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Synthesis and structures of hypervalent organoantimony and organobismuth chlorides containing asymmetric C,E,C-chelating (E = O, S) ligands†

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Two asymmetric tridentate C,E,C-chelating ligand precursors, 1-Br-2-[(2′-$BrC_6H_4CH_2E)CH_2]C_{10}H_6$ (E = O (**1**), E = S (**2**), were prepared in good yield. Lithiation of the two precursors was achieved by a reaction with *n*-BuLi, and was followed by treatment with $SbCl_3$ or $BiCl_3$ in a 1 : 1 molar ratio to give four air-stable hypervalent organoantimony and organobismuth chlorides with an asymmetric C,E,C-chelating ligand (E = O, S), *i.e.* $(C_6H_4CH_2OCH_2C_{10}H_6)SbCl$ (**3**), $(C_6H_4CH_2SCH_2C_{10}H_6)SbCl$ (**4**), $(C_6H_4CH_2OCH_2C_{10}H_6)BiCl$ (**5**) and $(C_6H_4CH_2SCH_2C_{10}H_6)BiCl$ (**6**). These compounds were characterized by NMR spectroscopy, elemental analysis and melting point determination. X-ray structure analysis of compounds **3–6** revealed that the donor atoms (O, S) are strongly coordinated to the metal atoms (Sb, Bi). Compounds **3–6** exhibit chirality and crystallize as racemic mixtures.

Introduction

In recent years, hypervalent organoantimony and organobismuth compounds bearing intramolecular E→M (E = N, O, S; M = Sb, Bi) coordinations have attracted much attention due to their intriguing chemistry, structure and applications in areas such as medicine, catalysis, and organic synthesis.[1–3] The majority of these compounds contain bidentate or tridentate aryl ligands with one or two pendant coordinating groups, *i.e.* the so-called C,E or E,C,E and C,E,C-chelating ligands (E = N, O, S). For example, the 2-$[Me_2NCH_2]C_6H_4$, 2,6-$(Me_2NCH_2)_2C_6H_3$, 2,6-$(ROCH_2)_2C_6H_3$ (R = Me, *t*-Bu) and $E(CH_2C_6H_4)_2$ (E = RN, O, S) moieties have often been applied to stabilize hypervalent organoantimony and organobismuth halides,[4] cations,[5] chalcogen derivatives[6] or compounds containing metal–metal bonds.[4d,6a,7] Among these compounds, those with intramolecular N→Sb or N→Bi interactions are well studied while those with E→M (E = O, S; M = Sb, Bi) intramolecular coordinations are somewhat less reported.[2,3] To the best of our knowledge, only the crystal structures of two compounds with S→Sb intramolecular coordinations, *viz.* CpFe-[2-$(RCH_2)C_5H_3$]$SbPh_2$ [R = SCH_2(furan)-2-yl][3,8] and [$S(CH_2$-2-$C_6H_4SbMe_3)_2]I_2$[9] have been determined by X-ray diffraction analysis.

In contrast to hypervalent organoantimony and organobismuth compounds containing symmetric tridentate E,C,E-ligands or C,E,C-ligands (E = N, O, S), the counterparts with asymmetric analogous ligands have been only scantily reported. Recently, a number of organoantimony and organobismuth compounds with asymmetric N,C,O-ligands, *i.e.* $LSbCl_2$, $LBiCl_2$ (L = [2-(Me_2NCH_2)-6-$(ROCH_2)C_6H_3$], R = Me,[10] *t*-Bu[11]) and $[LMCl]^+X^-$ (L = [2-(Me_2NCH_2)-6-(*t*-$BuOCH_2)C_6H_3$],[11] M = Sb, X = $[CB_{11}H_{12}]^-$; M = Bi, X = $CF_3SO_3^-$, $[CB_{11}H_{12}]^-$) as well as $(LME)_2$ (L = [2-$(Me_2NCH_2$-6-$(MeOCH_2)C_6H_3$],[12] M = Sb, E = S or Se; M = Bi, E = S) were synthesized and characterized. So far there are no organoantimony and organobismuth compounds with asymmetric C,E,C-chelating (E = N, O, S) ligands reported.

