Solid-state structure and solution behaviour of hypervalent organoantimony halides containing 2-(Me$_2$NCH$_2$)C$_6$H$_4$– moieties

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Hypervalent antimony(III) halides of the type R$_2$SbX [X = Cl (**1**), Br (**2**), I (**3**)] and RSbX$_2$ [X = Cl (**4**), Br (**5**), I (**6**)] [R = 2-(Me$_2$NCH$_2$)C$_6$H$_4$] have been prepared. Their dynamic solution behavior was investigated by ^{1}H and ^{13}C NMR spectroscopy. The structures of compounds **2**–**6** were determined by single-crystal X-ray diffraction and the observed trends in the degree of intramolecular coordination of the N atom of the pending CH$_2$NMe$_2$ arm are discussed. Compounds **2** and **3** are monomeric and exhibit distorted square-pyramidal (C,N)$_2$SbX cores. The molecular structure of the adduct R$_2$SbI·HI (**3·HI**) indicates the strong coordination of one of the N atoms to antimony. The second pendant arm is twisted away from the metal center, its N atom being protonated and thus converted into an ammonium group. The molecules of **4**–**6** contain a pseudo-trigonal bipyramidal geometry around the antimony atom, with the N atom strongly coordinated *trans* to a halogen atom. Different degrees of association through asymmetric Sb–X · · · Sb bridges [overall distorted square-pyramidal (C,N)SbX$_3$ cores] were found in the crystal of the dichloride **4** (polymeric chains) and dibromide **5** and diiodide **6** (centrosymmetric dimers), respectively. In an attempt to obtain [R$_3$SbI]I$_3$ by addition of I$_2$ to R$_3$Sb in 2 : 1 molar ratio, deep red-brown crystals of the new ionic species [R$_3$SbOH]$^+$[I$_3$]$^-$ (**7**) have been isolated. Crystals of **7** are built up from [R$_3$SbOH]$^+$ cations and linear non-symmetric [I$_3$]$^-$ anions.

Introduction

Organoantimony halides of the types RSbX$_2$, R$_2$SbX, R$_3$SbX$_2$ [X = Cl, Br, I] where R represents monodentate alkyl or aryl ligands have been studied for a long time with consideration of preparative and structural aspects.[1–5] They are important starting materials for organometallic syntheses although their use is often hampered by the air sensitivity of the compounds and by an unspecific reactivity resulting from ligand scrambling. Recently bulky ligands have been used to stabilise these compounds and to better control their chemistry. With steric protection also hydroxo halides of the type R$_3$Sb(OH)X were synthesized and two examples, a ionic derivative [(2,6-Me$_2$C$_6$H$_3$)$_3$SbOH]$^+$[I]$^-$,[6] and a covalent compound (Me$_3$SiCH$_2$)$_3$Sb-(Br)OH,[7] were characterized by single-crystal X-ray diffraction.

Another way to protect and to modify organoantimony halides and other organoantimony compounds is the use of the 2-(dimethylaminomethyl)phenyl group. This ligand is able to coordinate not only through the carbon center but also through the pendant amino group[8] and well protected hypervalent organoantimony compounds representing unusual coordination patterns result. Known examples of derivatives containing [2-(dimethylaminomethyl)phenyl]antimony(III) fragments are R$_3$Sb,[9] R(4-CH$_3$C$_6$H$_4$)$_2$Sb,[10,11] R$_2$SbCl (**1**),[12] R[(Me$_3$-Si)$_2$CH]SbCl,[13] R(4-CH$_3$C$_6$H$_4$)$_2$SbCl$_2$,[10,11] [R$_2$Sb]$^+$[PF$_6$]$^-$,[14] RSb[C$_6$H$_4${C(CF$_3$)$_2$O}-2],[15,16] and R[(Me$_3$Si)$_2$CH]SbH,[13] [R = 2-(Me$_2$NCH$_2$)C$_6$H$_4$]. In all these compounds intramolecular N→Sb interactions were observed both in the solid state and in solution. By contrast, in the asymmetric alkali metal diorganoantimonides, R[(Me$_3$Si)$_2$CH]SbLi·2THF and R[(Me$_3$Si)$_2$CH]-SbNa·TMEDA [R = 2-(Me$_2$NCH$_2$)C$_6$H$_4$],[13] the nitrogen atom of the pendant arm is interacting with alkali metal atom rather than the antimony center.

We report here on efficient synthetic pathways leading to the series of [2-(dimethylaminomethyl)phenyl]antimony(III) halides R$_2$SbX [X = Cl (**1**), Br (**2**), I (**3**)], RSbX$_2$ [X = Cl (**4**), Br (**5**), I (**6**)]
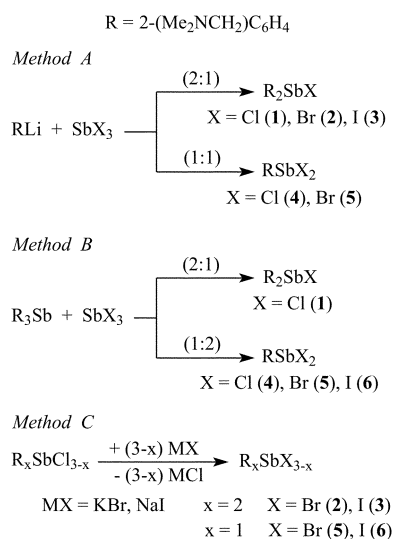
and on R$_2$SbI·HI (**3·HI**) and [R$_3$SbOH]$^+$[I$_3$]$^-$ (**7**) [R = 2-(Me$_2$-NCH$_2$)C$_6$H$_4$] two serendipitous products formed under hydrolytic conditions. The structures of **2**–**6**, **3·HI** and **7** were established by single-crystal X-ray diffraction. Our motivation for the investigation of these compounds stemmed from several considerations. First, we were interested to optimise preparative methods for new arylantimony(III) halides useful as starting materials for the synthesis of new organometallic species, including chiral compounds, stabilized through intramolecular coordination of the nitrogen atom of the pendant arm to the metal center. The use of the 2-(Me$_2$NCH$_2$)C$_6$H$_4$ ligand has allowed, for example, the isolation of the *cyclo*-(RBi)$_4$,[17] and a similar stabilizing effect is expected for organoantimony analogues. Second, interesting structural changes could result related to the halogen nature, its bridging potential and the competition between the halogen and the amine arm for potential supplemental coordination to the metal. Recently we have reported the isolation and characterization of the first functionalised organobismuth(III) derivatives of the type [2-(Me$_2$-NCH$_2$)C$_6$H$_4$]BiCl[(XPR$_2$)(YPR′$_2$)N][18] and a comparison with organoantimony(III) analogues would be of interest opening new perspectives for the synthesis of further mixed-ligand compounds and studies of hypervalent organometallic derivatives.

