Hypervalent diorganoantimony(III) fluorides via diorganoantimony(III) cations — a general method of synthesis†

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Introduction

The interest in the development of new sensors for the potentially toxic fluoride anion led to recent achievements based on main group chemistry and, particularly, organoantimony(III) and -antimony(v) compounds.1–4 A survey of the literature concerning organoantimony(III) fluorides revealed some interesting aspects with regard to the preparation of the few R2SbF2–14 and RSiF2 (ref. 11) species reported so far. In earlier works [NH3]2[PhSiF2] was used for phenylation of SbF3 in aqueous solution to give PhSbF.5–8 This is, so far, the only R2SbF species investigated by single-crystal X-ray diffraction; its solid state structure consisting of infinite chains of Ph2SbF units connected by strong intermolecular fluoride bridges.5 It should be noted here that organotin(v) fluorinating agents such as Me3Sn or [2-(Me2NCH2)2C6H4]Sn(Bu)2F were used successfully in halogen exchange reactions to prepare organoantimony(III) difluorides of the type [2,6-(YCH2)2C6H4]SbF2 (Y = Me, tBu, Me2N) from the corresponding dichlorides containing (O,C,N)- or (N,C,N)-pincer ligands.13 The difluoride [2,6-(Me2NCH2)2C6H4]SbF2 was also obtained by reacting the oxide [{2,6-(Me2NCH2)2C6H4}SbO] and HBF4-Et2O as a result of a polar group exchange.14

Several other methods failed to produce the desired Ph2SbF derivative.9 Thus, the reaction of Ph2SbCl with AgF in acetonitrile and AsF3 afforded the organoantimony(v) species Ph3SbF2 following a process of simultaneous oxidative fluorination and redistribution of the phenyl groups. The redistribution reaction between R3Sb and SbX3 (X = Cl, Br) in absence of any solvent,15–18 or the halogen exchange reaction between R3SbCl and KBr or NaI,19,20 worked very well for the preparation of chlorides, bromides or iodides. By contrast, no reaction occurs between Ph2Sb and SbF5 in CH2Cl2 or MeOH solutions, at reflux, or in absence of a solvent, or between Ph3Sb and KF even after long periods of heating at reflux in methanol.4

The fluorination was effective when the dibenzoazastibine chloride MeN(CH2C6H4)2SbCl was reacted with KF in DMF solution.4 While the partial phenylation of SbF5 with PhLi or PhMgBr reagents failed, the isolated product always being Ph3Sb regardless of the molar ratio of the reagents used,4 for other organolithium reagents the reaction with SbF5 led to the desired organoantimony(III) fluorides,10–12 even if the stoichiometry could not be fully controlled and from the reaction mixture both R2SbF and RSbF2 were isolated by fractional crystallization, e.g. for R = 2,4,6-tBu3C6H2.11,22

Taking into account the ability of the organoantimony(v) cations to react with the fluoride anions we have decided to investigate the possibility to prepare diorganoantimony(III) fluorides using ionic species such as the diorganoantimony(III) cation, [R2Sb]+. Monocations of this type can be stabilized by...
intermolecular coordination, e.g. $[\text{Ph}_2\text{Sb}(\text{OP(NMe}_2)_2)_2][\text{PF}_6]^-$, $[\text{Me}_2\text{Sb(SbMe}_3)_2][\text{GaCl}_4]^-$, $[\text{Ph}_2\text{Sb(PPPh}_3)_2][\text{PF}_6]^-$, $[\text{Ph}_2\text{Sb(PMe}_3)_2][\text{O}_2\text{SFC}_2]^-$ and $[\text{Ph}_2\text{Sb(PMe}_3)_2][\text{O}_2\text{SFC}_2]^-$, or by intramolecular coordination, e.g. $[\text{Ph}_{2}\text{NCH}_2\text{C}_6\text{H}_4\text{Sb}[\text{PF}_6]^-$ and $[\text{Ph}_2\text{Sb}(\text{OP(NMe}_2)_2)_2][\text{PF}_6]^-$.

We report herein a new route for the preparation of the diorganoantimony(III) fluorides via ionic diorganoantimony(III) derivatives stabilized by (C,N)-chelating ligands as well as their structural characterization both in solution and in the solid state.

**Results and discussion**

**Synthesis and characterization of ionic diorganoantimony(III) compounds**

The monohalides $\text{R}_2\text{SbBr}$, $(\text{R})\text{PhSbCl}$ ($\text{R}$

The monohalides $\text{R}_2\text{SbBr}$, $(\text{R})\text{PhSbCl}$ ($\text{R} = 2-(2',6',1\text{-Pr}_2\text{C}_6\text{H}_3\text{N} = \text{CH})\text{C}_6\text{H}_4\text{H}_0\text{ and } \text{R}''\text{SbBr}$ ($\text{R}'' = 2-(2',4',6',1\text{-Me}_3\text{C}_6\text{H}_2\text{N} = \text{CH})\text{C}_6\text{H}_4\text{H}_0$ were reacted with $\text{Tl}[\text{PF}_6]$ in THF, at room temperature, to give the ionic diorganoantimony(III) species $[\text{2-(Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Sb}[\text{PF}_6]^-$, $[\text{2-(2',6',1\text{-Pr}_2\text{C}_6\text{H}_3\text{N} = \text{CH})\text{C}_6\text{H}_4\text{Sb}[\text{PF}_6]^-$ and $[\text{2-(2',4',6',1\text{-Me}_3\text{C}_6\text{H}_2\text{N} = \text{CH})\text{C}_6\text{H}_4\text{Sb}[\text{PF}_6]^-$.