As part of our work on hypervalent organoantimony and organobismuth compounds with C,E,C-chelating (E = N, O, S)

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†Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR of **1–6** (Fig. S1–S12) and crystallographic details (Tables S1–S4). CCDC numbers 773956 (**3**), 827987 (**4**), 909196 (**5**) and 909197 (**6**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50922b

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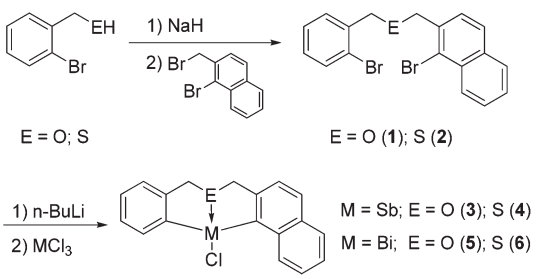
ligands, we report herein the synthesis and structures of four hypervalent organoantimony and organobismuth chlorides containing asymmetric C,E,C-chelating (E = O, S) ligands.

Results and discussion

Two asymmetric tridentate C,E,C-ligand (E = O, S) precursors, *viz.* 1-bromo-2-[(2-bromobenzyloxy)methyl]naphthalene (**1**) and (2-bromobenzyl)[(1-bromonaphthalen-2-yl)methyl]sulfane (**2**), were prepared by nucleophilic substitution of 1-bromo-2-bromomethylnaphthalene[13] with the nucleophilic reagent generated by reacting (2-bromophenyl)methanol or (2-bromophenyl)-methanethiol with NaH, respectively (Scheme 1). Both compounds were isolated as colorless transparent solids after recrystallization from CH_2Cl_2–hexane (92% for **1**, 87% for **2**). Compounds **1** and **2** were lithiated with *n*-BuLi at −30 °C, and the resulting dilithio compounds reacted with $SbCl_3$ or $BiCl_3$ in a 1 : 1 molar ratio to produce the corresponding chlorides, *i.e.* 14-chloro-7,14-dihydro-5*H*-benzo[*c*]naphtho[1,2-*f*][1,5]oxastibocine (**3**), 14-chloro-7,14-dihydro-5*H*-benzo[*c*]naphtho[1,2-*f*]-[1,5]thiastibocine (**4**), 14-chloro-7,14-dihydro-5*H*-benzo[*c*]-naphtho[1,2-*f*][1,5]oxabismocine (**5**) and 14-chloro-7,14-dihydro-5*H*-benzo[*c*]naphtho[1,2-*f*][1,5]thiabismocine (**6**) (Scheme 1). The crystals of compounds **3** and **4** are colorless and transparent while those of compounds **5** and **6** are yellow. Compounds **3–5** are well soluble in chlorinated solvents (CH_2Cl_2, $CHCl_3$) while compound **6** is only slightly soluble in chlorinated solvents (CH_2Cl_2, $CHCl_3$). Compounds **3–6** are air-stable and thermally stable up to 200 °C. The NMR and elemental analytical data of compounds **1–6** are consistent with their formulas.

The molecular structures of chlorides **3–6** determined by X-ray diffraction analysis of the single crystals obtained by slow diffusion of *n*-hexane into CH_2Cl_2 solutions are depicted in Fig. 1–4. Selected bond distances and angles are given in Table 1.

A common feature of organoantimony and organobismuth chlorides **3–6** is that the metal centre (Sb, Bi) is strongly coordinated with the donor O or S atom of the asymmetric tridentate C,E,C-ligand (E = O, S). The intramolecular E→Sb or E→Bi interactions result in the formation of "*chelate induced-M-chiral*" (M = Sb, Bi) compounds.[3,14] For compounds **3–6**, chirality (induced at Sb or Bi) can be described in terms of the C_M and



Scheme 1 Synthesis of compounds **1–6**.

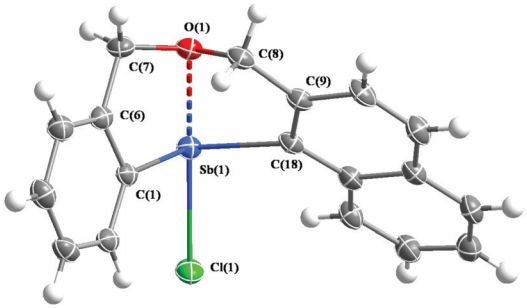


Fig. 1 A thermal ellipsoid plot of the (C_{Sb})-**3** isomer (50% probability level).