Results and discussion

Synthesis

The diarylantimony(III) halides, R$_2$SbX [X = Cl (**1**), Br (**2**), I (**3**)], and monoarylantimony(III) dihalides, RSbX$_2$ [X = Cl (**4**), Br (**5**), I (**6**)] [R = 2-(Me$_2$NCH$_2$)C$_6$H$_4$], were prepared in good yields *via* (i) salt elimination reactions between RLi and antimony trihalide (2 : 1 and 1 : 1 molar ratio), in toluene solution, at −78 °C (method A), (ii) redistribution reactions between [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_3$Sb and SbX$_3$ (2 : 1 and 1 : 2 molar ratio), carried out at 140 °C, in the absence of a solvent (method
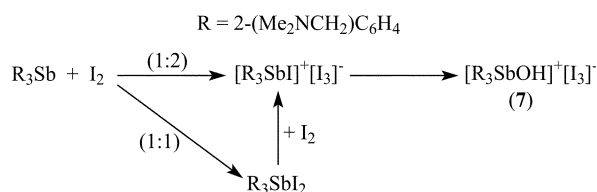
B), and (iii) halogen exchange reactions between $[2\text{-}(Me_2NCH_2)\text{-}C_6H_4]_xSbCl_{3-x}$ (x = 2, 1) and KBr or NaI, in acetone, at room temperature (method C) (Scheme 1). Previous attempts to prepare the monoarylantimony dichloride **4** by method A failed. Instead the monochloride **1** was isolated.[12] However, using the described procedure we were able to obtain both **4** (85%) and **5** (88%).

R = 2-(Me₂NCH₂)C₆H₄

Method A

RLi + SbX₃ →

(2:1) → R₂SbX
X = Cl (**1**), Br (**2**), I (**3**)

(1:1) → RSbX₂
X = Cl (**4**), Br (**5**)

Method B

R₃Sb + SbX₃ →

(2:1) → R₂SbX
X = Cl (**1**)

(1:2) → RSbX₂
X = Cl (**4**), Br (**5**), I (**6**)

Method C

R_xSbCl_{3-x} $\xrightarrow[\text{- (3-x) MCl}]{\text{+ (3-x) MX}}$ R_xSbX_{3-x}

MX = KBr, NaI   x = 2   X = Br (**2**), I (**3**)
                              x = 1   X = Br (**5**), I (**6**)

Scheme 1

The halides **1**–**6** are air-stable crystals. Compounds **1**, **2**, **4** and **5** are colorless, while the iodide derivatives **3** and **6** are yellow. Both mono- **1**–**3** and dihalides **4**–**6** are thermally stable and melt without decomposition. In the solid state they are also stable to hydrolysis and oxidation. Elemental analytical data, together with MS and NMR data are consistent with the anticipated formulas.

Red–brown, air-stable crystals of $[R_3SbOH]^+[I_3]^-$ (**7**) were isolated as product of the reaction of R_3Sb with I_2 in 1 : 2 molar ratio in Et_2O and subsequent hydrolysis (Scheme 2). Attempts to isolate and to characterise the intermediate R_3SbI_2 or $[R_3SbI]^+[I_3]^-$ failed. Recently, the reaction of R_3P with iodine in 1 : 2 molar ratio was reported to afford the isolation of the ionic $[R_3PI]^+[I_3]^-$ derivatives.[19,20] Their deep red–brown coloration is consistent with the presence of the $[I_3]^-$ anion. All the syntheses were carried out in strictly anaerobic and anhydrous conditions, the compounds being moisture sensitive. When R_3P (R = i-Pr) was reacted with iodine in 1 : 1 molar ratio the ionic $[R_3PI]^+[I]^-$ was isolated. The presence of moisture leads to the formation of $[R_3POH]^+[I]^-$ (R = i-Pr), which exhibits P–O–H $\cdots$ I cation–anion contacts in solid state.[20]

R = 2-(Me₂NCH₂)C₆H₄

R₃Sb + I₂ $\xrightarrow{(1:2)}$ [R₃SbI]⁺[I₃]⁻ ⟶ [R₃SbOH]⁺[I₃]⁻ (**7**)

(1:1) ↘   ↑ + I₂

R₃SbI₂

Scheme 2

Solid-state and solution behavior

In order to reveal the extent to which the NMe_2 groups are coordinated to the antimony center and the changes induced by the nature of the halogen atoms, the molecular structure of compounds **2**–**7** were determined by single-crystal X-ray diffraction. A previous structure determination of the monochloride **1** revealed that the nitrogen atom of one amine pendant arm is strongly coordinated to antimony [Sb(1)–N(1)

2.463(2) Å], while the nitrogen atom of the other amine group exhibits only a weak intramolecular interaction [Sb(1)–N(2) 3.216(3) Å].[12] The crystals of both **2** and **3** contain discrete monomers which resemble the molecular structure of the chloride analogue. The intramolecular coordination of the nitrogen atom to antimony in the molecular unit of **1**–**3** induces chirality at the Sb center. Indeed, the X-ray diffraction studies revealed that the monohalides $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbX$ crystallize as racemates. The molecular structures of the *R* isomer of **2a** and the *S* isomer of **3** are shown in Figs. 1 and 2 [with the C(1)–C(6) aromatic ring and the N(1) atom as chiral plane and pilot atom, respectively].[21]
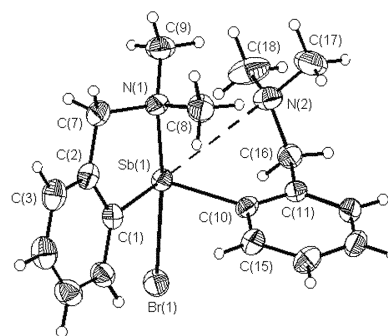

Fig. 1 ORTEP representation at 50% probability and atom numbering scheme for *R*-**2a** isomer.
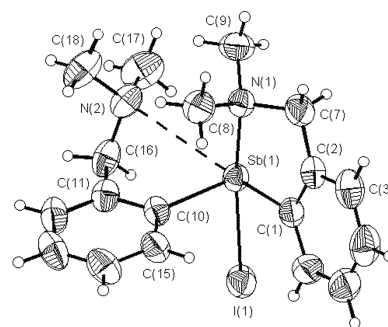

Fig. 2 ORTEP representation at 50% probability and atom numbering scheme for *S*-**3** isomer.

Two independent, very similar molecules **2a** and **2b** are present in the unit cell of the bromide **2** and in the subsequent discussion we will refer only to molecule **2a**. Selected bond distances and angles are given in Table 1. In both cases strong internal coordination of one of the Me_2N groups *trans* to the Sb–halogen bond leads to distorted ψ-trigonal-bipyramidal SbC(C,N)X cores, with the carbon atoms in equatorial positions and the N(1) atom *trans* to the halogen atom [**2a**, N(1)–Sb(1)–Br(1) 165.74(7)°; **3**, N(1)–Sb(1)–I(1) 170.47(8)°]. This deviation from the ideal angle of 180° is due to the constraints imposed by the coordinated amine arm. The Sb(1)–N(1) distances [**2a**, 2.423(3) Å; **3**, 2.417(3) Å] lie between the sums of the respective covalent $[\Sigma_{cov}(Sb,N)\ 2.11\ Å]$ and van der Waals radii $[\Sigma_{vdW}(Sb,N)\ 3.74\ Å]$.[22] Similar values were also found for the Sb–N distances in the chloride analogue **1** [2.463(2) Å][12] and $[2\text{-}(Me_2NCH_2)C_6H_4][(Me_3Si)_2CH]SbCl$ [2.533(7) Å].[13] The *trans*-Sb-halogen bonds [**1**, Sb(1)–Cl(1) 2.579(9) Å;[12] **2a**, Sb(1)–Br(1) 2.7775(8) Å; **3**, Sb(1)–I(1) 3.0105(5) Å] are significantly elongated compared to that of the related monomeric Ph_2SbX [Sb–Cl 2.409(1) Å;[23] Sb–Br 2.553(1) Å;[24] Sb–I 2.771(1) Å[25]], a behavior consistent with the σ*-orbital bonding model, *i.e.* the Lewis acidity of organoantimony(III) halides being related to the Sb–X σ* orbitals (X = halogen).[12,13] The second nitrogen atom of the molecular unit exhibits only a weak Sb(1)–N(2) intramolecular interaction [**2a**, 3.276(3) Å; **2b**, 3.351(3) Å; **3**, 3.211(3) Å], however well shorter than the sum of the van der Waals radii for Sb and N atoms. The Sb(1)–N(2) vector lies

