**Faculty of Chemistry & Chemical Engineering**

**Inorganic Chemistry Department**

**Babes-Bolyai University**

**Cluj-Napoca, 400028**

**PhD Thesis Abstract**

# HOMO- AND HETERONUCLEAR ORGANOANTIMONY COMPOUNDS

**Ana-Maria PREDA**

**Scientific advisor:**
**Prof. Dr. Cristian SILVESTRU**

**Cluj-Napoca**

**2012**

**Jury**

| | |
|---|---|
| President: Prof. Dr. Ion Grosu | Babes-Bolyai University |
| Scientific advisor: Prof. Dr. Cristian Silvestru | Babes-Bolyai University |
| 1. Reviewer: Prof. Dr. Vasile Pârvulescu | University of Bucharest |
| 2. Reviewer: Prof. Dr. Michael Mehring | Chemnitz University of Technology |
| 3. Reviewer: Conf. Dr. Ing. Monica Venter | Babes-Bolyai University |

Date of public defense: January 27, 2012

# TABLE OF CONTENTS

**Keywords:** Antimony / Hypervalent compounds / Chalcogenides / Ionic derivatives / Diorganotetrahaloantimonates / NMR studies / X-ray diffraction studies

## *Aims of the present study*

The aim of the present work was the synthesis and structural characterization, both in solution and in solid state, of new organoantimony(III) compounds containing ligands with intramolecular coordinating ability and also of new ionic organoantimony(V) derivatives.

Mono- and diorganoantimony(III) halides are important starting materials in the organometallic chemistry of antimony. Another aspect of the present work was to prove the reactivity of organoantimony(III) halides to hydrolysis, thiolysis and the investigation of the potential of the new hypervalent organoantimony(III) compounds to coordinate to metalcarbonyl fragments.

The synthesis and investigation of new ionic organoantimony compounds stabilized by intramolecular coordination was achieved.

The halogen exchange reactions between the organoantimony bromides and potassium fluoride did not work. A new route was established for the synthesis of new organoantimony(III) fluorides.

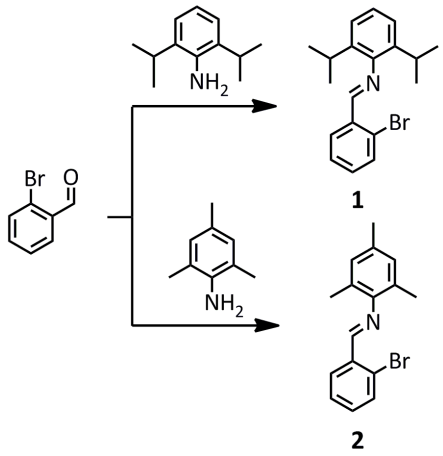
Another interest was to investigate some new onium diorganotetrafluoro-, -chloro- and –bromoantimonates, *i.e.* the structure of the tetrahedral cations and the octahedral anions with the organic groups in *trans* positions.

## III.A. Organoantimony(III) halides containing the 2-[(2',6'-$^{i}Pr_2C_6H_3$)N=CH]$C_6H_4$ and 2-[(2',4',6'-$Me_3C_6H_2$)N=CH]$C_6H_4$ fragments

### III.A.2. Preparation

The aim of the present work was the synthesis and structural characterization, both in solution and in the solid state, of new organoantimony compounds containing bulky organic ligands with intramolecular coordinating ability. Our interest was to study the behavior of these new organoantimony derivatives.

The organic imine ligands were synthesized in high yields using reported procedures,[68] *i.e.* by condensation of 2-bromobenzaldehyde with the corresponding amine in toluene, using a Dean-Stark receiver (**Scheme 1**). Their formation was confirmed by $^{1}H$ and $^{13}C$ NMR spectroscopy.