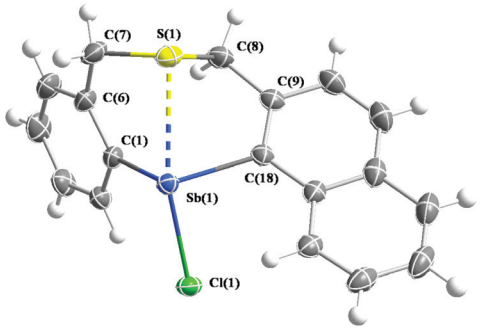


Fig. 2 A thermal ellipsoid plot of the (A_{Sb})-**4** isomer (50% probability level).

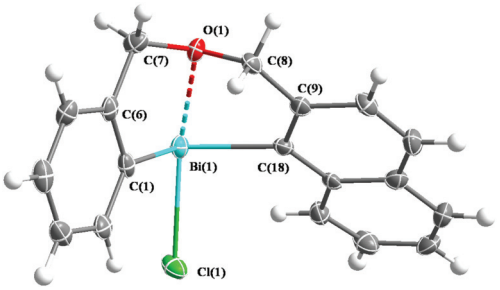


Fig. 3 A thermal ellipsoid plot of the (C_{Bi})-**5** isomer (50% probability level).

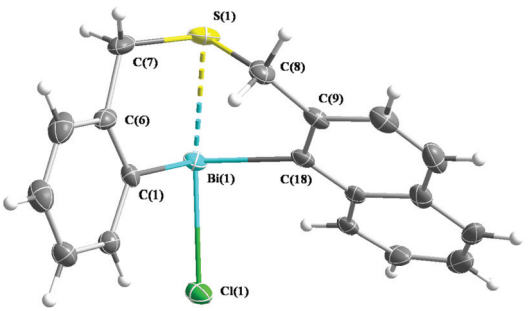


Fig. 4 A thermal ellipsoid plot of the (C_{Bi})-**6** isomer (50% probability level).

A_M isomers having *pseudo*-trigonal bipyramidal cores.[3,14] It is apparent that compounds **3–6** crystallize as racemates.

One can see that the coordination polyhedron around the centre metal (Sb, Bi) of compounds **3–6** can be best described

Table 1 Selected bond lengths [Å] and angles [°] of **3–6**

3			
Sb(1)–C(1)	2.176(4)	C(1)–Sb(1)–C(18)	101.55(13)
Sb(1)–C(18)	2.165(3)	C(1)–Sb(1)–O(1)	72.74(11)
Sb(1)–O(1)	2.425(2)	C(18)–Sb(1)–O(1)	73.77(11)
Sb(1)–Cl(1)	2.4793(10)	C(1)–Sb(1)–Cl(1)	88.81(10)
O(1)–C(7)	1.433(4)	C(18)–Sb(1)–Cl(1)	98.12(10)
O(1)–C(8)	1.437(4)	O(1)–Sb(1)–Cl(1)	157.43(7)
4			
Sb(1)–C(1)	2.186(3)	C(1)–Sb(1)–C(18)	106.01(10)
Sb(1)–C(18)	2.184(3)	C(1)–Sb(1)–S(1)	76.19(7)
Sb(1)–S(1)	2.7515(7)	C(18)–Sb(1)–S(1)	73.24(7)
Sb(1)–Cl(1)	2.5260(7)	C(1)–Sb(1)–Cl(1)	89.78(7)
S(1)–C(7)	1.799(3)	C(18)–Sb(1)–Cl(1)	89.55(7)
S(1)–C(8)	1.815(3)	S(1)–Sb(1)–Cl(1)	153.39(2)
5			
Bi(1)–C(1)	2.289(4)	C(1)–Bi(1)–C(18)	100.59(13)
Bi(1)–C(18)	2.270(4)	C(1)– Bi(1)–O(1)	70.10(12)
Bi(1)–O(1)	2.548(2)	C(18)–Bi(1)–O(1)	71.35(12)
Bi(1)–Cl(1)	2.5803(10)	C(1)–Bi(1)–Cl(1)	88.77(10)
O(1)–C(7)	1.446(4)	C(18)–Bi(1)–Cl(1)	95.87(9)
O(1)–C(8)	1.460(6)	O(1)–Bi(1)–Cl(1)	152.02(13)
6			
Bi(1)–C(1)	2.296(7)	C(1)–Bi(1)–C(18)	100.3(3)
Bi(1)–C(18)	2.292(7)	C(1)– Bi(1)–S(1)	74.0(2)
Bi(1)–S(1)	2.819(2)	C(18)–Bi(1)–S(1)	74.3(2)
Bi(1)–Cl(1)	2.655(2)	C(1)–Bi(1)–Cl(1)	88.7(2)
S(1)–C(7)	1.788(9)	C(18)–Bi(1)–Cl(1)	92.1(2)
S(1)–C(8)	1.817(8)	S(1)–Bi(1)–Cl(1)	155.32(7)