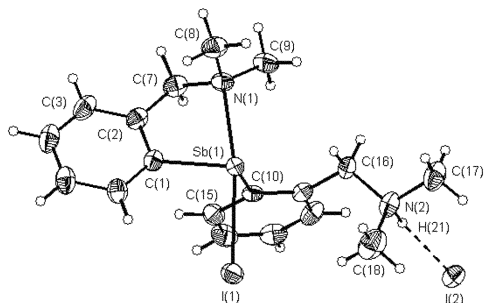**Table 1** Selected bond distances (Å) and angles (°) for compounds **2**, **3** and **3·HI**

Molecule 2a		Molecule 2b		3	3·HI
Sb(1)–C(1)	2.162(3)	Sb(2)–C(19)	2.161(3)	Sb(1)–C(1) 2.162(4)	2.165(6)
Sb(1)–C(10)	2.170(3)	Sb(2)–C(28)	2.159(3)	Sb(1)–C(10) 2.165(4)	2.167(5)
Sb(1)–Br(1)	2.7775(8)	Sb(2)–Br(2)	2.7562(8)	Sb(1)–I(1) 3.0105(5)	2.9448(11)
Sb(1)–N(1)	2.423(3)	Sb(2)–N(3)	2.437(3)	Sb(1)–N(1) 2.417(3)	2.432(5)
Sb(1)–N(2)	3.276(3)	Sb(2)–N(4)	3.351(3)	Sb(1)–N(2) 3.211(3)	4.393(22)[a]
				N(2)–H(21)	0.96(6)
				I(2)–H(21)	2.51(6)
C(1)–Sb(1)–C(10)	97.55(10)	C(19)–Sb(2)–C(28)	98.54(11)	C(1)–Sb(1)–C(10) 96.78(14)	96.3(2)
C(1)–Sb(1)–N(1)	75.08(10)	C(19)–Sb(2)–N(3)	74.51(10)	C(1)–Sb(1)–N(1) 76.03(13)	75.3(2)
C(1)–Sb(1)–Br(1)	90.82(9)	C(19)–Sb(2)–Br(2)	91.37(9)	C(1)–Sb(1)–I(1) 94.45(10)	94.87(16)
C(10)–Sb(1)–N(1)	92.18(10)	C(28)–Sb(2)–N(3)	87.39(10)	C(10)–Sb(1)–N(1) 92.99(12)	87.59(17)
C(10)–Sb(1)–Br(1)	87.45(9)	C(28)–Sb(2)–Br(2)	87.23(9)	C(10)–Sb(1)–I(1) 87.76(10)	89.35(13)
N(1)–Sb(1)–Br(1)	165.74(7)	N(3)–Sb(2)–Br(2)	163.96(7)	N(1)–Sb(1)–I(1) 170.47(8)	169.35(12)
N(2)–Sb(1)–C(1)	150.07(9)	N(4)–Sb(2)–C(19)	154.52(8)	N(2)–Sb(1)–C(1) 148.62(11)	
N(2)–Sb(1)–C(10)	65.91(8)	N(4)–Sb(2)–C(28)	66.34(8)	N(2)–Sb(1)–C(10) 66.76(11)	
N(2)–Sb(1)–N(1)	80.61(8)	N(4)–Sb(2)–N(3)	84.07(8)	N(2)–Sb(1)–N(1) 78.31(10)	
N(2)–Sb(1)–Br(1)	112.05(5)	N(4)–Sb(2)–Br(2)	107.48(5)	N(2)–Sb(1)–I(1) 110.60(7)	
				N(2)–H(21)–I(2)	167.42

[a] Non-bonding distance.

approximately *trans* to the C(1) atom [C(1)–Sb(1)–N(2) **2a**, 150.07(9)°; **2b**, 154.52(8)°; **3**, 148.62(11)°]. If this weak interaction is taken into account, distorted square-pyramidal Sb(*C,N*)$_2$X cores can be considered.

There are also weak interactions between the halogen atom and the proton *ortho* to antimony in the organic ligand establishing the strong intramolecular Sb–N interaction [**2a**, Br ··· H 2.82 Å; **3**, I ··· H 3.10 Å], which are shorter than the sums of van der Waals radii of the corresponding atoms [Σ_{vdW}(Br,H) 3.15 Å; Σ_{vdW}(I,H) 3.35 Å].[22] Similar weak Cl ··· H interactions were found in **1** (2.72 Å)[12] or [2-(Me$_2$NCH$_2$)-C$_6$H$_4$][(Me$_3$Si)$_2$CH]SbCl (2.643 Å),[13] which caused a large downfield shift of the resonance for the corresponding proton in the ^{1}H NMR spectra.
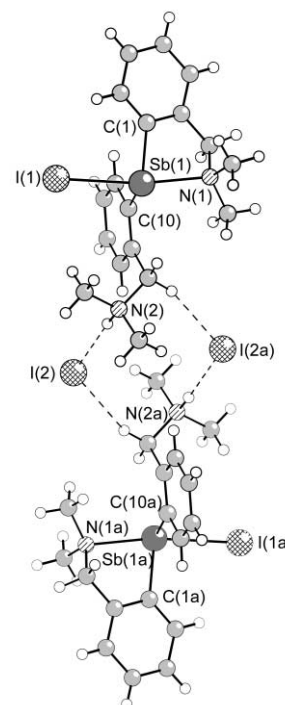
Our first attempts to obtain single crystals of **3** gave yellow crystals of the adduct R$_2$SbI·HI (**3·HI**), probably obtained by partial hydrolysis of the compound. Selected bond distances and angles are given in Table 1. The molecular structure determination revealed that only the N(1) atom of one amine arm is coordinated to the antimony atom [Sb(1)–N(1) 2.432(5) Å], thus resulting in distorted, equatorially vacant trigonal-bipyramidal geometry [N(1)–Sb(1)–I(1) 169.35(12)°, C(1)–Sb(1)–C(10) 96.3(2)°]. The second pendant arm is twisted away from the metal center [non-bonding Sb(1)–N(2) 4.39 Å], its N(2) atom being protonated [the H(21) atom was localised from the electron density map]. The compound can be described as an ammonium salt of the type [{2-(Me$_2$NCH$_2$)C$_6$H$_4$}Sb-{C$_6$H$_4$(CH$_2$NHMe$_2$)-2}]$^+$[I]$^-$. A hydrogen bond is established between the cation and the iodide anion [I(2) ··· H(21) 2.51(6) Å; N(2)–H(21) ··· I(2) 167.6(1)°] (Fig. 3 shows the *R* isomer,

with the C(1)–C(6) aromatic ring and the N(1) atom as chiral plane and pilot atom, respectively).[21]

The I(1) atom is again involved in a weak interaction with the proton *ortho* to antimony in the (C,N)-ligand (3.06 Å). The compound crystallizes as racemates, pairs of the *R* and *S* isomers being associated into "dimer units" through weak intermolecular interactions (3.00 Å) between the I(2) atom and a hydrogen of the CH$_2$ group of the protonated pendant arm (Fig. 4). Similar halogen–methylene proton weak interactions leading to "dimer units" were reported for **1**.[12] Moreover, there are further additional weak Sb–anion (4.20 Å) and I(1)–aromatic hydrogen (3.10 Å) interdimer interactions [*cf.* Σ_{vdW}(Sb,I) 4.35 Å; Σ_{vdW}(I,H) 3.35 Å],[22] thus resulting in a tri-dimensional network.