Using a similar procedure, treatment of the monochloride $\text{R''}\text{SbCl}$ ($\text{R''} = 2-(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Sb}[\text{PF}_6]^-$ gave the iodine compound $[\text{2-(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Sb}[\text{PF}_6]^-$ (Scheme 1). The species $[\text{2-(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Sb}[\text{PF}_6]^-$ was prepared in situ from the corresponding monochloride ($\text{R'}\text{PhSbCl}$ and $\text{Ag[SbF}_6]$ and converted, without isolation, into the fluoride (Scheme 2).

The compounds were isolated in fair good yields as pale yellow (1, 2, 3) and white (4) solids, soluble in chlorinated solvents. The spectroscopic data as well as elemental analytical data are consistent with the anticipated formulas. For compounds 1-3 the IR spectra exhibit a $\nu(\text{CH} = \text{N})$ stretching vibration of medium intensity in the region 1620–1600 cm$^{-1}$, which is typical for compounds containing Schiff-base ligands. In addition, strong $\nu(\text{E-F})$ stretching vibrations corresponding to the inorganic $\text{EF}_x$$^-$ anions were observed, as expected, in the regions 835–800 cm$^{-1}$ (E = P) for compounds 1–3 and around 750 cm$^{-1}$ (E = Sb) for compound 4. In the ES1$^+$ (for 1, 3, 4) and APCh$^+$ (for 2) mass spectra the base peaks were assigned to the corresponding fragments $[\text{R}_2\text{Sb}^+][\text{R''}_2\text{Sb}^+]$ and $[\text{R''}_2\text{Sb}^+]$, respectively.

All ionic compounds were investigated by multinuclear NMR spectroscopy in CDCl$_3$ solution, at room temperature. The assignment of the resonances was based on 2D NMR spectra, according to the numbering schemes illustrated in Scheme S1 (see ESI†). The $^1\text{H}$ NMR spectra of 1 and 2 exhibit two doublet resonances for the methyl protons. This indicates a diastereotopic behaviour of the isopropyl groups as well as non-equivalence of the two halves of a $2',6',1\text{-Pr}_2\text{C}_6\text{H}_3$ moiety, the free rotation of the bulky aromatic group around the C–N(–C) single bond being blocked. This is also supported, for example, by the presence of two singlet resonances for the methine C$7\text{'},\text{6}$ and C$7\text{'},\text{1}$ atoms in the $^1\text{C}$ NMR spectra ($\delta$ 30.21 and 28.96 ppm for 1 and $\delta$ 29.15 and 28.13 ppm for 2, respectively). By contrast, for the cation of 3 both $^1\text{H}$ and $^1\text{C}$ NMR spectra exhibit only two sharp resonances assigned to the methyl protons (1:2 integral ration) of the $2',4',6',1\text{-Me}_3\text{C}_6\text{H}_2$ moieties attached to the metal atom, suggesting that there is no restriction of free rotation of the mesityl groups around the C–N(–C) single bond. This different freedom of rotation around a C–N(–C) single bond observed for compounds 1 (or 2) and 3, respectively, in CDCl$_3$, solution at room temperature, is related to the bulkiness of the organic group attached to nitrogen. The presence of only one set of resonances in the $^1\text{H}$ and $^1\text{C}$ NMR spectra for the two organic groups in the cations of 1, 3 and 4 is consistent with equivalence of the aromatic ligands attached to the same metal atom. The room temperature $^1\text{H}$ and $^1\text{C}$ NMR spectra of 4 show one set of singlet resonances for the methyl and methylene groups, respectively, suggesting a fast dynamic behaviour which involves de-coordination – re-coordination of nitrogen to the metal centre. The presence of the octahedral fluorine-containing anions is indicated by the doublet $^1\text{F}$ resonance ($\delta_{\text{F}} = 713$ Hz) observed for compounds 1–3 and the multiplet $^1\text{F}$ resonance observed for compound 4. Consequently, the $^3\text{P}$ NMR spectra of 1–3 exhibit a septet resonance centered at $\delta$ –144 ppm.

Single crystals of 1·2$\text{CH}_2\text{Cl}_2$ and 3·2$\text{CHCl}_3$ were investigated by X-ray diffraction. The crystals contain the corresponding diorganoantimony(III) cations and hexafluorophosphate anions. The structure of the cations of 1 and 3 are depicted in Fig. 1 and S5,$^+$ respectively, and the important bond lengths and angles are listed in Table 1.

In the cations of 1 and 3 both nitrogen atoms are coordinated to antimony in an almost trans arrangement $[\text{N(1)} = \text{Sb(1)} = \text{N(2)} 159.67(10)\text{}$ for 1; 155.02(17)$^\circ$ for 3 resulting in a pseudo-trigonal bipyramidal (“see-saw”) coordination geometry at antimony, with the ipso carbon atoms placed in equatorial positions $[\text{C(1)} = \text{Sb(1)} = \text{C(20)} 105.05(14)^\circ$ for 1; $\text{C(1)} = \text{Sb(1)} = \text{C(17)} 102.8(2)^\circ$ for 3]. The antimony–nitrogen bond distances $[\text{Sb–N}^\circ$ (Scheme 1).

![Scheme 1](image1.png)

**Scheme 1** Preparation of the ionic species 1–3 and the fluorides 5 and 6.

![Scheme 2](image2.png)

**Scheme 2** Preparation of the ionic species 4 and the fluorides 7 and 8.

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2.353(3)/2.367(3) Å for \( \text{1·2CH}_2\text{Cl}_2 \); 2.365(5)/2.395(5) Å for \( \text{3·2CHCl}_3 \) compare well with those found in the related ionic species \([\text{2·(Me}_2\text{NCH}_2\text{)}\text{C}_6\text{H}_4\text{Sb}]^+\) [PF₆]⁻ \([\text{Sb-N 2.412(3)/2.416(4) Å}],^{19}\) but are shorter than in the bromide precursor \([\text{2·(2',6'-Pr}_2\text{C}_6\text{H}_3\text{N} (=\text{CH})}\text{C}_6\text{H}_4\text{SbBr}]^-\) [Sb-N 2.498(4)/2.996(4) Å]¹⁹ [cf. sums of the corresponding covalent, \(\Sigma_{\text{c}}\text{(Sb,N)}\) 2.11 Å, and van der Waals radii, \(\Sigma_{\text{vdW}}\text{(Sb,N)}\) 3.74 Å]²⁷ due to the more electrophilic nature of the antimony in the cation.

