a bond distances are nearly identical within the central core, 2.4666(7) and 2.4834(7) Å for **5**, 2.4536(12) and 2.4619(12) Å for **7**. These values are comparable to the Sb−S bond distances observed for the N,C-chelated analogue $[2\text{-}(Me_2NCH_2)C_6H_4SbS]_2$, although in this case both Sb−S bond lengths are a bit more distinct, 2.5338(12) vs 2.4245(12) Å.[10] The angles S1−Sb1−S1a are more acute in comparison to Sb1−S1−Sb1a in both cases (85.75(2)° and 94.26(2)° for **5** and 86.22(4)° and 93.78(2)° for **7**). The oxygen donor atoms O1 and O2 are coordinated to the central atom through weak intramolecular interactions (2.6323(17) and 2.8362(18) Å for **5**, 2.717(3) and 2.894(3) Å for **7**) mutually in *cis* fashion (O1−Sb1−O2 = 116.20(5)° for **5** and 118.58(8)° for **7**). The coordination polyhedron of the central antimony atom can be described as a bicapped trigonal pyramid which is formed by *ispo*-carbon C1 of the ligand and both sulfur atoms (sum of angles of $SbCS_2$ girdle, 290.9° for **5** and 283.6° for **7**).

Although some molecular structures of dimeric monoorganoantimony sulfides $[RSbS]_2$ have been determined,[10] to the best of our knowledge, all of them can be described as *trans* type with the substituent R located mutually on the opposite sides of the central ring. The *cis* position was in some compounds caused by coordination of the antimony or the sulfur atom to a transition metal.[10,13] The molecular structure of *cis*-**6** is depicted in Figure 3 and represents the first example of a "free" *cis* isomer of monorganoantimony sulfide characterized by X-ray diffraction in the solid state. The *cis* position of both ligands L^2 in **6** resulted in significant puckering of the central Sb_2S_2 ring (see Figure 3). This is in direct contrast to the planar central core detected in **5** and **7**. The bond distances Sb−S within the central ring are again nearly identical, Sb1−S1 = 2.460(3) Å and Sb1−S1b = 2.463(3) Å, as are the bonding angles, Sb1−S1−Sb1b = 91.30(10)°, S1−Sb1−S1b = 84.89(9)°. As a result of weak coordination of both oxygen donor atoms (Sb1−O1 = 2.792(8) Å and Sb1−O2 = 2.775(8) Å), the coordination polyhedron around each antimony atom is a bicapped trigonal pyramid similar to those in **5** and **7**.

In the case of compound **8**, the unit cell contains two independent molecules, but both differ only marginally in the structural parameters (Table 2), so only the selected one is depicted in Figure 4 and is described here in detail. The molecular structure of organobismuth sulfide *trans*-**8** is analogous to those of previously published compounds containing N,C,N-chelating ligand $[2,6\text{-}(Me_2NCH_2)_2C_6H_3BiS]_2$.[11] Compound **8** has a centrosymmetric dimeric structure with a Bi_2S_2 core (Bi1−S1 = 2.560(3) Å and Bi1−Sb1a = 2.555(3) Å), in which both ligands are located in *trans* positions. Both donor atoms are weakly coordinated to the central metal (Bi1−O1 = 2.825(6) Å and Bi1−O2 = 2.809(7) Å, $\sum_{vdW}$(Bi,O) = 3.86 Å)[12] in *cis* fashion (O1−Bi1−O2 = 113.44(19)°), leading to the bicapped trigonal pyramidal environment around each bismuth atom analogously to sulfides **5**−**7**.

The dimeric structure of sulfides **5**−**8** is retained in $CDCl_3$ solution as shown by ^1H and ^{13}C NMR spectroscopy. The ^1H and ^{13}C NMR spectra contained two sets of signals in the case of all compounds **5**−**8** in $CDCl_3$ at room temperature. The presence of two sets of signals in ^1H and ^{13}C NMR spectra of organoantimony sulfides bearing a similar N,C-chelating ligand was attributed to the formation of two possible isomers—*cis* and *trans* with respect to the position of the ligands on the central Sb_2S_2 ring.[10] Both isomers are present in 0.05 M $CDCl_3$ solutions of **5**−**8** in approximately 1:0.85 (**5**, **6**), 1:0.59 (**7**), and 1:0.56 (**8**) molar ratios based on the integration of the signal of the OCH_2 groups in the ^1H NMR spectra (see the Supporting Information). Although the resonances of the OCH_2 groups could not be definitely assigned to each isomer, most probably the *trans* isomer is the preferred one for steric reasons. It is evident that even in the case of sterically crowded sulfide **7** both isomers are formed in solution, although their ratio of 1:0.59 under the same conditions points to an increased preference for the *trans* isomer.