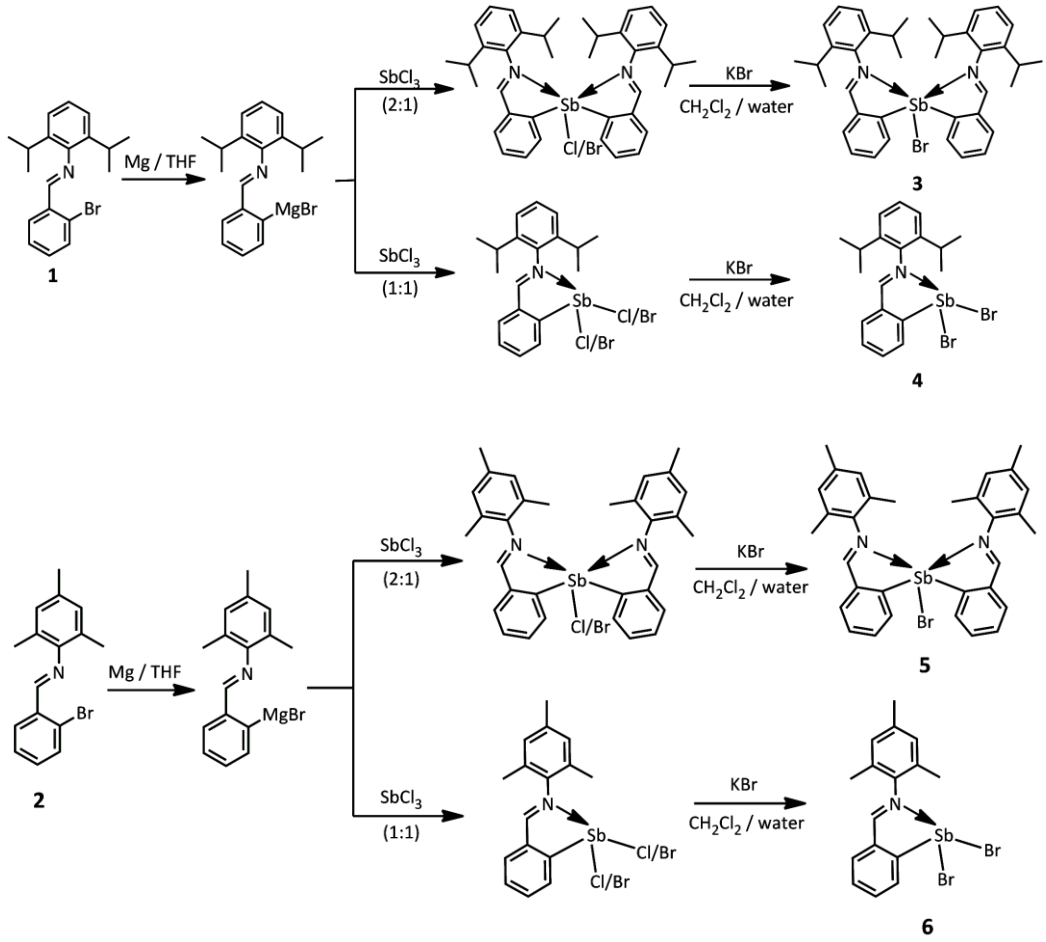



**Scheme 1.**

Grignard reagents were used to obtain the new organoantimony(III) halides of the type [2-{(2',6'-$^{i}Pr_2C_6H_3$)N=CH}$C_6H_4$]$_2SbCl_nBr_m$, [2-{(2',4',6'-$Me_3C_6H_2$)N=CH}$C_6H_4$]$_2SbCl_nBr_m$ (n + m = 1), and [2-{(2',6'-$^{i}Pr_2C_6H_3$)N=CH}$C_6H_4$]$SbCl_nBr_m$, [2-{(2',4',6'-$Me_3C_6H_2$)N=CH}$C_6H_4$]$SbCl_nBr_m$ (n + m = 2), followed by halogen exchange reactions between the mixture of chloro / bromo derivatives and KBr in $CH_2Cl_2$ / water mixture, at room temperature (**Scheme 2**).[61]

The Grignard reactions were performed in inert atmosphere (argon), using Schlenk techniques, and the solvents were dried and freshly distilled prior to use. The organoantimony(III) bromides $R_2SbBr$ (**4**), $RSbBr_2$ (**4**) [R = 2-(2',6'-$^{i}Pr_2C_6H_3$N=CH)$C_6H_4$] and $R'_2SbBr$ (**5**) and $R'SbBr_2$ (**6**) [R' = 2-(2',4',6'-$Me_3C_6H_2$N=CH]$C_6H_4$] were isolated as yellow, air-stable crystalline products, which are thermally stable and melt without decomposition.

The identity of compounds **3–6** was confirmed by NMR and IR spectroscopy, elemental analysis, mass spectrometry and the molecular structures were determined by single crystal X-ray diffraction.




**Scheme 2.** Preparation of organoantimony(III) bromides **3**–**6**.

## *III.A.5. NMR spectroscopy*

The solution behavior of monobromide $R_2SbBr$ (**3**) was investigated by NMR spectroscopy. The $^1H$ NMR spectrum was measured in $CDCl_3$ and DMSO-$d_6$ at room temperature. In the $^1H$ NMR spectrum measured in DMSO-$d_6$, (**Figure 1**) the resonances are better resolved and exhibits in the aliphatic region six doublets resonances which correspond to the methyl protons of the isopropyl groups and three unresolved heptet resonances, which were assigned to the methine protons of the isopropyl groups. Also the aromatic region exhibits two types of resonances for the aromatic protons. This result suggests that the organic ligands are non-equivalent. The non-equivalence of the organic groups is given by the intramolecular N→Sb interactions in solution at room temperature which are present also in the solid state.

In one of the organic group the free rotation around Sb–C bond is blocked by the strong coordination of the nitrogen atom of the pendant arm to the antimony whereas in the other ligand the presence of a weaker coordination of the nitrogen atom to the antimony does not block the free rotation of the 2-(2',6'-$^iPr_2C_6H_3N{=}CH)C_6H_4$.

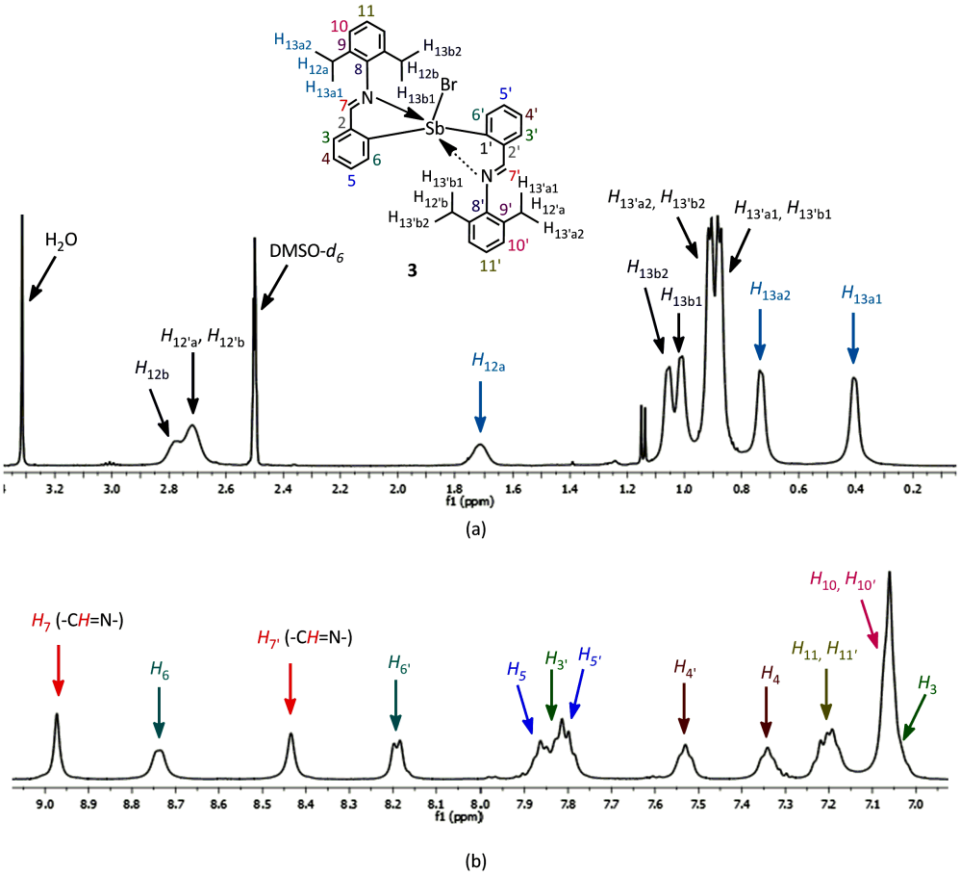



**Figure 1.** $^{1}$H NMR (DMSO-d$_6$, 500 MHz, r.t.) spectrum of compound R$_2$SbBr (**3**); (a) aliphatic region; (b) aromatic region.