The solution behavior of the monohalides **1**–**3** was investigated by NMR spectroscopy. For all three compounds the [1]H

Fig. 3 ORTEP representation at 50% probability and atom numbering scheme for **3·HI** (*R* isomer).

Fig. 4 View of the "dimer units" in the crystal of **3·HI**.

NMR spectra at 18 °C in CDCl₃ exhibit rather broad singlet resonances for the NMe₂ and CH₂ protons, as well as for the ring proton *ortho* to antimony. At 18 °C the ¹³C NMR spectra contain singlet signals for the NMe₂ and CH₂ carbons, as well as six singlet resonances in the aromatic region. No changes were noted when the NMR spectra of **1**–**3** were recorded at room temperature in DMSO-d₆. This pattern of the NMR spectra at room temperature suggests a rapid equilibrium between the strongly N(1) and the weak N(2) bound pendant arms or dissociation of the Sb–N bonds of both pendant arms. In order to study the dynamic processes NMR spectra of **1** were recorded with a variation of the temperature between 18 and −60 °C. A set of ¹H NMR spectra of **1** in CDCl₃ in this temperature range is shown in Fig. 5. New patterns of signals emerge when the solution is cooled. At −60 °C there are three resonances in the 1 : 2 : 1 ratio of intensities for the NMe₂ groups and the signals for the CH₂ protons can be assigned to two AB systems [δ A: 3.31, B: 4.02 ($^2J_{HH}$ = 11.7 Hz), and A: 3.72, B: 3.79 ($^2J_{HH}$ = 14.7 Hz)]. Consistent with the ¹H NMR data, the ¹³C NMR spectrum at −55 °C shows two singlet resonances for methyl carbons (δ 44.98, 46.14 ppm) and methylene carbons (δ 65.28, 65.66 ppm), respectively. The aromatic region of the ¹H and ¹³C NMR spectra shows two sets of signals, indicating non-equivalence of the aromatic rings.
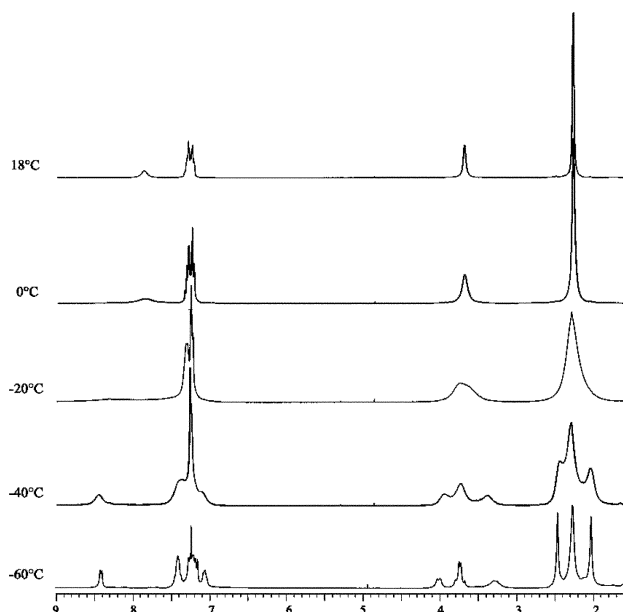

Fig. 5 Variable-temperature ¹H NMR spectra of **1** in CDCl₃.

The NMR spectra indicate that the dynamic process is frozen at −60 °C and the two organic ligands in **1** become non-equivalent probably due to different degrees of the intramolecular coordination of the N atoms to the antimony center. These findings correspond to the results of X-ray diffraction studies.

The solid-state molecular structure of the dihalides **4**–**6** features a similar strong coordinated amine arm to the antimony center [Sb(1)–N(1) **4**, 2.407(5) Å; **5**, 2.409(3) Å; **6**, 2.408(4) Å] *trans* to the Sb(1)–X(1) bond [N(1)–Sb(1)–X(1) **4**, 163.76(13)°; **5**, 167.00(7)°; **6**, 169.34(9)°]. This accounts for the longer Sb(1)–X(1) bond distance [**4**, 2.5612(19) Å; **5**, 2.7529(7) Å; **6**, 2.9960(5) Å] in comparison with the Sb(1)–X(2) bond [**4**, 2.4063(18) Å; **5**, 2.548(7) Å; **6**, 2.8161(5) Å] in the molecular unit. The latter compare well with the metal–halogen distances found in the related PhSbX₂ derivatives [Sb–Cl 2.411(2), 2.376(2) Å; Sb–Br 2.563(1), 2.526(1) Å; Sb–I 2.753(1), 2.738(1) Å].[26] As in the case of the monohalides **1**–**3**, due to the chelating nature of the organic ligand, the dihalides **4**–**6** crystallize as racemates. The geometry at the antimony center is distorted

Table 2 Selected bond distances (Å) and angles (°) for compounds **4**–**6**

	4 (X = Cl)	**5** (X = Br)	**6** (X = I)
Sb(1)–C(1)	2.147(5)	2.147(3)	2.150(4)
Sb(1)–N(1)	2.407(5)	2.409(3)	2.408(4)
Sb(1)–X(1)	2.5612(19)	2.7529(7)	2.9960(5)
Sb(1)–X(2)	2.4063(18)	2.5848(7)	2.8161(5)
Sb(1)–X(1a)	3.2942(17)	3.2894(8)	3.505(2)
C(1)–Sb(1)–N(1)	75.18(18)	75.88(10)	75.51(15)
C(1)–Sb(1)–X(1)	91.18(15)	91.95(8)	94.49(12)
C(1)–Sb(1)–X(2)	94.25(15)	92.88(8)	96.92(11)
N(1)–Sb(1)–X(1)	163.76(13)	167.00(7)	169.34(9)
N(1)–Sb(1)–X(2)	84.97(13)	87.36(7)	88.43(10)
X(1)–Sb(1)–X(2)	87.33(6)	88.72(3)	89.131(15)
X(1a)–Sb(1)–C(1)	78.23(13)	82.69(7)	86.18(12)
X(1a)–Sb(1)–N(1)	96.73(12)	97.94(6)	99.36(8)
X(1a)–Sb(1)–X(1)	88.90(5)	84.80(1)	83.39(1)
X(1a)–Sb(1)–X(2)	171.51(5)	172.01(1)	172.12(1)