Reactions of Organoantimony Sulfides 5−7 with I_2. Recently, we have shown that the reaction of intramolecularly coordinated organotin(IV) sulfides with I_2 gives the corresponding organotin iodides with concomitant elimination of elemental

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Table 3. Crystallographic Data for 3, 5−8, 10, and 12

	3	**5**	**6**	**7**	**8**	**10**	**12**
empirical formula	$C_{26}H_{28}Cl_2O_2Sb$	$C_{20}H_{26}O_4S_2Sb_2$	$C_{34}H_{54}Cl_4O_4S_2Sb_2$	$C_{56}H_{66}O_5S_2Sb_2$	$C_{32}H_{50}Bi_2ClO_4S_2$	$C_{26}H_{29}I_2O_2Sb$	$C_{24}H_{32}I_2O_4Sb_2$
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1$	$P2_1/n$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a(Å)	11.8007(3)	9.3281(2)	19.6912(9)	15.8025(14)	10.6653(8)	8.1363(2)	23.1689(11)
b(Å)	17.1360(12)	7.2572(2)	8.8823(12)	13.7531(16)	10.8035(10)	10.7204(8)	10.7841(9)
c(Å)	12.3284(11)	17.1797(4)	27.4682(13)	13.8521(18)	19.7842(19)	15.9477(8)	24.7928(12)
α (deg)	90	90	90	90	102.245(8)	82.391(6)	90
β (deg)	102.596(5)	99.6414(14)	109.581(13)	108.412(8)	92.040(8)	77.112(3)	115.407(13)
γ (deg)	90	90	90	90	96.605(7)	79.080(6)	90
Z	4	2	4	2	2	2	8
μ (mm^{-1})	1.374	2.561	1.553	1.061	8.138	3.389	4.164
D_x (Mg m^{-3})	1.543	1.848	1.433	1.310	1.528	1.877	2.093
cryst size (mm)	0.31 × 0.21 × 0.15	0.25 × 0.15 × 0.08	0.36 × 0.24 × 0.15	0.47 × 0.26 × 0.11	0.36 × 0.19 × 0.06	0.75 × 0.43 × 0.16	0.28 × 0.13 × 0.11
θ range (deg)	1−27.5	1−27.5	1−27.5	1−27.5	1−27.5	1−27.5	1−27.5
T_{min}, T_{max}	0.554, 0.778	0.679, 0.870	0.656, 0.785	0.782, 0.917	0.084, 0.648	0.119, 0.592	0.503, 0.719
no. of reflns measd	19804	16 501	41 237	26 422	40 961	24 250	41 882
no. of unique reflns, R_{int}[a]	10097, 0.036	2641, 0.036	4918, 0.045	6536, 0.049	10119, 0.078	6019, 0.084	6396, 0.044
no. of obsd reflns [$I > 2\sigma(I)$]	9927	2311	4114	4962	7303	5624	5044
no. of params	559	130	222	316	433	280	289
w_1/w_2[b]	0.0799/2.9367	0.0135/1.3119	0.0236/195.0838	0.0526/5.0147	0.0555/24.8677	0.1127/3.9669	0.0797/168.2457
S,[c] all data	1.055	1.12	1.298	1.094	1.061	1.108	1.070
final R[d] indices [$I > 2\sigma(I)$]	0.041	0.022	0.087	0.044	0.059	0.065	0.059
wR2[d] indices (all data)	0.109	0.049	0.205	0.123	0.153	0.177	0.177
$\Delta\rho$ (max, min) (e $Å^{-3}$)	0.672, −1.188	1.051, −0.569	2.871, −2.469	1.087, −0.688	3.169, −2.288	3.226, −4.876	2.454, <23.2.821

[a] $R_{int} = \sum|F_o^2 - F_{o,mean}^2|/\sum F_o^2$. [b] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$. [c] $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$. [d] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{1/2}$.

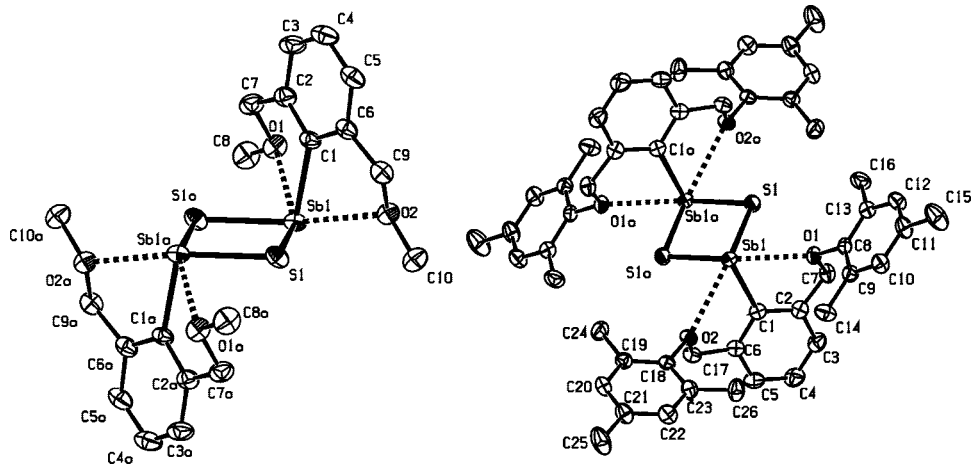

Figure 2. ORTEP drawings (50% probability atomic displacement ellipsoids) of *trans*-**5** (left) (symmetry code a: $-x, -y, -z$) and *trans*-**7** (right) (symmetry code a: $-x, -y + 1, 1 - z$). Hydrogen atoms and the THF molecule (in *trans*-**7**) have been omitted for clarity.