The $^{1}$H NMR spectrum of monobromide R'$_2$SbBr (**5**) was measured in $CDCl_3$ and exhibited in the aliphatic region two singlet resonances for the methyl protons placed in *orto* ($\delta$ 1.65 ppm) and *para* ($\delta$ 2.20 ppm) positions, respectively, of the mesityl moiety. Also the aromatic region of **5** showed the expected proton resonances. The singlet resonance for the -C*H*=N- group was found at $\delta$ 8.29 ppm (see **Figure 2**).

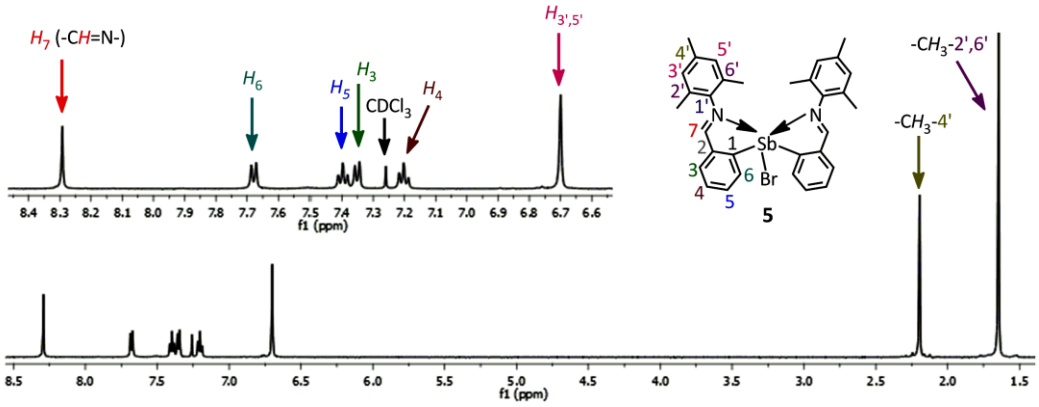



**Figure 2.** $^{1}$H NMR ($CDCl_3$, 500 MHz, r.t.) spectrum of compound R'$_2$SbBr (**5**).

The $^{1}H$ and $^{13}C$ NMR spectra of dibromides **4** and **6** were measured in a solution of $CDCl_3$, at room temperature.

The $^{1}H$ NMR spectrum of dibromide **4** shows in the aliphatic region two doublets resonances which correspond to the methyl protons -CH($CH_3$)$_2$ of the isopropyl groups ($\delta$ 1.16 ppm, 1.28 ppm) due to diastereotopicity and a heptet resonance for the methine, -$CH$($CH_3$)$_2$, protons of the isopropyl groups ($\delta$ 2.98 ppm). The $^{1}H$ NMR spectrum of dibromide **6** exhibits in the aliphatic region two singlet resonances for the methyl protons placed in *orto* ($\delta$ 2.24 ppm) and *para* ($\delta$ 2.32 ppm) positions of the mesityl moiety. The aromatic region of $^{1}H$ NMR spectra of compounds **4** and **6** contains each three resonances for the four different protons of the $C_6H_4$ group, one multiplet resonance for the protons which belong to the 2',6'-$^{i}Pr_2C_6H_3$ group in the case of **4** ($\delta$ 7.28 ppm) and 2',4',6'-$Me_3C_6H_2$ group in the case of **6** ($\delta$ 6.96 ppm) and one singlet resonance for the -C$H$=N- group ($\delta$ 8.48 ppm for **4** and $\delta$ 8.54 ppm for **6**). The most deshielded resonance is the resonance which corresponds to the protons in the *ortho* position to the antimony atom ($\delta$ 8.90 ppm for **4** and $\delta$ 8.84 ppm for **6**) (**Figure 3**). The $^{13}C$ NMR spectra contain the expected singlet resonances for the aliphatic and aromatic carbons, in the case of both dibromides **4** and **6**.