as a strongly distorted *pseudo*-trigonal bipyramid (hypervalent 10-Sb-4 or 10-Bi-4 species[15]). The O(1) or S(1) and Cl(1) atoms are located at the apical positions, and the C(1)and C(18) atoms at the equatorial positions along with a lone pair of Sb or Bi. Due to the constrains imposed by the intramolecular E→M (E = O, S; M = Sb, Bi) coordinations, the E–M–Cl angles in compounds **3–6** [**3**, O(1)–Sb(1)–Cl(1): 157.43(7)°; **4**, S(1)–Sb(1)–Cl(1): 153.39(2)°; **5**, O(1)–Bi(1)–Cl(1): 152.02(13)°; **6**, S(1)–Bi(1)–Cl(1): 155.32(7)°] significantly deviate from the ideal case of 180°. Furthermore, compared with the C–M–C angles of organoantimony and organobismuth chlorides containing symmetric tridentate C,E,C-ligands (E = N, O, S), [such as CyN-$(CH_2C_6H_4)_2$SbCl: 92.95(10)°,[4l] *t*-BuN$(CH_2C_6H_4)_2$BiCl: 93.6(1)°,[4e] PhN$(CH_2C_6H_4)_2$BiCl: 92.90(2)°,[4i] CyN$(CH_2C_6H_4)_2$BiCl: 96.72(19)°[4i] and S$(CH_2C_6H_4)_2$BiCl: 98.90(5)°[4i]] the C–M–C angles of chlorides **3–6** are wider, [C(1)–Sb(1)–C(18): 101.55(13)° for **3** and 106.01(10)° for **4**; C(1)–Bi(1)–C(18): 100.59(13)° for **5** and 100.3(3)° for **6**], which is plausibly a result of steric hindrance induced by the naphthyl group.

The Sb(1)–O(1) distance [2.425(2) Å] of **3** is shorter than that (2.626 Å) of 12-phenylethynyl-5*H*-7,12-dihydrodibenz[*c*,*f*][1,5]oxastibocine[4g] with a symmetric tridentate C,O,C-ligand. However, the Bi(1)–O(1) distance [2.548(2) Å] of **5** is longer than that [2.417(7) Å] of organobismuth triflate $[O(CH_2C_6H_4)_2Bi(OH_2)]^+[OSO_2CF_3]^-$[5i] with a 5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]oxabismocine framework, suggesting that the O→Bi coordination in **5** is weaker than that in the organobismuth cation containing a symmetric tridentate C,O,C-ligand. The Sb(1)–S(1) distance [2.7515(7) Å] in **4** is slightly shorter than the distances of the covalent single Sb–S bonds in organoantimony sulfides with intramolecular E→Sb interactions (E = N, O) [range of Sb–S bond lengths: 2.4109(15)–2.677(2) Å],[6a,e,g] and is significantly shorter than the Sb(1)–S(1) distance [3.555(2) Å] in $[S(CH_2\text{-}2\text{-}C_6H_4SbMe_3)_2]I_2$.[9] The Bi(1)–S(1) bond length [2.819(2) Å] of **6** is slightly shorter than that of $S(CH_2C_6H_4)_2BiCl$ [2.845(4) Å],[4i] suggesting that the S→Bi coordination of the former is slightly stronger than that of the latter, and longer than that of the organobismuth cations with a 5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]thiobismocine framework, *i.e.* $[S(CH_2C_6H_4)_2Bi(OH_2)]^+[ClO_4]^-$,[5d] $[S(CH_2C_6H_4)_2Bi(OH_2)]^+[BF_4]$,[5f] $[S(CH_2C_6H_4)_2Bi(OH_2)]^+[OSO_2C_4F_9]^-$[5j] and $[S(CH_2C_6H_4)_2Bi(OH_2)]^+[OSO_2C_8F_{17}]^-$[5e] [range of Bi–S bond lengths: 2.693(3)–2.713(1) Å], indicating that the S→Bi coordination in **6** is weaker than that of the organobismuth cations containing a symmetric tridentate C,S,C-ligand. A similar value for the Bi–S bond distance was found in 4,8-di-*tert*-butyl-6-iodo-2,10-dimethyldibenzo[*d*,*g*][1,3,6,2]dioxathiabismocine [Bi(1)–S(1) 2.8165(15) Å].[16] The Sb–Cl and Bi–Cl bond distances in **4** [2.5260(7) Å] and **6** [2.655(2) Å] containing S→M (M = Sb, Bi) coordinations are slightly longer than those in **3** [2.4793(10) Å] and **5** [2.5803(10) Å] containing O→M (M = Sb, Bi) interactions. The phenomenon is ascribable to the stronger electron-donating ability of the S atom compared with that of the O atom, which is consistent with the Lewis acidity of the Sb or Bi centre associated with the Sb–X or Bi–X σ* orbitals.[4b,c,d]