ψ-trigonal-bipyramidal [Sb(C,N)X₂ core] as shown in Fig. 6 for the *R*-**4** isomer, with the deviations of the bond angles at the metal atom from the ideal values mainly due to the constraints imposed by the coordinated amine arm (Table 2). There are also weak interactions between the X(1) atom and the proton *ortho* to antimony in the organic ligand [**4**, Cl ⋯ H 2.76 Å; **5**, Br ⋯ H 2.82 Å; **6**, I ⋯ H 3.07 Å] and X(2) atom and a N–CH₃ proton [**4**, Cl ⋯ H 2.70 Å; **5**, Br ⋯ H 2.94 Å; **6**, I ⋯ H 3.08 Å], respectively. The former accounts for the downfield shift of the resonance for the corresponding proton in the ¹H NMR spectra.
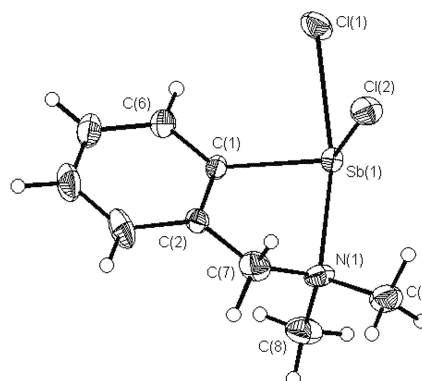

Fig. 6 ORTEP representation at 50% probability and atom numbering scheme for *R*-**4** isomer.

In the crystal, only one of the halogen atoms in the molecules of [2-(Me₂NCH₂)C₆H₄]SbX₂ establishes a Sb–X ⋯ Sb bridge, the presence of the intramolecular N→Sb dative interaction preventing the formation of doubly bridged polymeric chains involving both halogen atoms of a molecular unit, as found for the related PhSbX₂ derivatives.[26] The bridging halogen is always the X(1) atom *trans* to the nitrogen in the molecules of **4**–**6**, thus resulting in distorted square-pyramidal Sb(C,N)X₃ cores, with the carbon atom in apical position. The intermolecular Sb–X(1a) interactions are stronger [**4**, 3.2942(17) Å; **5**, 3.2894(8) Å; **6**, 3.505(2) Å] than those in the PhSbX₂ derivatives [Sb ⋯ Cl 3.443(2), 3.865(3)Å; Sb ⋯ Br 3.620(1), 4.058(1) Å; Sb ⋯ I 3.819(1), 4.078(1) Å].[26] Sb–X(1a) vector is *trans* to the X(2) atom, consistent with increased Lewis acidity of the metal center in the σ*-orbital bonding model. However, there are differences in the degree of association. Thus, the crystals of **4** contain parallel infinite chains (Fig. 7) built from *R* and *S* isomers, respectively, while for compounds **5** and **6** dimers between pairs of *R*–*S* isomers are formed as shown in Fig. 8 for the dibromide derivative.

The solution behavior of the dihalides **4**–**6** was also investigated by NMR spectroscopy. The ¹H and ¹³C NMR spectra at
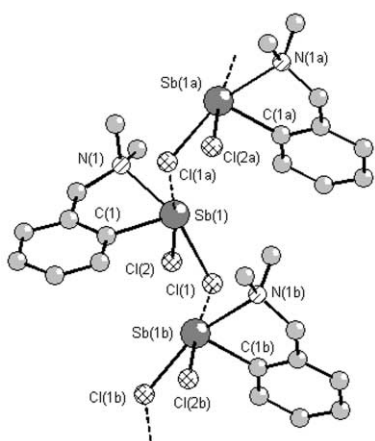
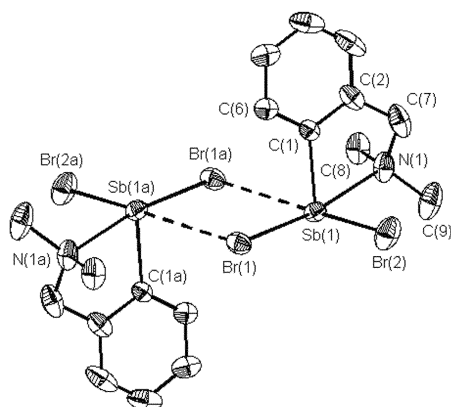**Fig. 7** View of the chain polymeric association of *R* isomers in the crystal of **4**.

Sb(1)–C(1)	2.106(5)	Sb(1)–N(1)	2.679(5)
Sb(1)–C(10)	2.145(5)	Sb(1)–N(3)[a]	3.592(4)
Sb(1)–C(19)	2.121(5)	Sb(1)–N(3)	2.785(5)
Sb(1)–O(1)	1.930(4)		
O(1)–H(1)	0.76(6)	H(1)–N(2)	2.04(6)
I(1)–I(2)	2.9758(7)	I(2)–I(3)	2.8531(7)
O(1)–Sb(1)–C(1)	99.8(2)	C(1)–Sb(1)–C(10)	103.36(19)
O(1)–Sb(1)–C(10)	94.38(18)	C(1)–Sb(1)–C(19)	137.20(19)
O(1)–Sb(1)–C(19)	101.8(2)	C(10)–Sb(1)–C(19)	111.3(2)
N(1)–Sb(1)–O(1)	172.54(14)	N(3)–Sb(1)–O(1)	81.08(17)
N(1)–Sb(1)–C(1)	72.77(16)	N(3)–Sb(1)–C(1)	72.76(15)
N(1)–Sb(1)–C(10)	87.23(16)	N(3)–Sb(1)–C(10)	166.98(16)
N(1)–Sb(1)–C(19)	84.38(16)	N(3)–Sb(1)–C(19)	70.84(17)
N(1)–Sb(1)–N(3)	105.79(14)		
I(1)–I(2)–I(3)	175.90(2)	O(1)–H(1)–N(2)	165(5)

[a] Non-bonding distance.

Fig. 8 ORTEP representation at 50% probability and atom numbering scheme for the dimer association in the crystal of **5**. Hydrogen atoms are omitted.
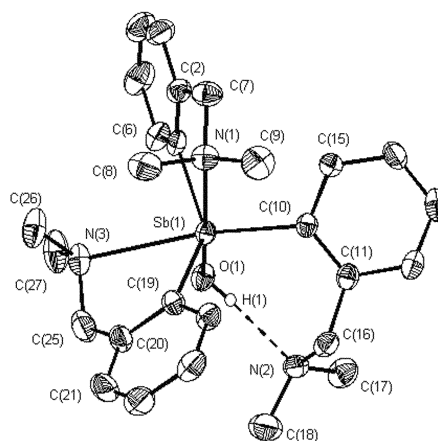

Fig. 9 ORTEP representation at 30% probability and atom numbering scheme for the *R* isomer of the cation in **7**. Hydrogen atoms less H(1) on oxygen are omitted.

18 °C in CDCl$_3$ or DMSO-d$_6$ exhibit sharp singlets for the NMe$_2$ and CH$_2$ protons and carbons, respectively. Cooling solutions of compound **4** in CDCl$_3$ to −60 °C does not change the pattern of the signals. This result suggests that dissociation of the bond between the nitrogen and antimony atoms is very fast even at this temperature.