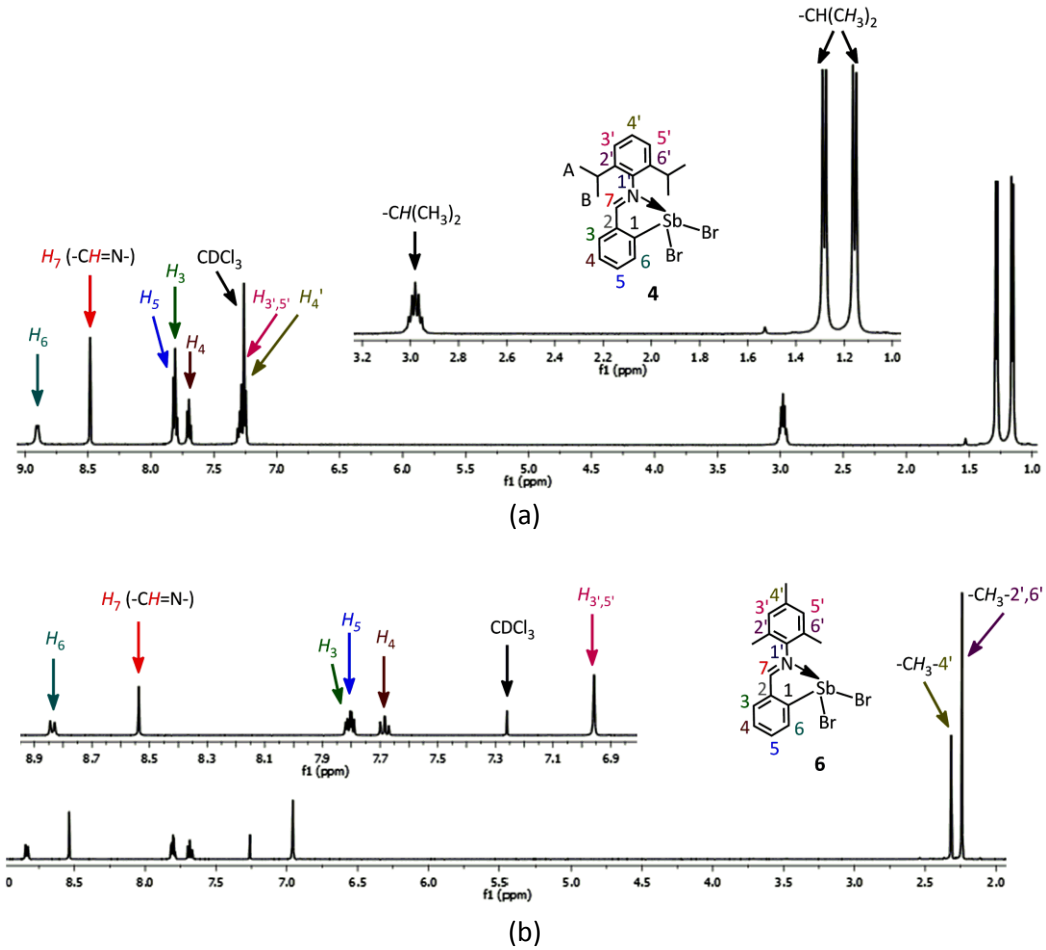



**Figure 3.** $^{1}H$ NMR ($CDCl_3$, 500 MHz, r.t.) spectra of compounds **4** (a) and **6** (b).

### *III.A.6. Single-crystal X-ray diffraction studies*

The molecular structures of compounds [2-{(2',6'-$^{i}Pr_2C_6H_3$)N=CH}$C_6H_4$]$_2$SbBr (**3**), [2-{(2',6'-$^{i}Pr_2C_6H_3$)N=CH}$C_6H_4$]SbBr$_2$ (**4**) and [2-{(2',4',6'-$Me_3C_6H_2$)N=CH}$C_6H_4$]SbBr$_2$ (**6**) were determined by single-crystal X-ray diffraction studies. In the case of compound [2-{(2',4',6'-$Me_3C_6H_2$)N=CH}$C_6H_4$]$_2$SbBr (**5**) no good crystals were obtained.

The crystal monobromide [2-{(2',6'-$^{i}Pr_2C_6H_3$)N=CH}$C_6H_4$]$_2$SbBr (**3**), **Figure 4** contains discrete molecules. The molecule displays a distorted square bipyramidal coordination geometry around antimony, with nitrogen atoms of both organic substituents coordinated to antimony. The nitrogen atoms are located in equatorial positions, with N(1) atom *trans* to the halogen atom [N(1)-Sb(1)-Br(1) 165.43(10)°. The nitrogen atom N(1) is strongly coordinated to antimony [Sb(1)-N(1) 2.498(4) Å] whereas the nitrogen atom N(2) of the molecular unit exhibits a weaker intramolecular interaction [Sb(1)-N(2) 2.996(7) Å], its vector lying almost *trans* to a carbon atom. The resulting $SbC_3N$ rings are basically planar. If both intramolecular N→Sb interactions per metal are taken into account, the geometry around the antimony atom is distorted square pyramidal [(*C,N*)$_2$SbBr core; hypervalent 12-Sb-5 species[70,71]], with the C(20) atom in the apical position.

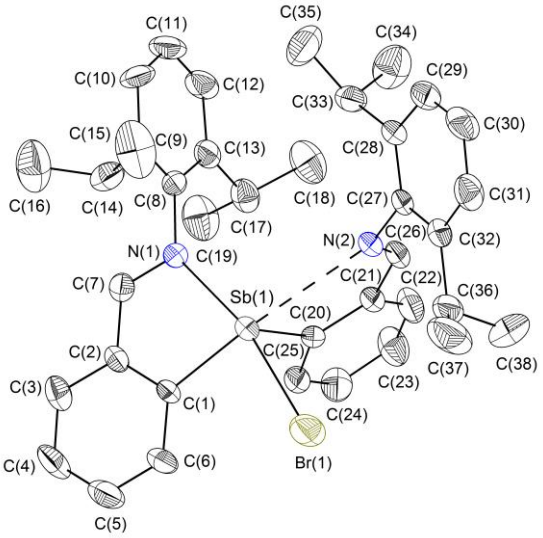



**Figure 4.** ORTEP representation at 30% probability ellipsoids of the molecular structure of the ($C_{Sb}$)-**3** isomer, showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

The two organic ligands bearing the pendant arm are non-equivalent (the aromatic rings are placed in apical and equatorial positions, respectively, of the overall metal coordination core)[62] and therefore the chirality at the antimony atom can be described in term of $C_{Sb}$ (clockwise) and $A_{Sb}$ (anticlockwise) isomers.[69] Indeed, the crystal of **3** contains a 1:1 mixture of ($C_{Sb}$) and ($A_{Sb}$) isomers.

The solid state molecular structures of the dihalides [2-{(2',6'-$^{i}Pr_2C_6H_3$)N=CH}$C_6H_4$]SbBr$_2$ (**4**) and [2-{(2',4',6'-$Me_3C_6H_2$)N=CH}$C_6H_4$]SbBr$_2$ (**6**), (**Figure 5**)show that the nitrogen atom of the pendant arm is coordinated to the antimony atom [Sb(1)-N(1) 2.395(3) Å for **4**; 2.346(3) Å for **6**] *trans* to a bromine atom [N(1)-Sb(1)-Br(1) 164.82(5)° for **4**; 163.60(7)° for **6**]. The resulting geometry around antimony is distorted *pseudo*-trigonal-bipyramidal [(*C,N*)SbBr$_2$ core], with a planar $SbC_3N$ ring.

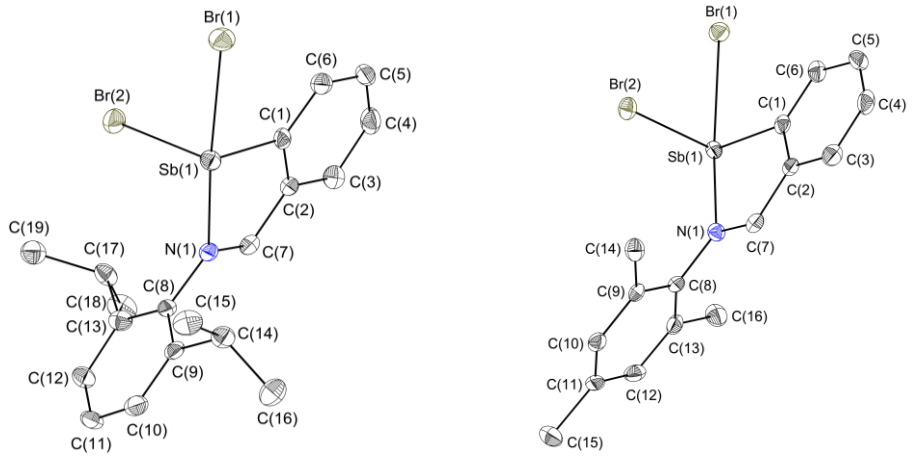



**Figure 5.** ORTEP representation at 50% probability and atom numbering scheme for (a) ($C_{Sb}$)-**4**, and (b) ($A_{Sb}$)-**6** isomers. Hydrogen atoms are omitted for clarity.