The cations of both these ionic species exhibit a helical structure due to the \((C,N)\)-chelating ligands. The corresponding configurations at the metal can be given as \(\Delta_{\text{Sn}}\) (or \(\rho_{\text{Sn}}\)) and \(\Delta_{\text{Sb}}\) (or \(\rho_{\text{Sb}}\)) with respect to the right-handed or left-handed helicity of the two chelate rings along the \(C_2\)-axis passing through the centre of the \(C-C\) edge (carbon atoms attached to antimony), the metal ion and the centre of the \(N-N\) edge.²⁸ Both compounds 1 and 3 crystallize as a 1 : 1 mixture of \(\Delta_{\text{Sn}}\)- and \(\Delta_{\text{Sb}}\)-cations. No cation–anion interactions between heavy atoms were observed. However, for both compounds supramolecular associations are built through halogen⋯hydrogen and C-H⋯π (\(\text{Ar}_{\text{centroid}}\)) interactions. Thus, in the crystal of \(\text{1·2CH}_2\text{Cl}_2\) chain polymers are formed based on F⋯H\(_{\text{H}_{\text{mine}}}\) contacts between anions and \((\Delta_{\text{Sn}})\)– or \((\Delta_{\text{Sb}})\)-cations (see Fig. S3, ESI†). Alternating, parallel, polymeric chains containing \((\Delta_{\text{Sn}})\)- and \((\Delta_{\text{Sb}})\)-cations, respectively, are connected through Cl\(_{\text{solvent}}\)⋯H contacts into a layer (see Fig. S4, ESI†). By contrast, in the crystal of \(\text{3·2CHCl}_3\) centrosymmetric dinuclear units are formed from \((\Delta_{\text{Sn}})\)- and \((\Delta_{\text{Sb}})\)-cations based on C-H\(_{\text{ethanol}}\)⋯π \(\text{Ar}_{\text{centroid}}\) interactions \((\text{i.e. H⋯\text{Ar}_{\text{centroid}}\) contacts shorter than 3.1 Å, with an angle \(\gamma\) between the normal to the aromatic ring and the line defined by the H atom and \(\text{Ar}_{\text{centroid}}\) smaller than 30º)²⁹ \(\text{C(16)}\)-H(16B)methyl⋯\(\text{Ar}_{\text{centroid}}\) (C(24)′-C(29)′) 2.85 Å \((\gamma = 3.8°)\). These dinuclear units are further connected through anions and solvent molecules into chain polymers (see Fig. S8, ESI†). In the crystals there are no further contacts between parallel layers (for \(\text{1·2CH}_2\text{Cl}_2\)) or polymeric chains (for \(\text{3·2CHCl}_3\)).

**Synthesis and characterization of diorganooantimony(III) fluorides**

The treatment of the ionic compounds 1, 2, 4 and \([\text{2·(Me}_2\text{NCH}_2\text{)}\text{C}_6\text{H}_4\text{Sb}]^-\) [SbF₆]⁻ \([\text{Sb-F 181.3, 176.9 and 169.2 ppm in CDCl}_3 \text{ solution.}]^{18}\) with \([\text{Bu}_4\text{NF} \cdot 3\text{H}_2\text{O}\) in acetonitrile, at room temperature, followed by extraction with \(\text{Hexane}\), leads to the isolation of the organoantimony(III) fluorides: \([\text{2·2',6'-Pr}_2\text{C}_6\text{H}_3\text{N} (=\text{CH})}\text{C}_6\text{H}_4\text{SbF}]^-\) [Scheme 1], \([\text{2·(Me}_2\text{NCH}_2\text{)}\text{C}_6\text{H}_4\text{Sb}]^-\) (Scheme 2). The fluorides were obtained as air-stable, yellow \((5, 6)\) or white \((7, 8)\) solids. They are easily soluble in chlorinated organic solvents as \(\text{CHCl}_3\), a behaviour consistent with their molecular structure observed in solid state. In the case of fluorides 5 and 6 an absorption band was observed at 1641 and 1622 cm\(^{-1}\), respectively, which was assigned to the \(\text{C}_\text{F} = \text{N}\) stretching vibration, consistent with the presence of the imine ligand. In the ESI(+) (for 5, 7 and 8) and APCl(+) (for 6) mass spectra the base peaks were assigned to the corresponding fragments \([\text{R}_2\text{Sb}]^+\), \([\text{R}^+\text{Sb}]^+\) and \([\text{RPhSb}]^+\), respectively. The mass spectrum of 6 showed a fragment with \(m/z\) value \((i.e. 945)\) higher than that corresponding to the molecular ion, which was assigned to the dinuclear cation containing fluorine bridge between metal atoms, \([\text{RPhSb}]PF_6\). The \(^{19}\text{F}\) NMR spectra of the new fluorides exhibit a sharp singlet resonance at \(\delta = -181.3, -174.7, -176.9\) and -169.2 ppm (for 5, 6, 7 and 8, respectively), a behaviour consistent with the presence of only one species in the solution of these compounds. The structure of the fluorides 5-8 in \(\text{CDCl}_3\) solutions was investigated by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy at room temperature. The assignment of the observed resonances, according to the numbering schemes illustrated in Scheme S1 (see ESI†), was based on 2D NMR spectra. For the fluoride 5, the NMR spectra at room temperature are consistent with a similar behaviour as observed previously for the analogous chloride²⁸ and bromide,²⁸ i.e. the presence in the same molecule of one organic ligand for which the free rotation around the \(C\text{-N(=C)}\) single bond is blocked (non-equivalence of the two
halves of a 2′,6′-Pr₂C₆H₃ moiety and one organic ligand with no restriction of free rotation around the C–N(═C) single bond. A similar restricted rotation around the C–N(═C) single bond was observed for the imine ligand in 6, at room temperature. This is consistent with four doublet ¹H resonances for the methyl protons and two septet resonances for the methine protons of the ¹Pr groups indicating that the two halves of the 2′,6′-Pr₂C₆H₃ moiety are not equivalent. The NMR spectra of fluorides 7 and 8 are consistent with the expected structures. For 7 only one set of resonances was observed suggesting a dynamic behaviour which results in equivalent organic ligands on the NMR time scale, at room temperature. The fluoride 8, with different organic groups attached to antimony, exhibits two singlet ¹H resonances, a behaviour consistent with the presence of intramolecular N→Sb interaction in solution. Interesting, an evident AB system was not observed for the CH₂ group of the pendant arm due to isochronous chemical shifts of the methylene protons. It should be also noted that for several carbon atoms the corresponding resonances appear as doublets due to carbon–fluorine couplings at two or even three bond distances.