The molecular structure of the ionic antimony(V) derivative **7** was also determined by single-crystal X-ray diffraction. The deep red–brown crystals are built up from [R$_3$SbOH]$^+$ cations and linear non-symmetric [I$_3$]$^-$ anions [I(1)–I(2)–I(3) 175.90(2)°]. Compound **7** crystallizes as a racemate and no cation–anion interactions are present in the crystal. In the cation the four covalent bonds describe a flattened trigonal-pyramidal SbC$_3$O core, with the carbon atoms in the corners of the base and the oxygen in the apex (Table 3). The metal atom is displaced 0.339 Å from the basal C$_3$ plane towards the oxygen atom. The nitrogen atoms of two pendant arms are capping two trigonal faces, establishing strong interactions [Sb(1)–N(1) 2.679(5) Å; Sb(1)–N(3) 2.785(5) Å] with the metal center. Alternatively, the overall SbC(C,N)$_2$O core can be described as distorted octahedral, with N(1) *trans* to O(1) and N(3) *trans* to C(10) [N(1)–Sb(1)–O(1) 172.54(14)°; N(3)–Sb(1)–C(10) 166.98(16)°] [isomer *R* shown in Fig. 9 – the O(1)/N(3)/C(19) face of the octahedral core observed from the side remote from the face C(1)/C(10/N(1)].[19] The *trans* effect of the more electronegative oxygen atom is reflected in the shorter Sb(1)–N(1) bond length. The N(2) atom of the third pendant arm is involved in an intramolecular hydrogen bonding with the H(1) atom of the hydroxy group. The antimony oxygen bond distance [Sb(1)–O(1) 1.930(4) Å] compares well with that observed in the tetrahedral cation of the related [(2,6-Me$_2$C$_6$H$_3$)$_3$-SbOH]$^+$[I]$^-$ [Sb–O 1.907(2) Å].[6]

Conclusions

New [2-(dimethylaminomethyl)phenyl]antimony(III) halides, R$_2$SbX and RSbX$_2$ [X = Cl, Br, I], were prepared and their hypervalent nature was investigated in solution and the solid state. The strong intramolecular N→Sb interactions induce chirality at the metal center and their strength is little influenced by the nature of the halogen atoms attached to the metal center. For RSbX$_2$ the degree of association in solid state through Sb–X ··· Sb bridges is halogen-dependent. The described synthetic procedures are efficient and provide useful starting materials for the preparation of new hypervalent organo-antimony(III) derivatives.

Experimental

General procedures

were dried and freshly distilled prior to use. Antimony(III) trihalogenide, *N,N*-dimethylbenzylamine and butyllithium (15% in hexane) were commercially available. SbX₃ were freshly sublimed prior to use. [2-(Me₂NCH₂)C₆H₄]Li, prepared from Me₂NCH₂C₆H₅ and BuLi in anhydrous hexane at room temperature,[27] was isolated as a white solid and was stored under argon atmosphere. [2-(Me₂NCH₂)C₆H₄]₃Sb was obtained according to the published method.[9]

Synthesis of [2-(Me₂NCH₂)C₆H₄]₂SbCl (1). *Method A.* The reaction of SbCl₃ (8.62 g, 0.038 mol) with [2-(Me₂NCH₂)-C₆H₄]Li (10.67 g, 0.076 mol) was carried out according to the literature procedure[12] and yielded 14.4 g (90%) of the title compound.

Method B. A mixture of [2-(Me₂NCH₂)C₆H₄]₃Sb (5.34 g, 0.01 mol) and SbCl₃ (1.16 g, 0.005 mol) was melted and stirred for 3 h at 140 °C, in the absence of any solvent. After cooling at room temperature, the solid product was washed with Et₂O and then recrystallized from chloroform to give 6 g (92%) of the title compound as colorless crystals, mp 115 °C.(lit.[12] mp 118 °C). ^{1}H NMR (+18 °C, CDCl₃): δ 2.26 (12 H, s, br, NCH₃), 3.68 (4 H, s, br, CH₂), 7.27 (7 H, m, C₆H₄), 7.86 (1 H, s, br, C₆H₄-*ortho* to antimony). ^{1}H NMR (−60 °C, CDCl₃): δ 2.05 (3 H, s, NCH₃), 2.29 (6 H, s, NCH₃), 2.48 (3 H, s, NCH₃), AB spin system with A: 3.31, B: 4.02 (2 H; CH₂, $^2J_{HH}$ 11.7 Hz), AB spin system with A: 3.72, B: 3.79 (2 H; CH₂, $^2J_{HH}$ 14.7 Hz), 7.27 (7 H, m, C₆H₄), 7.86 (1 H, s, br, C₆H₄-*ortho* to antimony). ^{13}C NMR (+18 °C, CDCl₃): δ 45.62 (s, NCH₃), 66.00 (s, CH₂), 127.94 (s, br, CH, C₆H₄), 128.29 (s, CH, C₆H₄), 128.94 (s, CH, C₆H₄), 136.18 (s, br, CH, C₆H₄), 143.40 (s, C-*ipso*, C₆H₄), 147.03 (s, C-*ipso*, C₆H₄). ^{13}C NMR (−55 °C, CDCl₃): δ 44.98 (s, NCH₃), 44.98 (s, NCH₃), 65.28 (s, CH₂), 65.66 (s, CH₂), 126.00, 128.17, 128.75, 128.94, 129.70, 133.88, 137.31 (s, CH, C₆H₄), 142.94 (s, C-*ipso*, C₆H₄), 146.07 (s, C-*ipso*, C₆H₄). MS (EI, 70 eV, 144 °C), *m/z* (%): 424 (3) [M⁺], 389 (25) [M⁺ − Cl], 292 (32) [(Me₂NCH₂C₆H₄)SbCl⁺ + 2H], 134 (75) [Me₂NCH₂C₆H₄⁺], 91 (100) [C₆H₄CH₂⁺ + H], 58 (64) [CH₂NMe₂⁺].

[2-(Me₂NCH₂)C₆H₄]₂SbBr (2). *Method A.* A solution of BuLi in hexane (63 ml 15%) was added dropwise, at room temperature, under argon, to a stirred solution of Me₂NCH₂C₆H₅ (13.5 g, 0.1 mol) in 100 ml anhydrous hexane. The reaction mixture was stirred for 5 h. The white precipitate of [2-(Me₂-NCH₂)C₆H₄]Li was washed with 3 × 30 ml of hexane. The solid product (11.80 g, 0.084 mol) was suspended in 50 ml toluene and added dropwise under stirring to a cooled (−78 °C) solution of SbBr₃ (15.11 g, 0.042 mol) in 100 ml toluene. After the addition of the organolithium reagent was completed, the reaction mixture was stirred for 1 h at −78 °C, then stirred over night to reach the room temperature. The reaction mixture was filtered and the solvent removed under vacuum. The white solid residue was recrystallized from toluene to give 14 g (71%) of the title compound as colorless crystals.