Due to the chelating nature of the organic ligand, the dihalides [2-{(2',6'-$^{i}Pr_2C_6H_3$)N=CH}$C_6H_4$]$SbBr_2$ (**4**) and [2-{(2',4',6'-$Me_3C_6H_2$)N=CH}$C_6H_4$]$SbBr_2$ (**6**) exhibit chirality at the antimony atom and crystallize as racemates, *i.e.* 1:1 mixtures of ($C_{Sb}$) and ($A_{Sb}$) isomers of **4** and **6**, respectively. The crystals of **4** and **6** contain centrosymetric dimer associations built from ($C_{Sb}$) and ($A_{Sb}$) isomers via bridging interactions involving the Br(1) atom, which is located in *trans* to the nitrogen atom in the molecular unit.

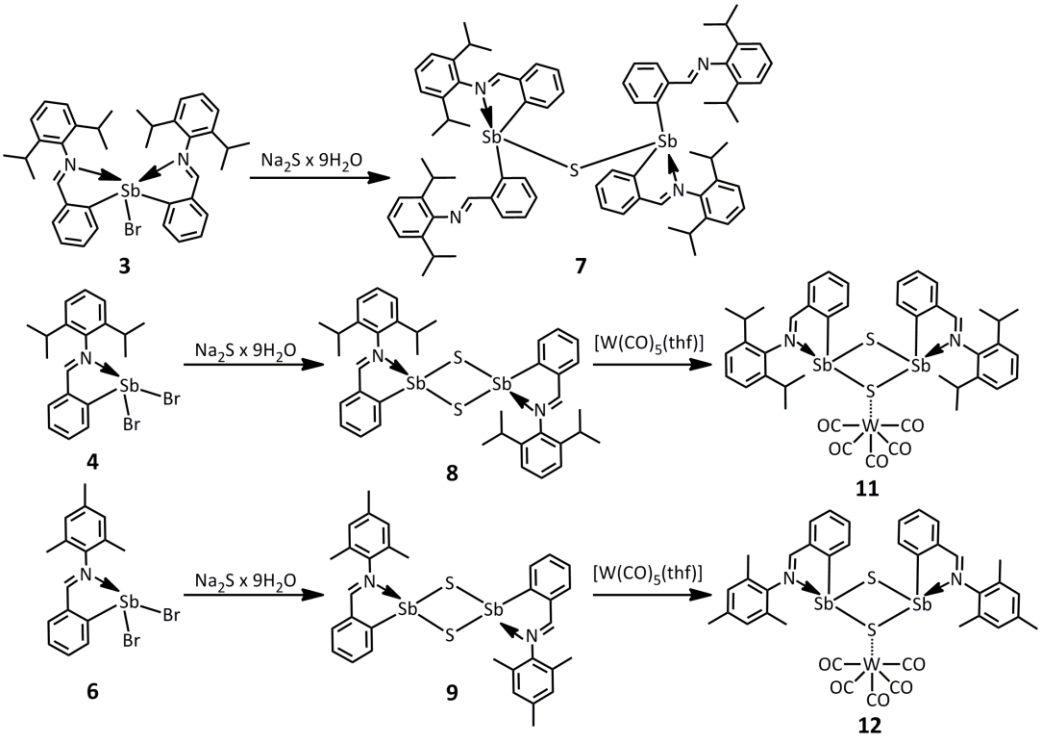
## *III.A.7. Conclusions*

- New organoantimony(III) bromides with organic imine ligands containing nitrogen atom(s) able to coordinate intramolecularly to antimony were obtained and structurally characterized both in solution and in solid state.
- Non-equivalence of the organic ligands in solution as well as in the solid state was observed for the monobromide [2-{(2',6'-$^{i}Pr_2C_6H_3$)N=CH}$C_6H_4$]$_2$SbBr (**3**). The free rotation of the aromatic group attached to nitrogen is blocked due to the presence of the strong coordination of the nitrogen atom of the pendant arm to the antimony atom.
- In the solid state the intramolecular coordination of the nitrogen atoms to antimony induces chirality at the antimony atom.
- Due to the chelating nature of the organic ligand, the dihalides **4** and **6** crystallize as racemates, *i.e.* 1:1 mixtures of ($C_{Sb}$) and ($A_{Sb}$) isomers.
- The dimers **4** and **6** are composed of ($C_{Sb}$) and ($A_{Sb}$) isomers and are formed by centrosymetric association via bridging bromine; this results in overall distorted square pyramidal (*C,N*)$SbBr_3$ coordination cores (12-Sb-5 species).

## III.B. Organoantimony(III) chalcogenides containing the 2-[(2',6'-$^{i}Pr_2C_6H_3$)N=CH]$C_6H_4$ and 2-[(2',4',6'-$Me_3C_6H_2$)N=CH]$C_6H_4$ fragments

### III.B.2. Preparation

In our study, the sulfides [{2-((2',6'-$Pr^{i}_2C_6H_3$)N=CH)$C_6H_4$}$_2$Sb]$_2$S (**7**), *cyclo*-[{2-((2',6'-$^{i}Pr_2C_6H_3$)N=CH)$C_6H_4$}SbS]$_2$ (**8**) and *cyclo*-[{2-((2',4',6'-$Me_3C_6H_2$)N=CH)$C_6H_4$}SbS]$_2$ (**9**) were prepared by the reaction of $R_2SbBr$ (**3**) with $Na_2S$ (for **7**), or $RSbBr_2$ (**4**) and $R'SbBr_2$ (**6**) with $Na_2S$ (for **8** and **9**, respectively) in water/toluene mixtures (**Scheme 3**). The oxide *cyclo*-[{2-((2',6'-$^{i}Pr_2C_6H_3$)N=CH)$C_6H_4$}SbO]$_3$ (**10**) was obtained by the reaction between **4** and KOH in water/toluene mixture (**Scheme 4**).