Single crystals of the diorganooantimony(III) fluorides 5–8, suitable for X-ray diffraction studies, were obtained by slow evaporation of their n-hexane solutions. The molecular structures are depicted in Fig. 2, 3, S20 and S24.† Selected bond lengths and angles are listed in Table 2.

The crystals of all four fluorides 5–8 contain discrete molecules with no intermolecular contacts between heavy atoms. This contrasts with the chain polymeric structure of Ph₂SbF in the related halides [Sb(1)–N(1) 2.693(6) Å in 5, and 2.512(5) Å in 7] in trans position to the fluorine atom [F(1)–Sb(1)–N(1) 158.66(18)° in 5, and 161.74(16)° in 7]. Due to a stronger trans influence of the fluorine atom these N→Sb distances are considerably longer for both 5 and 7 than observed in the related chlorides/bromides/iodides, i.e. [2-2′,6′-Pr₂C₆H₃N═CH]C₆H₄SbX [Sb–N 2.416(2) Å for X = Cl;³⁰ 2.498(4) Å for X = Br] or [2-(Me₂NCH₂)C₆H₄]SbX [Sb–N 2.463(2) Å for X = Cl;³¹ 2.423(3) Å for X = Br; 2.417(3) Å for X = I].³² The nitrogen atom of the second pendant arm in the molecule is placed in trans position to an ipso carbon atom and exhibits a slightly longer intramolecular bond in 5 [Sb(1)–N(2) 2.778(7) Å; N(2)–Sb(1)–C(1) 156.1(3)°], but being considerably longer in 7 [Sb(1)–N(2) 3.379(6) Å; N(2)–Sb(1)–C(1) 154.30(17)°; cf. sums of the respective covalent, ΣrΣr (Sb,N) 2.11 Å, and van der Waals radii, Σrvdw(Sb,N) 3.74 Å.³³ While for the fluoride 7 the length of the N→Sb bond placed in trans position to the carbon atom is similar to those observed for the other analogous halides [cf. Sb–N 3.216(3) Å for X = Cl;³⁰ 3.276(3) Å for X = Br; 3.211(3) Å for X = I]³⁴, for the imine derivative 5 this N→Sb distance is considerably shorter than in the corresponding chloride or bromide [Sb–N 2.952(3) Å for X = Cl;³⁰ 2.996(4) Å for X = Br].³⁵

In the molecules of the chiral fluorides 6 and 8, which contain one phenyl group and one organic ligand of the same type as in 5 and 7, again the nitrogen atom of the pendant arm is strongly coordinated to the metal atom [Sb(1)–N(1) 2.466(3) Å in 6, and 2.526(3) Å in 8] in trans position to the fluorine atom [F(1)–Sb(1)–N(1) 158.97(8)° in 6, and 161.48(9)° in 8]. The intramolecular N→Sb bond distance is longer than found in the related halides i.e. [2-2′,6′-Pr₂C₆H₃N═CH]C₆H₄SbX [Sb–N 2.433(2) Å]³⁶ or [2-(Me₂NCH₂)C₆H₄]PhSbX [Sb–N 2.452(2) Å for X = Cl;³¹ 2.444(4) Å for X = Br; 2.426(3) Å for X = I]³⁴. Fig. 3 Molecular structure of (C₃SB)-6, showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.
Table 2  Selected bond distances (Å) and angles (°) for compounds 5–8

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Taking into account both intramolecular N→Sb interactions the coordination geometry around the antimony atom in 5 and 7 is distorted square pyramidal [(C,N)2SbF core; hypervalent 12-Sb-5 species], with an ipso carbon atom in the apical position (Fig. 2 and S20†). For the fluorides 6 and 8, the molecules of which contain only one intramolecular N→Sb interaction, the coordination geometry is distorted pseudo-trigonal bipyramidal [(C,N)CSbF core; hypervalent 10-Sb-4 species], with the halogen and the nitrogen atoms placed in the axial positions. The intramolecular N→Sb interactions result in chelate induced-Sb-chirality,44,47 and therefore the crystals of the fluorides 5 and 6 contain 1:1 mixtures of (CNSb) and (Arcentroid) isomers.48 While the resulting SbCN rings are basically planar for the imine ligands in 5 and 6, the C2SbN rings in 7 and 8 are folded along the Sb–Cmethylene axis, with the N(sp3) atom lying out of the best plane through the residual SbC3 fragment. As result, in addition to the chirality at antimony, this folding induces planar chirality (with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively; for planar chirality the enantiomers are given as pSx and pRx).48 Indeed, the crystals contain racemic mixtures of (CNSb)p[RSCN(pNpS)]7(Arcentroid)5 and (CNSb)p[RSCN(pNpS)]8(Arcentroid)8 isomers, respectively.