sulfur.[14] The organoantimony sulfides **5**−**7** follow a similar reaction path, as shown by the reactions of **5**−**7** with 2 equiv of I_2. These reactions of **5** and **7**, as expected, gave intramolecularly coordinated diiodides $L^{1,3}SbI_2$ (L^1 (**9**) and L^3 (**10**)) in moderate yield. Compound **9** had been prepared previously and characterized by electrospray ionization (ESI) mass spectrometry and ^1H and ^{13}C NMR spectroscopy. All data of **9** are in good agreement with those reproted.[3b] The identity of compound **10** was established by elemental analysis, ESI mass spectrometry, and ^1H and ^{13}C NMR spectroscopy. The molecular structure of **10** was determined by the single-crystal X-ray diffraction technique (Figure 5). Only one of the donor oxygen atoms, O1, is coordinated to the central Sb atom by a medium strong intramolecular interaction (Sb1−O1 = 2.622(4) Å), while the second donor group remains pendant (Sb1−O2 = 5.006(4) Å). The overall geometry around the central antimony atom can be described as an equatorially vacant trigonal bipyramid. The axial positions are occupied by the oxygen donor atom O1 and I2 atom (O1−Sb1−I2 = 167.22(10)°), and the *ipso*-carbon C1 and the second iodine I1 are located in the equatorial positions. Closer inspection of the molecular structure of **10** revealed short intermolecular contacts Sb1−I2···Sb1a (3.8342(6) Å, $\sum_{vd\text{-}w}(Sb,I) = 4.24$ Å),[12] leading to a formation of weakly bound dimeric entities. Similar weak intermolecular contacts were observed in analogous O,C,O-chelated iodides.[3b]

Of particular interest is a weakening of the dative Sb−O intramolecular interaction on going from chloride **3** to iodide **10** (Table 1). In all other organoantimony halides containing ligands $L^{1,2}$ or N,C,N analogue L^4 [2,6-$(Me_2NCH_2)_2C_6H_3]^-$, using heavier halogens resulted in reinforcement of the present

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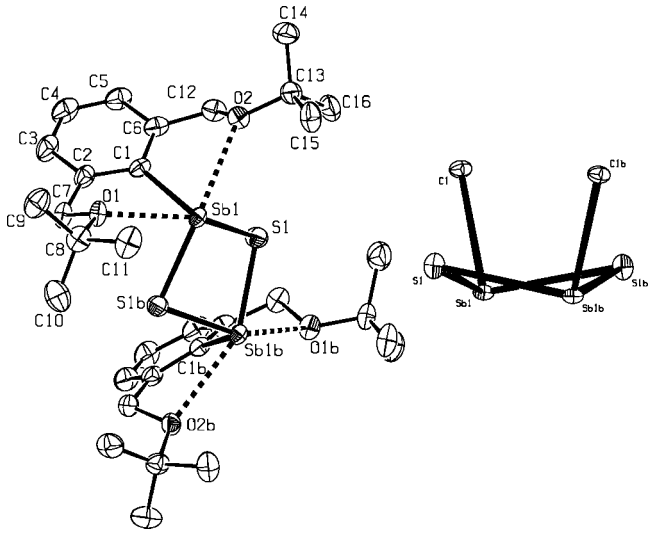


Figure 3. ORTEP drawings (50% probability atomic displacement ellipsoids) of *cis*-**6** (symmetry code b: $1 - x, -y, 1/2 - z$) and view on the puckered central Sb_2S_2 ring. Hydrogen atoms and the CH_2Cl_2 molecule have been omitted for clarity.

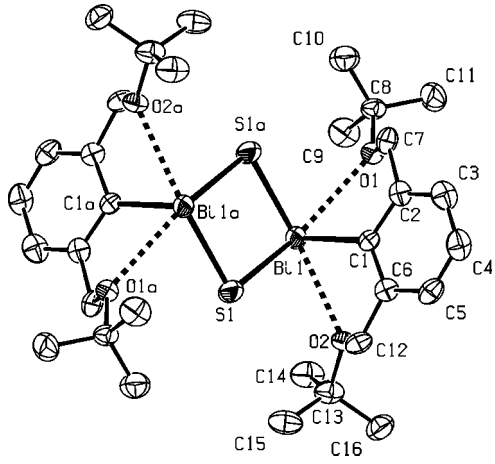


Figure 4. ORTEP drawings (50% probability atomic displacement ellipsoids, one of two independent molecules in the unit cell) of *trans*-**8** (symmetry code a: $-x + 1, -y + 2, -z + 1$). Hydrogen atoms and the $CHCl_3$ molecule have been omitted for clarity.

Sb−O(N) dative bonds. This tendency is especially evident between Cl and I congeners (Table 1).[3,4]

The reaction of **6** with 2 equiv of iodine yielded the expected diiodide L^2MI_2 (**11**) as the major product. This compound was characterized in the reaction mixture by ESI mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy.[3b] However, an unprecedented organoantimony compound, **12**, was obtained as the minor product in this reaction (Scheme 3). Compound **12** could be isolated in very low yield (∼10%) by repeated extraction of the reaction mixture with a 1:3 toluene/hexane mixture. Formation of oxastibol **12** can be explained as an intramolecular ether bond cleavage, leading to the cyclization of one of the ligand arms to a C_3SbO ring.[15,16] Similar reactions occur in the case