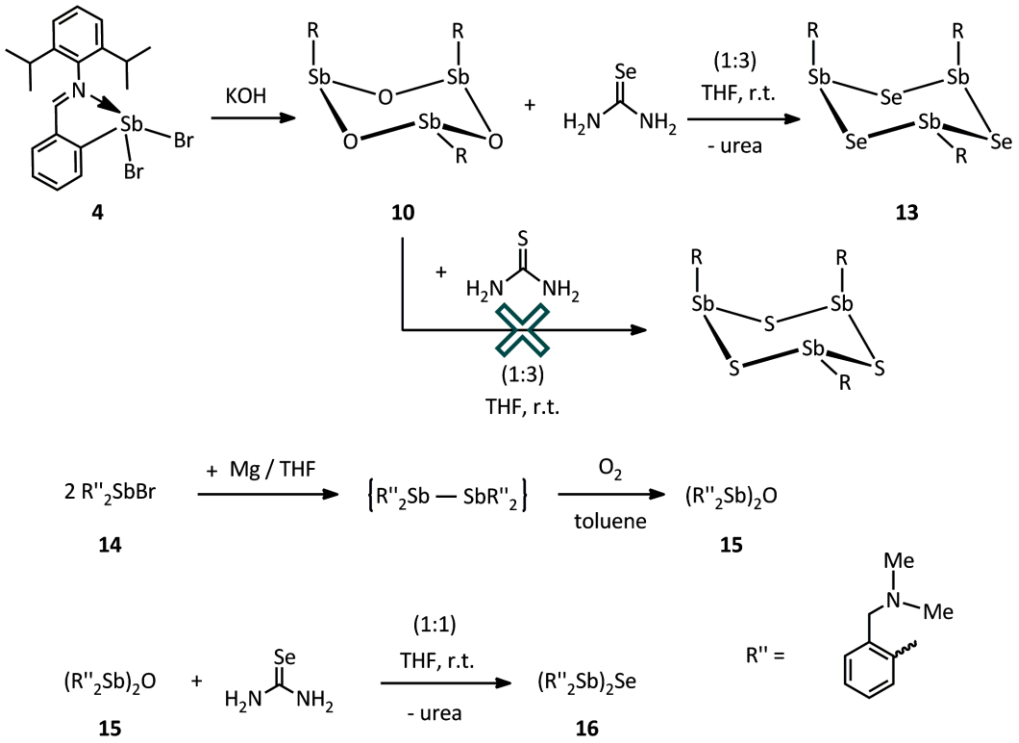



**Scheme 3.**

The metalcarbonyl complexes, *cis-cyclo*-[({2-((2',6'-$^{i}Pr_2C_6H_3$)N=CH)$C_6H_4$}SbS)$_2$-W(CO)$_5$] (**11**) and *cis-cyclo*-[({2-((2',4',6'-$Me_3C_6H_2$)N=CH)$C_6H_4$}SbS)$_2$W(CO)$_5$] (**12**) were prepared by the reaction between the heterocyclic sulfides *cyclo*-[RSbS]$_2$ (**8**) and *cyclo*-[R'SbS]$_2$ (**9**) with [W(CO)$_5$(thf)]. The reactions were performed in THF solution at ambient temperature, in a 1:1 molar ratio (**Scheme 3**).

Treatment of the oxide *cyclo*-[RSbO]$_3$ (**10**) with selenourea gave the corresponding selenide *cyclo*-[{2-((2',6'-$^{i}Pr_2C_6H_3$)N=CH)$C_6H_4$}SbSe]$_3$ (**13**) and urea as the by-product. When the oxide **10** was reacted with thiourea no chalcogen exchange reaction occurred. This fact was confirmed by $^{1}$H NMR spectroscopy which showed the pattern resonances belonging to the oxide **10**.

The monobromide R''$_2$SbBr (**14**) [R'' = 2-(Me$_2$NCH$_2$)C$_6$H$_4$] was reduced with Mg in THF to give the distibane R''$_2$Sb–SbR''$_2$, which was converted *in situ* into the oxide [{2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_2$Sb]$_2$O (**15**) by air oxidation.[63] Also the oxide (R''$_2$Sb)$_2$O (**15**) was treated with selenourea in THF, at room temperature to obtain the corresponding selenide [{2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_2$Sb]$_2$Se (**16**) (**Scheme 4**).




**Scheme 4.**

The treatment of the corresponding oxides with selenourea is a new route for the preparation of new organoantimony(III) complexes containing antimony-selenium bonds.

All compounds were characterized by NMR, IR spectroscopy, mass spectrometry, elemental analysis, and the molecular structures of most compounds were determined by single-crystal X-ray diffraction studies. Single-crystals suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into solutions of $CH_2Cl_2$ (3:1 v/v) (for compounds **7**–**9**, **11**, **16**) and a $CHCl_3$ solution (3:1 v/v) (for **15**).

### *III.B.5. NMR spectroscopy*

In the case of the chalcogenides [R$_2$Sb]$_2$S (**7**), *cyclo*-[RSbS]$_2$ (**8**) and *cyclo*-[R'SbS]$_2$ (**9**) the NMR data were recorded in $CDCl_3$. For **7** and **9** these data suggest a dynamic process concerned to the coordination of nitrogen to antimony which is very fast at room temperature.

The $^1$H NMR spectrum at room temperature of compound *cyclo*-[RSbS]$_2$ (**8**) (**Figure 8**) showed in the aliphatic region a broad singlet resonance and a heptet for the methyl protons and methine protons from the isopropyl groups, respectively.

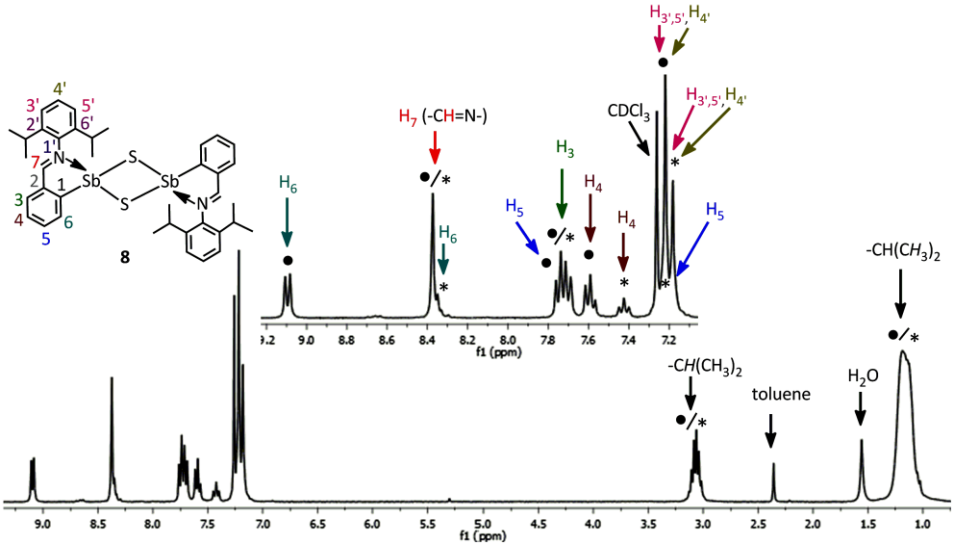



**Figure 8.** $^{1}$H NMR ($CDCl_3$, 500 MHz, r.t.) spectrum of compound *cyclo*-$[RSbS]_2$ (**8**); isomer **A** (•), isomer **B** (*).