A closer investigation of the crystal packing revealed that, in addition to intramolecular F⋯H contacts established in the molecules of all fluorides 5–8, intermolecular F⋯H and C⋯H⋯π (Arcentroid) interactions are present and lead to different supramolecular architectures (see ESI†). Thus, ribbon-like polymers of either (CNSb) or (Arcentroid) isomers based on C-Haryl⋯π (Arcentroid) interactions are formed in the crystal of 5. Parallel pairs of chains built from (CNSb)p[RScN(pNpS)]7 or (Arcentroid)5 p[RScN(pNpS)]7 isomers, respectively, through weak F(1)⋯H(3a)aryl contacts [2.49 Å; cf. sum of the corresponding van der Waals radii, ∑vdw(F, H) = 2.55 Å17 and C(14)–H(14)aryl⋯Arcentroid(C(10c)⋯C(15c)) (3.09 Å; γ = 13.3°) are developed along axis b in the crystal of 7. By contrast, in the crystal of 6 a 3D architecture is formed based on weak C⋯H⋯π (Arcentroid) contacts between parallel chain polymers of alternating (CNSb)6 and (Arcentroid)6 isomers connected through F(1)⋯H(7b)intermolecular (2.31 Å) interactions. Surprisingly, no intermolecular F⋯H contacts are present in the crystal of 8; in this case a dimer association of (CNSb)p[RScN(pNpS)]8 and (Arcentroid)p[RScN(pNpS)]8 is formed through C(7)⋯H(7b)methylene⋯Arcentroid(C(10a)⋯C(15a)) (2.99 Å; γ = 17.7°) contacts and these dimer units are further associated into a layer based on C(11)–H(11)aryl⋯Arcentroid[C(10a)⋯C(15a)] (3.02 Å; γ = 13.7°) contacts.

Experimental

Materials and instrumentation

The syntheses were performed under argon or nitrogen atmosphere using standard Schlenk techniques. THF was dried over sodium or potassium and distilled under argon prior to use. Reagents such as BuLi, Ti[PF6]3, Ag2[SnCl4] and [Bu4N]F were purchased from commercial suppliers and used without further purification. The other starting materials were prepared according to the literature procedures: (2′,6′,2′′,6′′-Pr3C6H3N=CH)C6H4Br, [2′(2′,6′,2′′,6′′-Pr3C6H3N=CH)C6H4]2SbBr, [2′(2′,4′,6′-Me3C6H3N=CH)C6H4]2SbBr,98 PhSbCl15,99 [2-(Me3NCH3)C6H4]2SbCl4.18 Elemental analyses were carried out with Perkin-Elmer 2400 and CHN-Analyzer Type FlashEA 1112 (Co. Thermo) instruments. The melting point of compounds was measured with an Electrothermal 9200 or a Melting Point B-540 (Co. Büchi) apparatus. The 1H, 13C, 19F NMR spectra were recorded at room temperature using Bruker Avance 300 (for 2, 7, 8), Bruker Avance II 400 (for 5, 6) and Bruker Avance III 500 (for...
Crystal structure determination

Single crystals of 1-2CH2Cl2 were obtained by slow diffusion of n-hexane into a solution of CH2Cl2 (3:1 v/v) or slow evaporation of a CHCl3 solution for 3-2CHCl3. Colorless crystals of 5-8 were grown by slow evaporation of a n-hexane solution. The details of the crystal structure determination and refinement are given in Tables S1 and S2 (see ESI†). The crystals were attached with Krytox™ to a glass fiber (1-2CH2Cl2, 3-2CHCl3) or mounted on cryoloops (5-8). For 3-2CHCl3, 5-8 data were collected at room temperature, while for 1-2CH2Cl2 the crystal was cooled under a nitrogen stream at low temperature. Data were collected on Oxford (Type Gemini S) (1-2CH2Cl2, 3-2CHCl3) and Bruker SMART APEX (5-8) diffractometers, using graphite-monochromated Mo-K\(\alpha\) radiation (\(\lambda = 0.71073\) Å), except for 3-2CHCl3, for which Cu-K\(\alpha\) (\(\lambda = 0.54184\) Å) radiation was used. The structures were refined with anisotropic thermal parameters. The 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. The drawings were created with the Diamond program.† CCDC reference numbers 1020707 (1-2CH2Cl2), 1020708 (3-2CHCl3), 1020709 (5), 10207010 (6), 10207011 (7) and 10207012 (8) contain the supplementary crystallographic data for this paper.†

Synthesis of \([2-(2',6',4',3')Pr2C6H3N=CH]C6H4\)2Sb\(\text{[PF}_6\text{]}^2\) (1).

A suspension of \(\text{TPF}_6\) (0.750 g, 2.15 mmol) in THF (20 mL) was added dropwise to a solution of \(2'-(2',6',4',3')\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH}\text{C}_6\text{H}_4\text{Sb}\) (1.570 g, 2.15 mmol) in THF (25 mL) at room temperature, resulting in immediate formation of a white precipitate. The reaction mixture was stirred for 1.5 h and then filtered off through Celite. The solvent was removed in vacuum from the clear yellowish solution to give 1 as a pale yellow solid (1.380 g, 81%), m.p. 235–237 °C. Anal. calc. for \(\text{C}_{40}\text{H}_{38}\text{SbF}_{12}\text{P}\) (795.49): C, 56.37; H, 5.58; N, 3.52. Found: C, 56.37; H, 5.46; N, 3.52.