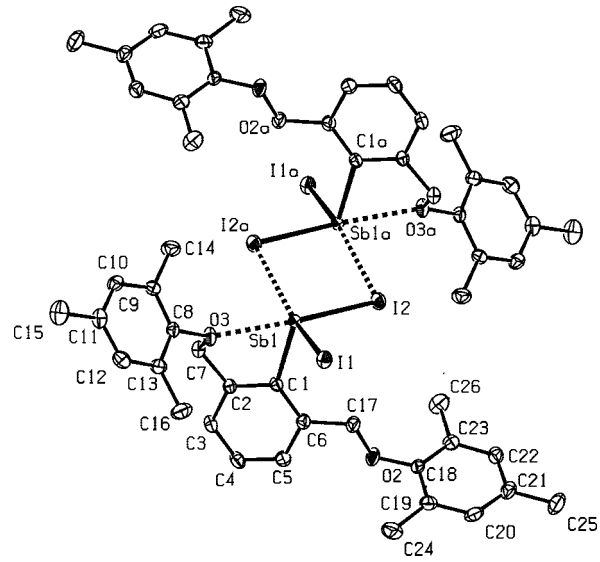
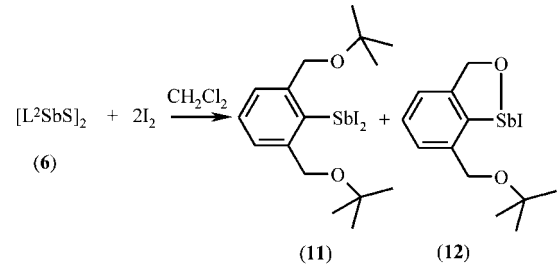


Figure 5. ORTEP drawings (50% probability atomic displacement ellipsoids) of **10** (symmetry code a: $-x, -y, -z$). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Sb1−O1, 2.622(4); Sb1−O2, 5.006(4); Sb1−I1, 2.7491(5); Sb1−I2, 2.8056(6); Sb1−C1, 2.177(6). Selected bond angles (deg): O1−Sb1−I2, 167.22(10); I1−Sb1−I2, 99.83(2); O3−Sb1−I1, 92.50(10); C1−Sb1−O3, 72.65(18); C1−Sb1−I1, 95.27(16); C1−Sb1−I2, 102.63(15).

Scheme 3. Reaction of Compound 6 with I_2



of organophosphorus analogues[17] and also in the reaction of **2** with the silver salt of triflate or $CB_{11}H_{12}^-$ cluster anions.[5] The identity of compound **12** was established by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR spectra contained two signals for OC*H*$_2$ groups (2:2 integral ratio), a broad signal at 5.59 ppm belonging to OC*H*$_2$ within the C_3SbO ring and a sharp one at 4.75 ppm appropriate for OC*H*$_2$ of the second ligand arm. There was only one signal detected in the region of *t*-Bu moieties at 1.47 ppm with an integral value of 9, clearly demonstrating that only one of the *t*-Bu groups is present in **12**. Also in the aromatic region of the ^{1}H NMR spectrum three signals were observed in a 1:1:1 ratio, indicating nonequivalence of three aromatic protons, which is in accordance with the proposed structure. Five resonances were observed in the aromatic region in the ^{13}C NMR spectrum (the signal of the *ipso*-carbon was not detected), and two signals for O*C*H$_2$ emerged; these findings confirm the proposed structure. Compounds containing a similar ligand system (the so-called Martin ligand) have been

(15) It is highly probable that compound **12** is formed by *t*-BuI elimination from **11** during the reaction. Similar fragmentation has been recently obtained in mass spectra of **11** (see ref 3b) and analogous organotin(IV) compounds (see ref 16). The mechanism of this type of reaction is currently being investigated in our laboratories. We thank one of the reviewers of this manuscript for suggestions concerning this phenomenon.

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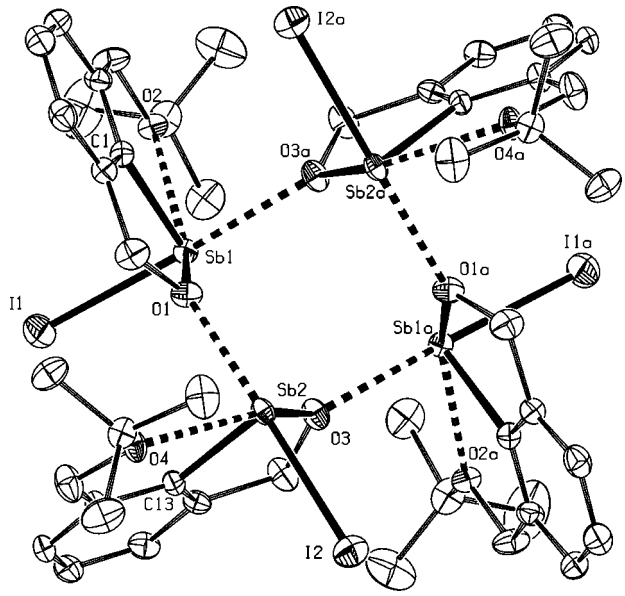

Figure 6. ORTEP drawings (40% probability atomic displacement ellipsoids) of **12** (symmetry code a: $-x+1, y, -z+1/2$). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Sb1−C1, 2.109(9); Sb1−O1, 2.029(7); Sb1−O2, 2.703(7); Sb1−I1, 2.7889(12); O1−Sb2, 2.468(7); Sb2−C13, 2.103(9); Sb2−O3, 2.037(7); Sb2−O4, 2.662(7); Sb2−I2, 2.8065(11); Sb1−O3a, 2.565(7). Selected bond angles (deg): C1−Sb1−O1, 80.6(3); O1−Sb1−O2, 148.4(2); I1−Sb1−O3a, 175.58(16); Sb1−O1−Sb2, 129.3(3); C13−Sb2−O3, 81.3(3); O3−Sb2−O4, 148.7(3); I2−Sb2−O1, 174.48(16); Sb2−O3−Sb1a, 135.0(3).