The aromatic region of *cyclo*-$[RSbS]_2$ (**8**) shows two sets of signals with an integral ratio of 1.8:1 for the aromatic protons, a behavior assumed to suggest that both *cis* and *trans* isomers are present in solution. The resonance which corresponds to the protons in the *ortho* position to antimony of one of the isomers ($\delta$ 9.09 ppm) is the more deshielded resonance and the resonances for the -C*H*=N- group were found at $\delta$ 8.35 ppm in the case of both isomers.

The room temperature $^{1}$H NMR spectrum of sulfide *cyclo*-$[R'SbS]_2$ (**9**) (**Figure 10**) was measured in $CDCl_3$ and is also consistent with the presence of two isomers in the integral ratio of 1.4:1. The aliphatic region exhibits three singlet resonances. The most shielded ones were assigned to the protons of the methyl groups placed in positions 2' and 6' of the organic ligand belonging to one of the two isomers. The third, most deshielded resonance is the result of overlapping of the resonances corresponding to the protons of methyl group placed in position 4' of the ligand, in both isomers. This was proved by an variable-temperature $^{1}$H NMR study (**Figure 11**).

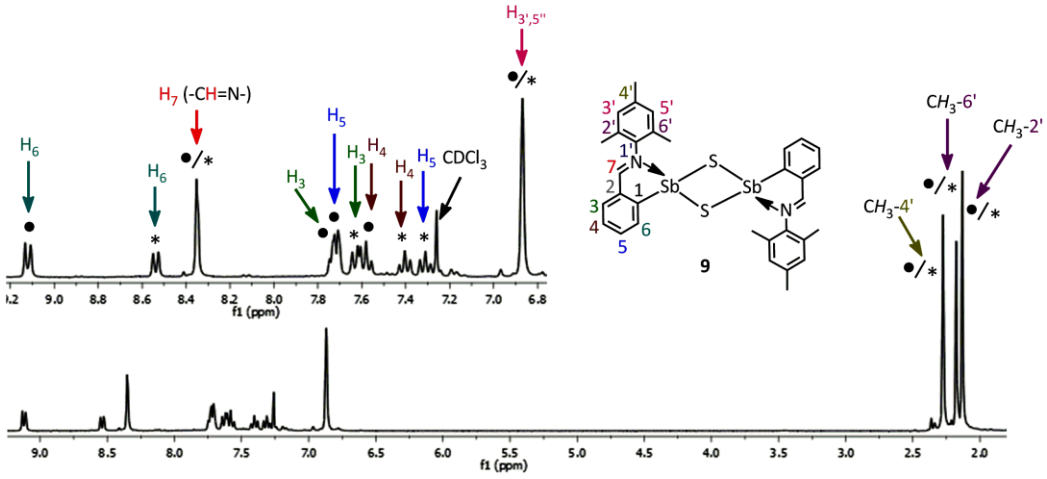



**Figure 10.** $^{1}$H NMR ($CDCl_3$, 500 MHz, r.t.) spectrum of compound *cyclo*-$[R'SbS]_2$ (**9**); isomer **A** (•), isomer **B** (*).

In the $^{1}$H NMR spectrum of **9** at –60 °C it could be observed that resonances which belong to the protons of the methyl group placed in position 4' of the organic ligand in the two isomers are now well separated.