The ^{1}H NMR spectra for compounds **1** and **2** in $CDCl_3$ at room temperature contain two singlet signals (**1**, δ 4.73, 4.95; **2**, δ 3.84, 4.09 ppm) ascribable to the two methylene units, which is consistent with their non-equivalence. For compounds **3–6** the signals for the two CH_2 groups exhibit two AB systems, *i.e.* two pairs of doublet signals as in the case of **4** (Fig. S7†) and **6** (Fig. S11†) as a result of intramolecular E→M (E = O, S; M = Sb, Bi) coordinations. In compound **5**, the two doublet signals of the CH_2 protons at a lower field partially overlap and look like a triplet (Fig. S9†). On the other hand, by chance the two signals from one of the CH_2 groups of **3** showed an identical chemical shift and appeared as a singlet with 2H integration (Fig. S5†), while the signals from the other CH_2 group appeared as the usual doublet pair.

Conclusions

In summary, two asymmetric tridentate C,E,C-chelating (E = O, S) ligand precursors **1**, **2** and four hypervalent organoantimony and organobismuth chlorides **3–6** containing an asymmetric C,E,C-chelating ligand (E = O, S), *i.e.* $(C_6H_4CH_2OCH_2C_{10}H_6)$-SbCl (**3**), $(C_6H_4CH_2SCH_2C_{10}H_6)$SbCl (**4**), $(C_6H_4CH_2OCH_2C_{10}H_6)$-BiCl (**5**) and $(C_6H_4CH_2SCH_2C_{10}H_6)$BiCl (**6**), were synthesized and characterized. To the best of our knowledge, compounds **3–6** are the first examples of Sb and Bi (heavy group 15 elements) compounds bearing an asymmetric tridentate C,E,C-ligand. X-ray structure analysis of **3–6** revealed that the donor atoms (O, S) are strongly coordinated to the metal atoms (Sb, Bi). The four compounds exhibit chirality and crystallize as racemic mixtures.

Experimental

General

All manipulations of air-sensitive materials were performed in a glove box filled with argon or under a nitrogen atmosphere using the standard Schlenk techniques. The chemicals were purchased from Aldrich as well as some other chemical providers. They were used as received unless otherwise indicated. All solvents were dried by standard procedures and distilled prior to use. 1-Bromo-2-bromomethylnaphthalene was prepared according to literature procedures.[13] The NMR spectra were recorded at room temperature using a Bruker Avance III 400 spectrometer (Germany). Chemical shifts given in ppm are referenced to tetramethylsilane for ^{1}H NMR spectra (0.0 ppm) and to the solvent signal ($CDCl_3$) for ^{13}C NMR spectra (77.0 ppm), and coupling constants were reported in hertz. Elemental analysis was performed using a VARIO EL III (Germany). The melting points of the compounds were determined using a XT-4 micro apparatus (Beijing Tech Instrument Co. Ltd) and are not corrected.