extensively studied with both pentavalent and trivalent central antimony atoms.[18]

Finally, the molecular structure of **12** was established by single-crystal X-ray analysis (Table 3, Figure 6). In **12** one of the ligand arms was disrupted with formation of an Sb−O covalent bond, while the second one remained intact, proving the proposed structure in solution (vide supra and Figure 6). The bond distances Sb1−O1 = 2.029(7) Å and Sb2−O3 = 2.037(7) Å are comparable with $\sum_{cov}$(Sb,O) = 2.14 Å[12] indicating the presence of a covalent bond and formation of five-membered C_3SbO rings. These rings are not perfectly planar, but the methylene groups are a bit bent out. The other oxygen donor atoms O2 and O4 remain coordinated to the central antimony atoms through medium strong intramolecular interactions (Sb1−O2 = 2.703(7) Å and Sb2−O4 = 2.662(7) Å). One of the endocyclic oxygen atoms, O1, is involved in an intermolecular contact with the adjacent molecule, forming a dimeric unit. The Sb2−O1 = 2.468(7) Å bond length indicates strong intermolecular connection between both moieties. The geometry around O1 can be described as a nearly ideal trigonal planar environment (the sum of the angles of the girdle around O1 is 360.1°). In turn, the second endocyclic oxygen, O3, is joined with another molecule of an analogous dimer, forming the final centrosymmetric tetrameric structure of **12**. This connection, Sb1a−O3 = 2.565(7) Å, is significantly longer than intermolecular contacts within each dimer (Sb2−O1 = 2.468(7) Å), and the oxygen atom O3 is again located in a trigonal planar environment (the sum of the angles of the girdle around O5 is 359.6°). The central eight-membered Sb_4O_4 ring is strongly puckered (Figure 6), where two nearly planar Sb_2O_2 moieties are joined through weak Sb1(a)−O3(a) interactions. The iodine atoms are coordinated to the central antimony atoms through regular covalent bonds (Sb1−I1 = 2.7889(12) Å, Sb2−I2 = 2.8065(11) Å). The coordination geometry around each antimony atom (for example, Sb1) taking into account all coordinated oxygen atoms (for Sb1, i.e., O1, O2, and O3a) can be described as a distorted tetragonal pyramid, with the *ipso*-carbon atom C1 located in the apical position and O1, O2, O3a, and I1 atoms forming the basal plane, where atoms I1, O3a (175.58(16) Å) and O1, O2 (148.4(2) Å) are mutually placed in *trans* positions. The structure of a similar oxastibol has been recently described as well.[19] In this case the endocyclic oxygen atom is involved in OH···O hydrogen bonding.

Experimental Section

General Remarks. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX360 and Bruker500 Avance spectrometers, respectively, using 5 mm tunable broad-band probes. Appropriate chemical shifts in ^{1}H and ^{13}C NMR spectra were calibrated on the residual signals of the solvent ($CDCl_3$, $\delta(^1H)$ = 7.27 ppm and $\delta(^{13}C)$ = 77.23 ppm) or external Me_4Si ($\delta(^1H)$ = 0.0 ppm). In the case of organometallic sulfides **5**−**8** the integral values are not given in ^{1}H NMR data, because they coexist as two (*cis*, *trans*) isomers, and so the full description may be a bit confusing.

Positive-ion ESI mass spectra were measured on an ion trap analyzer, Esquire 3000 (Bruker Daltonics, Bremen, Germany), in the range *m*/*z* 50−1500. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 5 μL/min. The selected precursor ions were further analyzed by MS/MS analyses under the following conditions: isolation width *m*/*z* = 6, collision amplitude in the range 0.8−1.0 V depending on the precursor ion stability, ion source temperature 300 °C, tuning parameter compound stability 100%, flow rate and pressure of nitrogen 4 L/min and 10 psi, respectively. All masses listed in this section are related to the ^{121}Sb configuration.

Air- and moisture-sensitive operations were carried out under an argon atmosphere using the standard Schlenk technique, and solvents were purified by standard procedures. $Na_2S\cdot 9H_2O$ and a 1.6 M solution of *n*-BuLi in hexane were obtained from commercial suppliers and used as delivered. Starting compounds **1**, **2**, and **4** were prepared according to published procedures.[3b]

X-ray Structure Determination. Suitable single crystals of **3**, **5**−**8**, **10**, and **12** were mounted on a glass fiber with an oil and measured on a four-circle diffractometer, KappaCCD, with a CCD area detector by monochromatized Mo Kα radiation (λ = 0.71073 Å) at 150(1) K (Table 3). The numerical[20] absorption corrections from the crystal shape were applied for all crystals, and multiscan[21] was applied for **7**. The structures were solved by the direct method (SIR92[22]) and refined by a full matrix least-squares procedure based on F^2 (SHELXL97[23]). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$(pivot atom); for the methyl moiety a multiple of 1.5 was chosen. The final difference maps displayed no peaks of chemical

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significance as the highest peaks and holes are in close vicinity (~1 Å) of heavy atoms, except in compound **8**, where they are located between the chlorine atoms of a disordered solvate molecule (chloroform).