Method C. KBr (0.14 g, 1.18 mmol) was added at room temperature to a stirred solution of [2-(Me₂NCH₂)C₆H₄]₂SbCl (0.5 g, 1.18 mmol) in 30 ml acetone. The reaction mixture was stirred for 5 h, after which it was filtered and the solvent removed under vacuum. The white solid residue was recrystallized from acetone to give 0.4 g (72%) of the title compound, mp 130 °C. Anal. Calc. for C₁₈H₂₄BrN₂Sb (470.06): C, 45.99; H, 5.15. Found: C, 46.55; H, 5.10%. ^{1}H NMR (+18 °C, CDCl₃): δ 2.28 (12 H, s, br, NCH₃), 3.71 (4 H, s, br, CH₂), 7.28 (7 H, m, C₆H₄), 7.90 (1 H, s, br, C₆H₄-*ortho* to antimony). ^{1}H NMR (+18 °C, DMSO-d₆): δ 2.24 (12 H, s, br, NCH₃), 3.74 (4 H, s, br, CH₂), 7.33 (7 H, m, C₆H₄), 7.70 (1 H, s, br, C₆H₄-*ortho* to antimony). ^{13}C NMR (+18 °C, CDCl₃): δ 45.81 (s, NCH₃), 66.07 (s, CH₂), 128.02 (s, br, CH, C₆H₄), 128.35 (s, CH, C₆H₄), 129.03 (s, CH, C₆H₄), 137.04 (s, br, CH, C₆H₄), 143.43 (s, C-*ipso*, C₆H₄), 145.22 (s, C-*ipso*, C₆H₄). ^{13}C NMR (+18 °C, DMSO-d₆): δ 45.31 (s, NCH₃), 65.08 (s, CH₂), 127.80 (s, CH,

C₆H₄), 127.95 (s, br, CH, C₆H₄), 128.97 (s, CH, C₆H₄), 136.04 (s, br, CH, C₆H₄), 143.72 (s, C-*ipso*, C₆H₄), 145.03 (s, C-*ipso*, C₆H₄). MS (EI, 70 eV, 137 °C), *m/z* (%): 389 (100) [M⁺ − Br], 336 (12) [(Me₂NCH₂C₆H₄)SbBr⁺ + 2H], 134 (59) [Me₂-NCH₂C₆H₄⁺], 91 (58) [C₆H₄CH₂⁺ + H], 58 (38) [CH₂NMe₂⁺]. MS (CI, NH₃) *m/z* (%), positive: 602 (8) [(Me₂NCH₂C₆H₄)₃-SbBr⁺], 469 (50) [M⁺ + H], 389 (100) [M⁺ − Br], 134 (27) [Me₂NCH₂C₆H₄⁺], 91 (9) [C₆H₄CH₂⁺ + H]; negative: 549 (100) [M⁻ + Br], 494 (14) [(Me₂NCH₂C₆H₄)SbBr₃⁻], 79 (84) [Br⁻].

[2-(Me₂NCH₂)C₆H₄]₂SbI (3). *Method A.* As above, from [2-(Me₂NCH₂)C₆H₄]Li (11.8 g, 0.084 mol) and SbI₃ (21,16 g, 0.042 mol), in toluene, at −78 °C. The crude solid was recrystallized from toluene to give 15 g (69%) of the title compound as yellowish crystals.

Method C. As above, from NaI (0.18 g, 1.17 mmol) and [2-(Me₂NCH₂)C₆H₄]₂SbCl (0.5 g, 1.17 mmol), in acetone, at room temperature. The solid residue was recrystallized from acetone to give 0.33 g (54%) of the title compound, mp 155 °C. Anal. Calc. for C₁₈H₂₄IN₂Sb (517.06): C, 41.81; H, 4.68. Found: C, 41.34; H, 4.97%. ^{1}H NMR (+18 °C, CDCl₃): δ 2.34 (12 H, s, br, N–CH₃), 3.77 (4 H, s, br, CH₂), 7.30 (7 H, m, C₆H₄), 7.96 (1 H, s, br, C₆H₄-*ortho* to antimony). ^{13}C NMR (+18 °C, CDCl₃): δ 45.84 (s, NCH₃), 65.84 (s, CH₂), 128.27 (s, br, CH, C₆H₄), 128.65 (s, CH, C₆H₄), 129.40 (s, CH, C₆H₄), 138.90 (s, br, CH, C₆H₄), 141.86 (s, C-*ipso*, C₆H₄), 142.83 (s, C-*ipso*, C₆H₄).

[2-(Me₂NCH₂)C₆H₄]SbCl₂ (4). *Method A.* As above, from [2-(Me₂NCH₂)C₆H₄]Li (11.73 g, 0.083 mol) and SbCl₃ (18.96 g, 0.083 mol), in toluene, at −78 °C. The white solid residue was recrystallized from toluene to give 23 g (85%) of the title compound as colorless crystals.

Method B. As above, from [2-(Me₂NCH₂)C₆H₄]₃Sb (5.05 g, 9.6 mmol) and SbCl₃ (4.4 g, 19 mmol), melted in absence of a solvent. The solid product was washed with Et₂O and then recrystallized from chloroform to give 8.8 g (93%) of the title compound, mp 185 °C. Anal. Calc. for C₉H₁₂Cl₂NSb (326.86): C, 33.07; H, 3.70; Found: C, 33.04; H, 3.76%. ^{1}H NMR (+18 °C, CDCl₃): δ 2.56 (6 H, s, NCH₃), 4.09 (2 H, s, CH₂), 7.30 (1 H, m, C₆H₄), 7.43 (2 H, m, C₆H₄), 8.43 (1 H, m, C₆H₄-*ortho* to antimony). ^{1}H NMR (+18 °C, DMSO-d₆): δ 2.51 (6 H, s, NCH₃), 4.06 (2 H, s, CH₂), 7.35 (3 H, m, C₆H₄), 8.28 (1 H, d, $^3J_{HH}$ 6.3 Hz, C₆H₄-*ortho* to antimony). ^{13}C NMR (+18 °C, CDCl₃): δ 44.54 (s, –NCH₃), 64.69 (s, CH₂), 126.55, 128.47, 130.84, 135.95 (s, CH, C₆H₄), 143.77 (s, C-*ipso*, C₆H₄), 150.34 (s, C-*ipso*, C₆H₄). ^{13}C NMR (+18 °C, DMSO-d₆): δ 44.66 (s, –NCH₃), 64.17 (s, CH₂), 126.19, 127.45, 129.14, 134.34 (s, CH, C₆H₄), 143.59 (s, C-*ipso*, C₆H₄), 156.30 (s, C-*ipso*, C₆H₄). MS (EI, 70 eV, 36 °C), *m/z* (%): 325 (5) [M⁺], 290 (16) [M⁺ − Cl], 134 (21) [Me₂NCH₂C₆H₄⁺], 91 (37) [C₆H₄CH₂⁺ + H], 58 (100) [CH₂NMe₂⁺].

[2-(Me₂NCH₂)C₆H₄]SbBr₂ (5). *Method A.* As above, from [2-(Me₂NCH₂)C₆H₄]Li (5 g, 0.035 mol) and SbBr₃ (12.84 g, 0.035 mol), in toluene, at −78 °C. The white solid residue was recrystallized from chloroform to give 13 g (88%) of the title compound as colorless crystals.

Method B. As above, from [2-(Me₂NCH₂)C₆H₄]₃Sb (2.21 g, 4.2 mmol) and SbBr₃ (3.05 g, 8.4 mmol), melted in absence of a solvent. The solid residue was washed with Et₂O and then recrystallized from chloroform to give 3.8 g (72%) of the title compound.