Synthesis of 1-Br-2-[(2′-BrC$_6$H$_4$CH$_2$O)CH$_2$]C$_{10}$H$_6$ (1). To a suspension of NaH (1.50 g, 80% oil dispersion, 0.05 mol) in THF (50 mL), (2-bromophenyl)methanol (7.48 g, 0.04 mol) was added at 0 °C over 30 min, and the mixture was stirred for 2 h. Then, a solution of 1-bromo-2-bromomethylnaphthalene (12.0 g, 0.04 mol) in THF (80 mL) was added dropwise at 0 °C. The reaction mixture was heated at reflux for 4 h. After cooling, the reaction mixture was diluted with Et_2O (150 mL) and quenched with water (50 mL). The organic layer was separated, washed with NH_4Cl, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2–hexane to give compound **1** in the form of colorless crystals. Yield: 14.92 g (92%). Mp: 80–81 °C. Anal. calcd for $C_{18}H_{14}Br_2O$ (406.11): C, 53.23; H, 3.47; found: C, 53.14; H, 3.46. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 4.73 (2H, s), 4.95 (2H, s), 7.15 (1H, t, J = 8.0 Hz), 7.33 (1H, t, J = 7.6 Hz), 7.51(1H, t, J = 8.0 Hz), 7.54–7.60 (3H, m), 7.69 (1H, d, J = 8.4 Hz), 7.81 (2H, d, J = 8.4 Hz), 8.30 (1H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 72.02, 72.75, 122.43, 122.66, 125.88, 126.44, 126.95, 127.37, 127.42, 127.73, 128.10, 128.98, 129.05, 132.06, 132.49, 133.93, 135.56, 137.36.

Synthesis of 1-Br-2-[(2′-BrC$_6$H$_4$CH$_2$S)CH$_2$]C$_{10}$H$_6$ (2). To a suspension of NaH (1.20 g, 80% oil dispersion, 0.04 mol) in THF (40 mL), a solution of (2-bromophenyl)methanethiol (6.09 g, 0.03 mol) in THF (15 mL) was added dropwise at 0 °C over 30 min, and the mixture was stirred for 2 h. Then, a solution of 1-bromo-2-(bromomethyl)naphthalene (9.0 g, 0.03 mol) in THF (60 mL) was added dropwise at 0 °C. The reaction mixture was heated at reflux for 4 h. After cooling, the reaction mixture was diluted with Et_2O (100 mL) and quenched with water (40 mL). The organic layer was separated, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2–hexane to give compound **2** in the form of colorless crystals. Yield: 11.02 g (87%). Mp: 86–88 °C. Anal. calcd for $C_{18}H_{14}Br_2S$ (422.18): C, 51.21; H, 3.34; found: C, 51.14; H, 3.32. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 3.84 (2H, s), 4.09 (2H, s), 7.09 (1H, t, J = 7.6 Hz), 7.23 (1H, t, J = 8.4 Hz), 7.35 (1H, d, J = 7.6 Hz), 7.49–7.56 (3H, m), 7.59 (1H, t, J = 8.4 Hz), 7.74 (1H, d, J = 8.4 Hz), 7.79 (1H, d, J = 8.0 Hz), 8.30 (1H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 36.50, 37.49, 124.40, 124.63, 126.42, 127.43, 127.46, 127.51, 127.75, 127.82, 128.05, 128.65, 130.74, 132.42, 133.03, 133.57, 135.49, 137.21.

Synthesis of (C$_6$H$_4$CH$_2$OCH$_2$C$_{10}$H$_6$)SbCl (3). Compound **1** (4.06 g, 10.0 mmol) was dissolved in Et_2O (100 mL), and 8.8 mL (22 mmol, 2.5 M in hexane) of *n*-butyllithium was added dropwise to the solution at −30 °C. The mixture was gradually warmed to room temperature over a period of 3 h, and then a solution of $SbCl_3$ (2.28 g, 10 mmol) in Et_2O (100 mL) was added at −78 °C. The resulting mixture was gradually warmed to room temperature over a period of 12 h and then continuously stirred for 6 h at room temperature. After the removal of Et_2O under vacuum and toluene extraction, the insoluble material was filtered out, and the organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2–hexane to give compound **3** in the form of colorless crystals. Yield: 1.05 g (26%). Mp: 196–198 °C. Anal. calcd for $C_{18}H_{14}SbClO$ (403.52): C, 53.58; H, 3.50; found: C, 53.56; H, 3.49. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 4.87 (1H, d, J = 14 Hz), 5.04 (2H, s), 5.27(1H, d, J = 14 Hz), 7.12 (1H, d, J = 8.4 Hz), 7.28 (1H, d, J = 7.6 Hz), 7.39 (1H, t, J = 7.2 Hz), 7.47–7.52 (2H, m), 7.60 (1H, t, J = 8.0 Hz), 7.75 (1H, d, J = 8.4 Hz), 7.82 (1H, d, J = 8.0 Hz), 8.43 (1H, d, J = 7.2 Hz), 8.97 (1H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 73.74, 74.78, 121.81, 125.46, 125.92, 125.99, 128.52, 129.14, 130.01, 130.04, 130.29, 134.11, 135.78, 136.37, 137.21, 141.28, 141.89, 142.32.