Synthesis of 1,3-(2′,4′,6′-$(CH_3)_3C_6H_2OCH_2)_2C_6H_4$ (L^3). 1,3-$(CH_2Br)_2C_6H_4$ (12.4 g, 0.047 mol) in THF (100 mL) was added to 2,4,6-$(CH_3)_3C_6H_2O^-Na^+$ (14.8 g, 0.093 mol) in THF (300 mL) and the resulting mixture stirred overnight. NaBr was filtered, and the filtrate was evaporated in vacuo to dryness, providing a yellow oil, which was dissolved in hexane (50 mL). Colorless crystals were obtained after crystallization at −30 °C, collected by filtration, and dried in vacuo. Yield: 13.7 g (78%). Mp: 79−81 °C. Anal. Calcd for $C_{26}H_{30}O_2$ (MW 374.53): C, 83.4; H, 8.1. Found: C, 83.5; H, 8.2. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.30 (6H, s,*p*-C*H*$_3$-Mes), 2.32 (12H, s, *o*-C*H*$_3$-Mes), 4.86 (4H, s, OC*H*$_2$), 6.89 (4H, s, *m*-*H*-Mes), 7.48 (3H, m, Ar-*H3,4,5*), 7.65 (1H, s, Ar-*H1*). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 16.5 (s, *o*-*C*H$_3$-Mes), 20.9 (s, *p*-*C*H$_3$-Mes), 74.1 (s, O*C*H$_2$), 127.1 (s, Ar-*C*1), 127.4 (s, Ar-*C3,5*), 128.9 (s, Ar-*C4*), 129.7 (s, *m*-*C*-Mes), 130.9 (s, *o*-*C*-Mes), 133.5 (s, *p*-*C*-Mes), 138.4 (s, Ar-*C2,6*), 153.7 (s, *C*-O-Mes).

Synthesis of 2,6-(2′,4′,6′-$(CH_3)_3C_6H_2OCH_2)_2C_6H_3SbCl_2$ (3). *n*-BuLi (3.5 mL, 1.6 M solution in hexane, 5.6 mmol) was added to a solution of L^3 (2.07 g, 5.5mmol) in hexane (20 mL) and the resulting mixture stirred for an additional 24 h. During this time a white suspension of L^3Li formed and was collected by filtration, washed by a minimum amount of hexane (5 mL) and dried in vacuo, giving 1.47 g of L^3Li. The lithium salt was dissolved in Et_2O (30 mL) and added to a cooled (−70 °C) solution of $SbCl_3$ (0.88 g, 3.9 mmol) in Et_2O (50 mL); then the reaction mixture was allowed to reach room temperature and stirred for an additional 12 h. The solvent was evaporated in vacuo, and the resulting oily product was extracted by 2 × 30 mL of CH_2Cl_2. Insoluble material was filtered, the filtrate was evaporated, and the crude product was crystallized from a hexane/CH_2Cl_2 mixture. Yield: 1.27 g (58%). Mp: 181−184 °C. Anal. Calcd for $C_{26}H_{29}O_2Cl_2Sb$ (MW 566.18): C, 55.2; H, 5.2. Found: C, 55.5; H, 5.0. Positive-ion MS: *m*/*z* 1039 $[LSbOSbLCl]^+$; *m*/*z* 529 $[M - Cl]^+$; *m*/*z* 511 $[LSbOH]^+$, 100; *m*/*z* 493 $[M - Cl - HCl]^+$. Negative-ion MS: *m*/*z* 599 $[M + Cl]^-$, 100. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.24 (12H, s, *o*-C*H*$_3$-Mes), 2.31 (6H, s, *p*-C*H*$_3$-Mes), 5.52 (4H, s, OC*H*$_2$), 6.88 (4H, s, *m*-*H*-Mes), 7.31 (2H, d, Ar-*H3,5*), 7.41 (1H, t, Ar-*H4*). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 18.0 (s, *o*-*C*H$_3$-Mes), 20.9 (s, *p*-*C*H$_3$-Mes), 76.9 (s, O*C*H$_2$), 125.3 (s, Ar-*C3,5*), 129.7 (s, Ar-*C4*), 129.8 (s, *m*-*C*-Mes), 130.7 (s, *o*-*C*-Mes), 134.8 (s, *p*-*C*-Mes), 146.5 (s, Ar-*C2,6*), 151.5 (s, Ar-*C*1), 154.7 (s, *C*-O-Mes).

Synthesis of $[2,6\text{-}(MeOCH_2)_2C_6H_3SbS]_2$ (5). Compound **1** (450 mg, 1.26 mmol) was dissolved in toluene (20 mL), added to a water solution (20 mL) of $Na_2S \cdot 9H_2O$ (0.312 mg, 1.30 mmol), and stirred for an additional 12 h. Then the toluene fraction was separated, and the water layer was washed twice with toluene (10 mL). Combined toluene fractions were dried over Na_2SO_4 and evaporated in vacuo to dryness. The white material was washed with hexane (2 × 5 mL), giving a slightly yellow powder of **5**. Yield: 0.2 g (51%). Mp: 153−156 °C. Anal. Calcd for $C_{20}H_{26}O_4S_2Sb_2$ (MW 638.06): C, 37.7; H, 4.1. Found: C, 37.4; H, 4.4. Positive-ion MS: *m*/*z* 675 $[M + K]^+$; *m*/*z* 659 $[M + Na]^+$, 100; *m*/*z* 357 $[LSbS + K]^+$; *m*/*z* 341 $[LSbS + Na]^+$. ^{1}H NMR ($CDCl_3$): δ 3.35 and 3.37 (s, C*H*$_3$O), 4.48 and 5.04 (s, OC*H*$_2$), 6.87 and 7.18 (d, Ar-*H3,5*), 6.97 and 7.27 (t, Ar-*H4*). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 58.5, overlap of two signals (*C*H$_3$O), 75.4 and 75.6 (s, O*C*H$_2$), 125.6 and 126.3 (s, Ar-*C3,5*), 127.6 and 128.0 (s, Ar-*C4*), 144.9 and 145.7 (s, Ar-*C2,6*), Ar-*C*1 not obtained.