Method C. As above, from [2-(Me₂NCH₂)C₆H₄]SbCl₂ (0.5 g, 1.53 mmol) and KBr (0.36 g, 3.06 mmol), in acetone, at room temperature. The white solid residue was recrystallized from acetone to give 0.45 g (71%) of the title compound as colorless crystals, mp 205 °C. Anal. Calc. for C₉H₁₂Br₂NSb (415.76): C, 26.00; H, 2.91. Found: C, 26.12; H, 2.96%. ^{1}H NMR (+18 °C, CDCl₃): δ 2.64 (6 H, s, NCH₃), 4.11 (2 H, s, CH₂), 7.28 (1 H, m, C₆H₄), 7.43 (2 H, m, C₆H₄), 8.58 (1 H, m, C₆H₄-*ortho* to

Table 4 Crystallographic data for compounds 2–6, 3·HI and 7

	2	3	3·HI	4	5	6	7
Empirical formula	$C_{18}H_{24}BrN_2Sb$	$C_{18}H_{24}IN_2Sb$	$C_{18}H_{25}I_2N_2Sb$	$C_9H_{12}Cl_2NSb$	$C_9H_{12}Br_2NSb$	$C_9H_{12}I_2NSb$	$C_{27}H_{37}I_3N_3OSb$
M_r	470.05	517.04	644.95	326.85	415.77	509.75	922.05
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$Pna2_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	9.762(2)	9.6477(17)	15.432(3)	11.8382(13)	6.926(1)	9.9046(9)	16.3570(10)
b/Å	12.890(3)	16.244(3)	12.241(3)	14.6215(15)	14.515(3)	8.4738(8)	14.1663(9)
c/Å	16.109(3)	12.623(2)	12.299(4)	6.7329(10)	12.278(2)	15.8002(15)	14.0075(9)
a/°	93.11(3)	90	90	90	90	90	90.00
β/°	91.45(3)	90.399(3)	104.96(2)	90	92.63(3)	95.721(2)	91.0300(10)
γ/°	110.24(3)	90	90	90	90	90.00	90.00
V/Å³	1897.0(7)	1978.2(6)	2244.6(10)	1165.4(2)	1233.0(4)	1319.5(2)	3245.3(4)
Z	4	4	4	4	4	4	4
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Absorption correction	DIFABS[30]	Multi-Scan[31]	DIFABS[30]	DIFABS[30]	DIFABS[30]	Multi-Scan[31]	Multi-Scan[31]
μ(Mo-Kα)/mm⁻¹	3.560	2.954	3.981	2.782	8.678	6.733	3.727
$R1$ [$I > 2\sigma(I)$]	0.0227	0.0291	0.0395	0.0348	0.0198	0.0296	0.0454
$wR2$	0.0525	0.0673	0.1026	0.0929	0.0427	0.0663	0.0906
GOF	0.922	1.105	1.063	1.065	1.015	1.160	1.118

antimony). ^{13}C NMR (+18 °C, CDCl$_3$): δ 45.07 (s, NCH$_3$), 65.19 (s, CH$_2$), 126.65, 128.73, 130.87, 137.73 (s, CH, C$_6$H$_4$), 143.72 (s, C-*ipso*, C$_6$H$_4$), 146.48 (s, C-*ipso*, C$_6$H$_4$). MS (EI, 70 eV, 157 °C), *m/z* (%): 415 (2) [M$^+$], 334 (97) [(Me$_2$NCH$_2$C$_6$H$_4$)-SbBr$^+$], 134 (72) [Me$_2$NCH$_2$C$_6$H$_4^+$], 91 (100) [C$_6$H$_4$CH$_2^+$ + H], 58 (73) [CH$_2$NMe$_2^+$]. MS (CI, NH$_3$) *m/z* (%), positive: 551 (22) [M$^+$ + Br], 416 (71) [M$^+$ + H], 389 (82) [M$^+$ − Br], 336 (100) [(Me$_2$NCH$_2$C$_6$H$_4$)SbBr$^+$ + 2H], 134 (96) [Me$_2$NCH$_2$C$_6$H$_4^+$], 91 (25) [C$_6$H$_4$CH$_2^+$ + H]; negative: 496 (100) [M$^-$ + Br + 2H], 441 (80) [SbBr$_4^-$], 79 (3) [Br$^-$].

[2-(Me$_2$NCH$_2$)C$_6$H$_4$]SbI$_2$ (6). *Method B.* As above, from [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_3$Sb (1.25 g, 2.38 mmol) and SbI$_3$ (2.4 g, 4.77 mmol), melted in absence of a solvent.. The yellow solid residue was washed with Et$_2$O and then recrystallized from chloroform to give 1.65 g (45%) of the title compound as bright yellow crystals.

Method C. As above, from [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SbCl$_2$ (0.5 g, 1.53 mmol) and NaI (0.46 g, 3.06 mmol), in acetone, at room temperature. The yellow solid residue was recrystallized from acetone to give 0.58 g (75%) of the title compound as bright yellow crystals, mp 195 °C. Anal. Calc. for C$_9$H$_{12}$I$_2$NSb (509.76): C, 21.21; H, 2.37; Found: C, 20.93; H, 2.76%. ^1H NMR (+18 °C, CDCl$_3$): δ 2.69 (6 H, s, NCH$_3$), 4.04 (2 H, s, CH$_2$), 7.25 (1 H, m, C$_6$H$_4$), 7.42 (2 H, m, −C$_6$H$_4$−, H$_{4,5}$), 8.68 (1 H, m, C$_6$H$_4$-*ortho* to antimony). ^{13}C NMR (+18 °C, CDCl$_3$): δ 45.02 (s, NCH$_3$), 65.43 (s, CH$_2$), 126.71, 128.91, 130.78 (s, CH, C$_6$H$_4$), 137.55 (s, br, C-*ipso*, C$_6$H$_4$), 141.06 (s, br CH, C$_6$H$_4$), 143.49 (s, C-*ipso*, C$_6$H$_4$).

Crystal structures

The details of the crystal structure determination and refinement for compounds **2**–**6**, **3·HI** and **7** are given in Table 4.

Data were collected on Stoe IPDS (**2**, **5**), Bruker SMART APEX (**3**, **6**, **7**) and Siemens P4 four-cycle (**3·HI**,**4**) diffractometers, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). For this purpose the crystals were attached with Kel-F oil (**2**, **3·HI**,**4**, **5**) or epoxy glue (**3**, **6**, **7**) to a glass fiber. For **2**, **3·HI**, **4** and **5** the crystals were cooled under a nitrogen stream at 173 K, while data for **3**, **6**, **7** were collected at room temperature (297 K). The structures were refined with anisotropic thermal parameters. The hydrogen atoms attached to nitrogen in **3·HI** and oxygen atom in **7** were located from the difference map. The other hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.[28] The drawings were created with the Diamond program.[29]

CCDC reference numbers 211552 (**2**), 210849 (**3**), 211554 (**3·HI**), 211553 (**4**), 211555 (**5**), 210851 (**6**) and 210850 (**7**).

See http://www.rsc.org/suppdata/dt/b3/b306299f/ for crystallographic data in CIF or other electronic format.

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