\(\text{IR} (\text{ATR, cm}^{-1}):\) 3021, 2731, 1736, 1697, 1514, 1469, 1387, 1298, 1214, 802, 713. Synthesis of \([2-(2',6',4',3')\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH}]\text{C}_6\text{H}_4\text{PhSb}\)\(\text{[PF}_6\text{]}^2\) (2).

A solution of \(\text{^6}\text{BuLi in n-hexane (5.45 mL, 8.7 mmol, 1.6 M}) was added dropwise, at −78 °C to a stirred solution of \(2-(2',6',4',3')\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH}]\text{C}_6\text{H}_4\text{Br} (3.00 g, 8.7 mmol) in anhydrous n-hexane (40 mL) and the reaction mixture was stirred for 1.5 h. The resulting yellow-orange suspension of organolithium compound was added dropwise to a suspension of PhSbCl2 (2.35, 8.7 mmol) in n-hexane (30 mL), at −78 °C, and the mixture was stirred for 2 h at −78 °C, then for 12 h at room temperature. The solvent was removed, the residual yellow-orange solid was washed several times with cold n-hexane and then extracted with CHCl3. Evaporation of the solvent in vacuum gave 2.15 g (50%) of \([2-(2',6',4',3')\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH}]\text{C}_6\text{H}_4\text{PhSbCl}2\) as a yellow powder (m.p. 233–235 °C; cf. 238 °C (ref. 32)) which was used without further purification. To a solution of this chloride (1.00 g, 2.00 mmol) in THF (25 mL) a suspension of Tl[PF6] (0.70 g, 2.00 mmol) in THF (15 mL) was added dropwise, at room temperature. A white precipitate is formed immediately. The reaction mixture was stirred for 2 h and then filtered off through Celite. The solvent was removed under vacuum from the pale-yellow solution and the resulting precipitate was washed with n-hexane to give 2 as a pale yellow solid (0.873 g, 72%), m.p. 169–170 °C. Anal. calc. for \(\text{C}_{153}\text{H}_{169}\text{F}_{36}\text{P}\) (608.21): C, 49.37; H, 4.47; N, 2.50. Found: C, 49.02; H, 4.26; N, 2.33%. IR (ATR, cm−1): 1615(s) [\(\text{C}=\text{N}\)], 802(s) [\(\text{P}=\text{F}\)].

\(\text{H NMR} (500 \text{MHz, CDCl}_3): \delta 0.35 \text{[d,} \text{J}\text{H,H = 6.7 Hz, 3H, H}-8'a1, \text{CH(}	ext{CH}_3)_2\text{]}, 0.88 \text{[d,} \text{J}\text{H,H = 6.8 Hz, 3H, H}-8'a2, \text{CH(}	ext{CH}_3)_2\text{]}, 1.13 \text{[d,} \text{J}\text{H,H = 6.8 Hz, 3H, H}-8'b1, \text{CH(}	ext{CH}_3)_2\text{]}, 1.34 \text{[d,} \text{J}\text{H,H = 6.8 Hz, 3H, H}-8'b2, \text{CH(}	ext{CH}_3)_2\text{]}, 1.73 \text{[sept,} \text{J}\text{H,H = 6.8 Hz, 1H, H}-7'a, \text{CH(}	ext{CH}_3)_2\text{]}, 2.93 \text{[sept,} \text{J}\text{H,H = 6.8 Hz, 1H, H}-7'b, \text{CH(}	ext{CH}_3)_2\text{]}, 7.26 \text{[m,} \text{7H, H}-3', \text{H}-4', \text{C}_6\text{H}_4\text{H}], 7.34 \text{[sept,} \text{J}\text{H,H = 6.7 Hz, 2H, H}-7'a, \text{CH(}	ext{CH}_3)_2\text{]}, 7.46 \text{[m,} \text{4H, H}-3'b or H-3'a, \text{H}-4', \text{C}_6\text{H}_4\text{H}], 7.52 \text{[d,} \text{J}\text{H,H = 7.4 Hz, 2H, H}-6, \text{C}_6\text{H}_4\text{H}], 7.59 \text{[dd,} \text{J}\text{H,H = 7.5 Hz, J}^\text{H,H} = 1.2 Hz, 2H, H-5, \text{C}_6\text{H}_4\text{H}], 7.70 \text{[dd,} \text{J}\text{H,H = 7.5 Hz, J}^\text{H,H} = 1.1 Hz, 2H, H-4, \text{C}_6\text{H}_4\text{H}], 8.17 \text{[dd,} \text{J}\text{H,H = 7.6 Hz, J}^\text{H,H} = 0.9 Hz, 2H, H-3, \text{C}_6\text{H}_4\text{H}], 8.94 \text{[s, 2H, H}-7, \text{CH}=\text{N}]. \)
Synthesis of [2-(2',4',6'-Me6C6H3N=CH)C6H4]Sb][PF6]- (3). A suspension of [PF6]2 (0.120 g, 0.34 mmol) in THF (15 mL) was added dropwise to a solution of [2-(2',4',6'-Me6C6H3N=CH)C6H4]SbBr (0.222 g, 0.34 mmol) in THF (20 mL) at room temperature, resulting in immediate formation of a white precipitate. The reaction mixture was stirred for 1.5 h and then filtered off through Celite. The solvent was removed in vacuum from the clear yellowish solution to give 3 as a pale yellow solid (0.139 g, 57%). m.p. 200–202 °C. Anal. calc. for C25H27FNSb (482.25): C, 62.26; H, 5.64; N, 3.89%. IR (ATR, cm⁻¹): 1602(s) [v(CH=NH)], 825(s) [v(P=F)].