Synthesis of $[2,6\text{-}(t\text{-}BuOCH_2)_2C_6H_3SbS]_2$ (6). Compound **6** was prepared analogously to **5** using **2** (520 mg, 1.18 mmol) and $Na_2S \cdot 9H_2O$ (290 mg, 1.2 mmol). Yield: 0.26 g (54%). Mp: 123−127 °C. Anal. Calcd for $C_{32}H_{50}O_4S_2Sb_2$ (MW 806.38): C, 47.7; H, 6.3. Found: C, 47.4; H, 6.0. Positive-ion MS: *m*/*z* 843 $[M + K]^+$; *m*/*z* 827 $[M + Na]^+$, 100. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27, overlap of two signals ((C*H*$_3$)$_3$CO), 4.72 and 4.92 (s, OC*H*$_2$), 6.75 and 7.12 (d, Ar-*H3,5*), 6.83 and 7.19 (t, Ar-*H4*). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 27.7, overlap of two signals ((*C*H$_3$)$_3$CO), 65.3 and 65.4 (s, O*C*H$_2$), 75.7 and 75.8 (s, (CH$_3$)$_3$*C*O), 124.9 and 125.6 (s, Ar-*C3,5*), 127.1 and 127.4 (s, Ar-*C4*), 146.0 and 147.1 (s, Ar-*C2,6*), 145.3 and 148.3 (s, Ar-*C*1).

Synthesis of $[2,6\text{-}(2',4',6'\text{-}(CH_3)_3C_6H_2OCH_2)_2C_6H_3SbS]_2$ (7). Compound **7** was prepared analogously to **5** using **3** (345 mg, 0.61 mmol) and $Na_2S \cdot 9H_2O$ (150 mg, 0.62 mmol). Yield: 0.17 g (52%). Mp: 199−202 °C. Anal. Calcd for $C_{52}H_{58}O_4S_2Sb_2$ (MW 1054.67): C, 59.2; H, 5.5. Found: C, 59.0; H, 5.8. Positive-ion MS: *m*/*z* 1091 $[M + K]^+$, 100; *m*/*z* 1075 $[M + Na]^+$; *m*/*z* 565 $[LSbS + K]^+$; *m*/*z* 549 $[LSbS + Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.14 and 2.16 (s, *p*-C*H*$_3$-Mes), 2.17 and 2.25 (s, *o*-C*H*$_3$-Mes), 5.39 and 5.56 (4H, s, OC*H*$_2$), 6.80, overlap of two signals (*m*-*H*-Mes), 6.85 and 7.15 (d, Ar-*H3,5*), 6.90 and 7.26 (t, Ar-*H4*). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 17.3 and 17.6 (s, *p*-*C*H$_3$-Mes), 17.6 and 20.8 (s, *o*-*C*H$_3$-Mes), 77.0 and 77.1 (s, O*C*H$_2$), 125.0 and 125.7 (s, Ar-*C3,5*), 127.6 and 127.9 (s, Ar-*C4*), 129.5, overlap of two signals (*m*-*C*-Mes), 131.0 and 131.1 (s, *o*-*C*-Mes), 133.7, overlap of two signals (s, *p*-*C*-Mes), 145.5 and 146.4 (s, Ar-*C2,6*), 146.6 and 148.9 (s, Ar-*C*1), 155.2 and 155.4 (s, *C*-O-Mes).

Synthesis of $[2,6\text{-}(t\text{-}BuOCH_2)_2C_6H_3BiS]_2$ (8). Compound **8** was prepared analogously to **5**, with the exception that the reaction mixture was stirred only for 2 h, and during evaporation of toluene this solution must not be heated (use a vacuum); otherwise decomposition of the product is observed (see the Results and Discussion). Also the purity of starting **4** should be guaranteed, because only a small amount of bismuth chloride remaining from the preparation of **4** can hamper the whole synthesis. A 300 mg (0.6 mmol) portion of **4** and a 145 mg (0.6 mmol) portion of $Na_2S \cdot 9H_2O$ were used. Yield: 106 mg (38%). Mp: 148 °C dec. Anal. Calcd for $C_{32}H_{50}O_4S_2Bi_2$ (MW 980.84): C, 39.2; H, 5.1; Found: C, 39.5; H, 4.9. Positive-ion MS: *m*/*z* 1019 $[M + K]^+$; *m*/*z* 1003 $[M + Na]^+$, 100; *m*/*z* 981 $[M + H]^+$; *m*/*z* 529 $[LBiS + K]^+$; *m*/*z* 313 $[LBiS + Na]^+$; *m*/*z* 491 $[LBiSH]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 and 1.27 (s, (C*H*$_3$)$_3$CO), 4.77 and 4.96 (s, OC*H*$_2$), 6.88 and 7.26 (d, Ar-*H3,5*), 7.03 and 7.38 (t, Ar-*H4*). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 27.8, overlap of two signals ((*C*H$_3$)$_3$CO), 67.5 and 67.6 (s, O*C*H$_2$), 75.7, overlap of two signals ((CH$_3$)$_3$*C*O), 126.9 and 127.3 (s, Ar-*C3,5*), 128.0, overlap of two signals (Ar-*C4*), 149.6 and 150.6 (s, Ar-*C2,6*), Ar-*C*1 not obtained.