Synthesis of (C$_6$H$_4$CH$_2$SCH$_2$C$_{10}$H$_6$)SbCl (4). Compound **2** (2.12 g, 5 mmol) was dissolved in Et_2O (80 mL), and 4.4 mL (11 mmol, 2.5 M in hexane) of *n*-butyllithium was added dropwise to the solution at −30 °C. The mixture was gradually warmed to room temperature over a period of 3 h, and then a solution of $SbCl_3$ (1.14 g, 5 mmol) in Et_2O (50 mL) was added at −78 °C. The resulting mixture was gradually warmed to room temperature over a period of 12 h and then continuously stirred for 6 h at room temperature. After removal of Et_2O under vacuum and toluene extraction, the insoluble material was filtered out, and the organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2–hexane to give compound **4** in the form of colorless crystals. Yield: 0.46 g (22%). Mp: 210–212 °C. Anal. calcd for $C_{18}H_{14}SbClS$ (419.58): C, 51.53; H, 3.36; found: C, 51.50; H, 3.34. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 4.17 (1H, d, J = 14.4 Hz), 4.22(1H, d, J = 14.4 Hz), 4.33 (1H, d, J = 16.0 Hz), 4.38 (1H, d, J = 16.0 Hz), 7.22 (1H, d, J = 8.0 Hz), 7.30 (1H, d, J = 7.6 Hz), 7.36 (2H, m), 7.48 (1H, t, J = 7.6 Hz), 7.60 (1H, t, J = 8.4 Hz), 7.72 (1H, d, J = 7.6 Hz), 7.79 (1H, d, J = 8.0 Hz), 8.70 (1H, d, J = 7.2 Hz), 8.91 (1H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 39.17, 39.27, 125.43, 125.82, 126.03,

128.25, 128.90, 129.30, 129.38, 130.01, 131.79, 133.43, 137.40, 137.92, 138.08, 139.76, 144.78, 147.73.

Synthesis of $(C_6H_4CH_2OCH_2C_{10}H_6)BiCl$ (5). Compound **1** (4.06 g, 10.0 mmol) was dissolved in Et_2O (60 mL), and 8.8 mL (22 mmol, 2.5 M in hexane) of *n*-butyllithium was added dropwise to the solution at −30 °C. The mixture was gradually warmed to room temperature over a period of 3 h, and then a solution of $BiCl_3$ (3.17 g, 10 mmol) in Et_2O (100 mL) was added at −78 °C. The resulting mixture was gradually warmed to room temperature over a period of 12 h and then continuously stirred for 6 h at room temperature. After removal of Et_2O under vacuum and toluene extraction, the insoluble material was filtered out, and the organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2–hexane to give compound **5** in the form of yellow crystals. Yield: 1.86 g (38%). Mp: 230–231 °C. Anal. calcd for $C_{18}H_{14}BiClO$ (490.74): C, 44.05; H, 2.88; found: C, 44.02; H, 2.8. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 4.96 (1H, d, J = 14.0 Hz), 5.04 (1H, d, J = 13.2 Hz), 5.28 (2H, t, J = 16 Hz), 7.42 (1H, t, J = 7.6 Hz), 7.45–7.50 (2H, m), 7.57 (1H, d, J = 7.6 Hz), 7.61 (1H, d, J = 8.4 Hz), 7.69 (1H, t, J = 7.2 Hz), 7.81 (1H, d, J = 8.4 Hz), 7.93 (1H, d, J = 8.0 Hz), 9.05 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 76.13, 78.17, 124.82, 126.12, 126.26, 127.76, 128.29, 128.72, 129.03, 131.37, 132.99, 136.01, 139.03, 141.09, 141.47, 143.75, 145.75.