1H NMR (500 MHz, CDCl3): δ 6.37 (s, 6H, H-8, CH3), 2.45 (s, 12H, H-7, CH3), 7.11 (s, 4H, H-3',5', C6H4), 7.24 (d, JH-H = 7.5 Hz, 2H, H-6, C6H4), 7.55 (dd, JH-H = 7.5 Hz, JH-H = 1.2 Hz, 2H, H-5, C6H4), 7.62 (dd, JH-H = 7.5 Hz, JH-H = 1.1 Hz, 2H, H-4, C6H4), 8.12 (dd, JH-H = 7.5 Hz, JH-H = 0.8 Hz, 2H, H-3, C6H4), 8.94 (s, 2H, H, CH-N). 13C{1H} NMR (125.8 MHz, CDCl3): δ 20.25 (s, br, C-7', CH3), 21.07 (s, C-8', CH3), 279.19 (s, C-2',6'). 131C{1H} NMR (282.4 MHz, CDCl3): δ -72.8 (d, JH-H = 713.3 Hz). 31P{1H} NMR (202.5 MHz, CDCl3): δ -144.3 (s, JF-P = 713.3 Hz). MS (ESI+); CHCl3/CH3CN: m/z (%) 565 (100) [R2Sb+] [R = 2-(2',4',6'-Me6C6H3N=CH)C6H4].

Synthesis of [2-(MeNCH2)C6H4]Sb][PF6]- (4). A solution of [2-(MeNCH2)C6H4]SbCl2 (0.48 g, 1.13 mmol) in THF (15 mL) was added a suspension of AgCl (0.39 g, 1.13 mmol) in THF (10 mL), which lead to the immediate formation of a white precipitate. The flask was covered with aluminum foil against light. The reaction mixture was stirred for 30 minutes and then filtered off through Celite, resulting in a colorless solution.