Synthesis of $2,6\text{-}(MeOCH_2)_2C_6H_3SbI_2$ (9). A solution of I_2 (200 mg, 0.8 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **5** (250 mg, 0.4 mmol) in CH_2Cl_2 (30 mL). The resulting mixture was stirred for 12 h and then evaporated in vacuo. The residue was extracted with a minimum amount of chloroform. Filtration followed by evaporation of the solvent gave **9** as a pale yellow powder after washing with hexane. Yield: 208 mg (48%). Mp: 158−161 °C. Other analytical data correspond to those published elsewhere.[3b]

Synthesis of 2,6-(2′,4′,6′-$(CH_3)_3C_6H_2OCH_2)_2C_6H_3SbI_2$ (10). Compound **10** was prepared analogously to **9** using I_2 (144 mg, 0.56 mmol) and **7** (300 mg, 0.28 mmol). Yield: 230 mg (55%). Mp: 160−163 °C. Anal. Calcd for $C_{26}H_{29}O_2I_2Sb$ (MW 749.08): C, 41.7; H, 3.9. Found: C, 41.4; H, 4.2. Positive-ion MS: *m*/*z* 621 $[M - I]^+$; *m*/*z* 511 $[LSbOH]^+$, 100. Negative-ion MS: *m*/*z* 875 $[M + I]^-$; *m*/*z* 127 $[I]^-$, 100. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.27 (12H, s, *o*-C*H*$_3$-Mes), 2.28 (6H, s, *p*-C*H*$_3$-Mes), 5.43 (4H, s, OC*H*$_2$), 6.86 (4H, s, *m*-*H*-Mes), 7.50 (1H, t, Ar-*H4*), 7.61 (2H, d, Ar-*H3,5*). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 17.7 (s, *o*-*C*H$_3$-Mes), 20.9 (s, *p*-*C*H$_3$-Mes), 76.8 (s, O*C*H$_2$), 126.7 (s, Ar-*C3,5*), 129.7 (s, *m*-*C*-Mes), 130.7 (s, *o*-*C*-Mes), 130.9 (s, Ar-*C4*), 134.3 (s, *p*-*C*-Mes), 145.3 (s, Ar-*C2,6*), 153.9 (s, *C*-O-Mes), Ar-*C*1 not obtained.

Reaction of $[2,6\text{-}(t\text{-}BuOCH_2)_2C_6H_3SbS]_2$ and I_2. A solution of I_2 (265 mg, 1.04 mmol) in CH_2Cl_2 (10 mL) was added to a solution

of **6** (420 mg, 0.52 mmol) in CH_2Cl_2 (30 mL). The resulting mixture was stirred for 12 h and then evaporated in vacuo. ^1H and ^{13}C NMR spectra revealed besides signals of the expected product 2,6-(*t*-$BuOCH_2)_2C_6H_3SbI_2$ (**11**) (analytical data correspond to those in the literature[3b]) signals of novel compound 2-(OCH_2)-6-(*t*-$BuOCH_2$)-C_6H_3SbI (**12**); see the Results and Discussion. Compound **12** was isolated from this mixture as follows. The evaporated reaction mixture was extracted twice with a mixture of toluene/hexane (1:3), and evaporation of the solvents yielded a yellow powder, which was washed with pentane and dried in vacuo. Yield: 55 mg (12%). Mp: 108−110 °C. Anal. Calcd for $C_{12}H_{16}O_2ISb$ (MW 440.91): C, 32.7; H, 3.7. Found: C, 32.5; H, 3.9. Positive-ion MS: *m*/*z* 753 $[2M - I]^+$, 100; *m*/*z* 331 $[M - I + H_2O]^+$; *m*/*z* 313 $[M - I]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 1.47 (9H, s, $(CH_3)_3CO$), 4.75 (2H, s, $(CH_3)_3COCH_2$), 5.59 (2H, s (br), $SbOCH_2$), 7.17 (1H, d, Ar-*H*), 7.36 (1H, d, Ar-*H*), 7.39 (1H, dd, Ar-*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 28.4 (s, $(CH_3)_3CO$), 62.6 (s, $(CH_3)_3COCH_2$), 77.2 (s, $SbOCH_2$), 77.9 (s, $(CH_3)_3CO$), 120.8, 123.3, 130.3 143.9, 153.5 (s, Ar-*C*), Ar-*C*1 not detected.

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Supporting Information Available: ^1H NMR spectra of **5**−**7** and CIF data. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 670097 for **5** and 713304−713309 for **3**, **6**−**8**, **10**, and **12**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Rd., Cambridge CB2 1EY, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; URL, http://www.ccdc.cam.ac.uk).

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