Synthesis of $(C_6H_4CH_2SCH_2C_{10}H_6)BiCl$ (6). Compound **2** (1.69 g, 4 mmol) was dissolved in Et_2O (100 mL), and 3.5 mL (8.8 mmol, 2.5 M in hexane) of *n*-butyllithium was added dropwise to the solution at −30 °C. The mixture was gradually warmed to room temperature over a period of 3 h, and then a solution of $BiCl_3$ (1.26 g, 4 mmol) in Et_2O (50 mL) was added at −78 °C. The resulting mixture was gradually warmed to room temperature over a period of 12 h and then continuously stirred for 6 h at room temperature. After removal of Et_2O under vacuum and toluene extraction, the insoluble material was filtered out, and the organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2–hexane to give compound **6** in the form of yellow crystals. Yield: 0.38 g (19%). Mp: 247–249 °C. Anal. calcd for $C_{18}H_{14}BiClS$ (506.80): C, 42.66; H, 2.78; found: C, 42.62; H, 2.74. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 4.22 (1H, d, J = 14.0 Hz), 4.27 (1H, d, J = 16.4 Hz), 4.67(1H, d, J = 15.6 Hz), 4.99 (1H, d, J = 14 Hz), 7.48 (2H, t, J = 7.6 Hz), 7.55–7.65 (3H, m), 7.67 (1H, d, J = 7.6 Hz), 7.85 (1H, d, J = 8.4 Hz), 7.91 (1H, d, J = 8.0 Hz), 9.02 (1H, d, J = 8.8 Hz), 9.25 (1H, d, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 40.27, 41.74, 126.23, 126.73, 127.81, 128.31, 128.52, 128.96, 131.42, 131.78, 132.44, 134.62, 140.51, 141.12, 144.63, 150.82.

X-ray crystallography

Given in Table 2 are the results of the crystal structure determination and refinement for compounds **3–6**. X-ray single crystal diffraction analysis was performed at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences using a Bruker SMART APEX diffractometer. In all cases, the diffraction data were collected using graphite monochromated Mo-Ka radiation (λ = 0.71073 Å). The collected frames were processed with SAINT+[17] software and an absorption correction (SADABS)[18] was applied to the collected reflections. The structure was solved by the Direct method (SHELXTL)[19] in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F^2. The hydrogen atoms were generated in their idealized positions and all non-hydrogen atoms were refined anisotropically.

Table 2 Crystallographic data for compounds **3–6**

Compound	**3**	**4**	**5**	**6**
Empirical formula	$C_{18}H_{14}SbClO$	$C_{18}H_{14}SbClS$	$C_{18}H_{14}BiClO$	$C_{18}H_{14}BiClS$
M	403.49	419.55	490.72	506.78
T	293(2) K	293(2) K	133(2) K	293(2) K
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/n$	$Pna2(1)$	$P2(1)/n$
a/Å	11.7504(10)	11.4234(8)	20.5263(19)	11.6940(12)
b/Å	14.4272(12)	11.2183(8)	15.8560(15)	11.4596(12)
c/Å	8.9688(8)	13.3640(10)	4.5578(4)	12.4340(13)
α/°	90.00	90.00	90.00	90.00
β/°	93.251(2)	111.4280(10)	90.00	110.526(2)
γ/°	90.00	90.00	90.00	90.00
V/Å^3	1518.0(2)	1594.2(2)	1483.4(2)	1560.5(3)
Z	4	4	4	4
No. of reflections collected	8803	9412	10 320	9015
No. of unique reflections	3307	3129	3079	3063
R_{int}	0.1210	0.0284	0.0266	0.0852
R_1 [$I > 2\sigma(I)$]	0.0411	0.0257	0.0154	0.0482
R_1 (all data)	0.0455	0.0284	0.0190	0.0552
wR_2 [$I > 2\sigma(I)$]	0.1079	0.0658	0.0354	0.1084
wR_2 (all data)	0.1108	0.0672	0.0365	0.1118
GOF on F^2	1.053	1.052	0.965	1.029

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