Removal of the solvent under vacuum gave 4 as a white solid (0.35 g, 50%), m.p. 212–214 °C. Anal. calc. for C23H23FNSb (425.25): C, 62.62; H, 5.64; N, 3.80% Found: C, 61.46; H, 5.93; N, 3.61%. IR (ATR, cm⁻¹): 1622(s) [v(CH=NH)]. 1H NMR (400 MHz, CDCl3): δ 0.51 [d, JH-H = 6.7 Hz, 3H, H-8' a1], 1.06 [d, JH-H = 6.8 Hz, 3H, H-8' a2], 1.42 [d, JH-H = 6.8 Hz, 3H, H-8' b1], 1.82 [d, JH-H = 6.8 Hz, 3H, H-8' b2], 1.33 [d, JH-H = 6.8 Hz, 3H, H-8' b1], 1.82 [d, JH-H = 6.8 Hz, 3H, H-8' b2], 1.33 [d, JH-H = 6.8 Hz, 3H, H-8' b1], 1.82 [d, JH-H = 6.8 Hz, 3H, H-8' b2], 1.33 [d, JH-H = 6.8 Hz, 3H, H-8' b1], 1.82 [d, JH-H = 6.8 Hz, 3H, H-8' b2]. 13C{1H} NMR (75.5 MHz, CDCl3): δ 31.97 (s, C-7, CH a), 126.67 (s, C-4, CH a), 132.47 (s, C-3, CH a), 130.95 (s, C-5, CH a), 22.01 (s, C-6, CH a), 26.41 (s, C-8, CH a). Synthesis of [2-(2',6'-Pr2CH2N=CH)C6H4]Sb][PF6]- (5). A solution of [Bu4NF]-3H2O (0.088 g, 0.28 mmol) in acetonitrile (10 mL) was added to a solution of 1 (0.224 g, 0.28 mmol) in acetonitrile (15 mL). The reaction mixture was stirred for 16 h, then the color of the solution being changed from colourless to yellow. The solvent was removed in vacuum to obtain a yellow precipitate, which was extracted with n-hexane. Slow evaporation of the clear n-hexane solution gave yellow crystals of 5 (0.103 g, 55%), m.p. 166–168 °C. Anal. calc. for C25H25FNSb (669.53): C, 68.17; H, 6.62; N, 4.18. Found: C, 68.46; H, 6.81; N, 4.34%. IR (ATR, cm⁻¹): 1641(m) [v(CH=NH)]. 1H NMR (300 MHz, CDCl3): δ 0.44 [d, JH-H = 5.4 Hz, 3H, H-8'a1 (A), CH(CH3)2], 0.73 [d, JH-H = 5.3 Hz, 3H, H-8'a2 (A), CH(CH3)2], 0.88 [d, JH-H = 5.3 Hz, 6H, H-8' a1 (B), CH(CH3)2], 1.06 [m, 12H, H-8'b1 (A) + H-8'b2 (B) + CH(CH3)2], 1.91 [m, 1H, H-7'a (A), CH(CH3)2], 2.80 [m, 3H, H-7'b + H-7'B (B), CH(CH3)2], 6.98 [s, br, 1H, H-3'a (A), CH3], 7.11 [s, br, 5H, H-3'b (A) + H-4' (A) + H-3' (B) + H-4' (B), C6H5], 7.22 [s, br, 1H, H-6 (B), C6H5], 7.26 [s, br, 1H, H-5 (B), C6H5], 7.44 [dd, 1H, JH-H = 6.4 Hz, H-4 (B), C6H5], 7.62 [m, 2H, H-4 (A) + H-3 (B), C6H5], 7.74 [dd, JH-H = 7.3 Hz, 1H, H-5 (A), C6H5], 7.85 [dd, JH-H = 6.7 Hz, 1H, H-3 (A), C6H5], 8.38 [m, 3H, H-6 (A), C6H5, H-7 (A) + H-7 (B), CH=NH]. 13C{1H} NMR (75.5 MHz, CDCl3): δ 22.12 [s, C-8'a1 (A), CH(CH3)2], 23.78 [s, C-8' (B), CH(CH3)2], 24.03 [s, C-8'' (B), CH(CH3)2], 24.92 [s, C-8'a2 (A), CH(CH3)2], 25.32 [s, C-8'' (B), CH(CH3)2], 28.14 [s, br, C-7'a (A) + C-7'' (B), CH(CH3)2], 28.31 [s, C-7'' (B), CH(CH3)2], 122.99 [s, C-3'a (A) + C-4'' (A) or C-4'' (B)], 123.97 [s, C-3'' (B)], 124.42 [s, C-4'' (B) or C-4' (A)], 126.32 [s, C-3' (A), C-7 (A) + C-7 (B)], 128.95 [s, C-4 (A)], 129.69 [s, C-4 (B)], 131.96 [s, C-5 (B), C-3 (A) + C-3 (B)], 134.53 [s, C-6 (A)], 136.06 [s, C-6 (B)], 138.57 [s, C-2' (B)], 139.00 [s, C-2' (B)], 139.47 [s, C-2'' (B)], 140.64 [s, C-2'' (A) + C-2'' (A)], 144.69 [s, C-1' (A)], 148.15 [s, C-1' (B)], 148.53 [s, C-1 (B)], 160.00 [s, C-1 (A)], 164.74 [s, C-7 (B), CH=NH], 168.76 [s, C-7 (A), CH=NH]. 19F{1H} NMR (282.4 MHz, CDCl3): δ -181.3 (s). MS (ESI+, CH3CN): m/z (%) 649 (100) [R2Sb+] [R = 2-(2',6'-Pr2CH2N=CH)C6H4].
Synthesis of [2-(Me₂NCH₂)C₆H₄]₂SbF (7). A solution of [Bu₄NF]·H₂O (0.131 g, 0.42 mmol) in acetonitrile (15 mL) was added to a solution of [2-(Me₂NCH₂)C₆H₄]₂SbF₄ (4) (0.260 g, 0.42 mmol) in acetonitrile (15 mL). The reaction mixture was stirred for 16 h, then the solvent was removed in vacuum to yield a white solid, which was extracted with hexane. Slow evaporation of the clear n-hexane solution gave white crystals of [2-(Me₂NCH₂)C₆H₄]₂SbF (7). A solution of [Bu₄NF]·H₂O (0.051 g, 43%), m.p. 164 °C. Anal. calc. for C₁₅H₁₃N₃F₁₀Sb: C, 39.0; H, 2.7; N, 7.0%.1H NMR (300 MHz, CDCl₃): δ 2.01 (s, 3H, H-8a, C₆H₅), 2.71 (s, 6H, H-8b, C₆H₅), 3.72 (m, 3H, H-meta, para), 7.37 (dd, J = 7.4 Hz, 1H, H-4, C₆H₅), 7.47 (dd, J = 7.4 Hz, 1H, H-3, C₆H₅), 7.52 (m, 2H, H-ortho, C₆H₅), 8.16 (d, J = 7.4 Hz, 1H, H-6, C₆H₅).13C{¹H} NMR (75.5 MHz, CDCl₃): δ 45.48, 45.50 (s, C-8a, C-8b), 65.45 (s, C-7), 126.51 (s, C-3), 128.32 (s, C-5), 128.90 (s, C-meta), 129.18 (s, C-14), 129.46 (s, C-para), 134.67 (d, J = 1.1 Hz, C-ortho, C₆H₅), 135.22 (d, J = 6.9 Hz, C-6), 143.22 (s, C-2), 144.07 (d, J = 10.1 Hz, C-ipsos), 148.27 (d, J = 7.7 Hz, C-1).19F{¹H} NMR (282.4 MHz, CDCl₃): δ −167.9 (s, br). MS [M++H]: 409 (3) [M+H]: 389 (100). [R²PhSB⁺] [R²' = 2-(Me₂NCH₂)C₆H₄].

Conclusions

The present work reports on a new general method for the synthesis of hypervalent diorganooammonium(III) fluorides containing either one or two organic ligands with a pendant arm, e.g. [2’-(Me₂NCH₂)C₆H₄N=CH]⁺[C₆H₄SBF₆] (5), [2’-(Me₂NCH₂)C₆H₄N=CH]⁺[C₆H₄PhSBF₆] (6) (Scheme 1), [2-(Me₂NCH₂)C₆H₄]₂SbF₄ (7) and [2-(Me₂NCH₂)C₆H₄]²⁺[PC₆H₄(SbF₆)₃] (8), using as starting materials diorganooammonium(III) cations stabilized by intramolecular N→Sb interactions. It is worthwhile to mention that the diorganooammonium(III) fluorides could be obtained just by [Bu₄NF]·H₂O addition to in situ prepared cationic species. The ionic species [2’-(Me₂NCH₂)C₆H₄N=CH]⁺[C₆H₄SBF₆] (5) and [2’-(Me₂NCH₂)C₆H₄N=CH]⁺[C₆H₄PhSBF₆] (6) exhibit helical chirality and crystallize as 1 : 1 mixture of (ΔSb)⁺ and (ΔSb)⁻cations. In contrast to Ph₃SbF, which exhibits a chain polymeric structure based on almost symmetric Sb–F...Sb bridges, the crystals of the novel fluorides 5-8 contain discrete molecules as result of intramolecular N→Sb interactions.

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