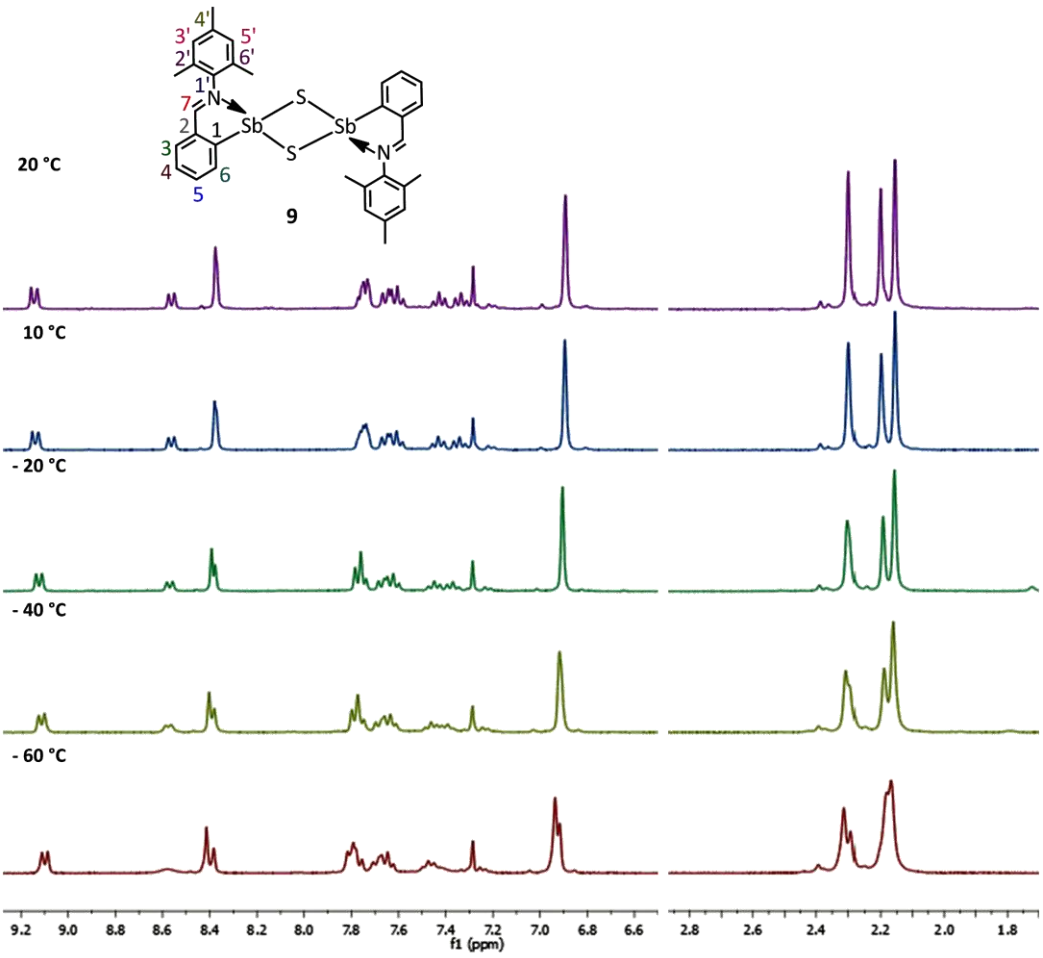



**Figure 11.** Variable-temperature $^{1}$H NMR ($CDCl_3$, 300 MHz) spectra of **9**.

The $^{1}$H NMR spectrum of compound *cyclo*-$[RSbO]_3$ (**10**) was recorded in $CDCl_3$, at room temperature. The aliphatic region shows two complex multiplets for the methyl protons and for the methine protons, respectively, of the isopropyl groups of the organic ligands placed in *trans* and *cis* positions with respect to the six-membered $Sb_3O_3$ ring of chair conformation. The aryl region of the $^{1}$H NMR spectrum contains two sets of signals with an integral ratio of 2:1 for the aromatic protons (**Figure 12**). The $^{13}$C NMR spectrum of the oxide **10** also exhibits two sets of aromatic resonances for the ligands placed in *trans* and *cis* positions (**Figure 13**).

For the metalcarbonyl complex *cis-cyclo*-$[(RSbS)_2W(CO)_5]$ (**11**) the $^{1}$H NMR spectrum (**Figure 14**) shows only one set of resonances, *i.e.* two multiplets resonances in the aliphatic region which were assigned to the methyl and methine protons belonging to the the isopropyl groups, as well as the expected resonances in the aromatic region.

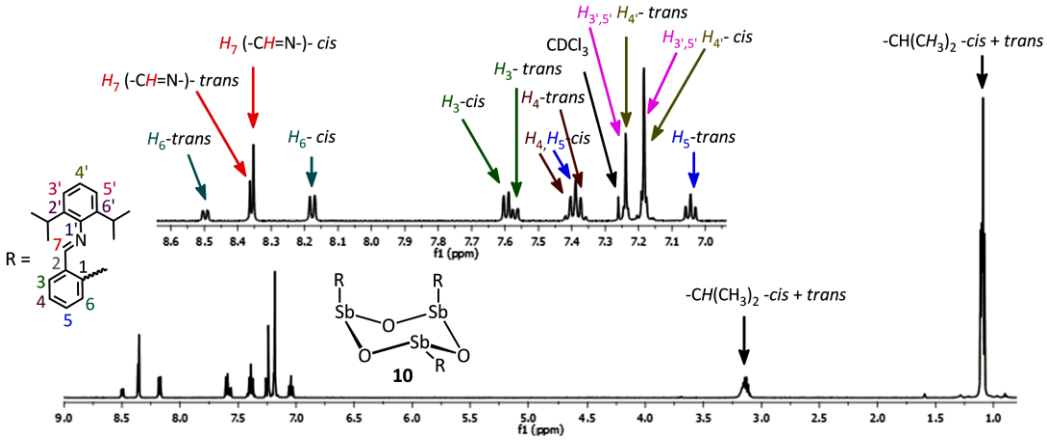
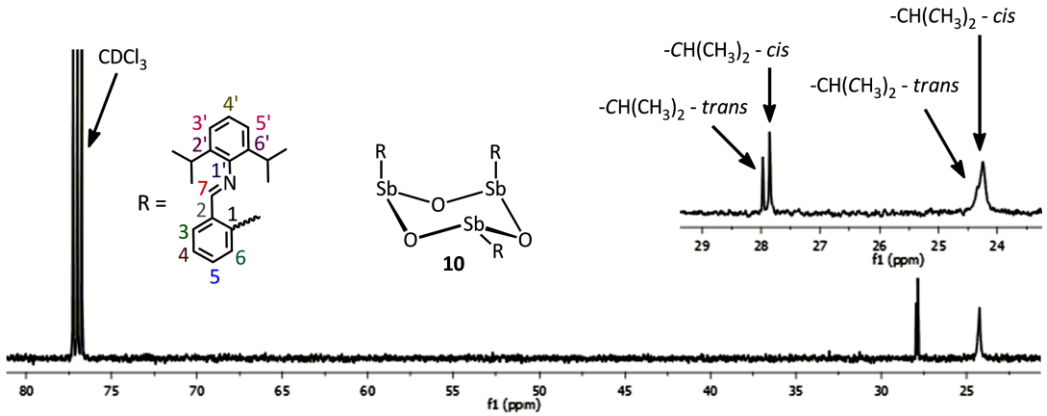
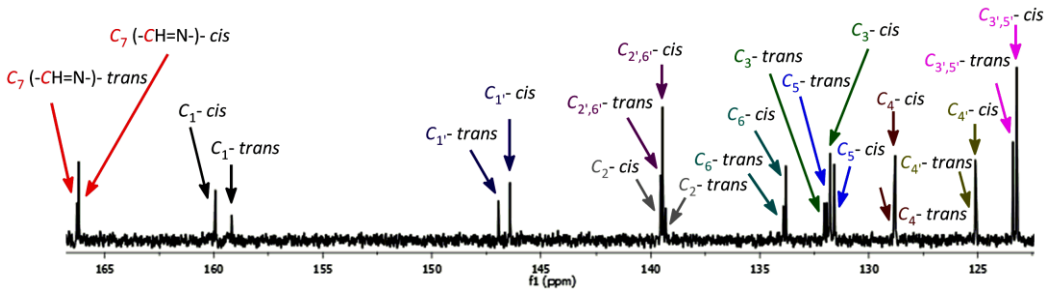



**Figure 12.** $^{1}$H NMR ($CDCl_3$, 500 MHz, r.t.) spectrum of **10**.




(aliphatic region)




(aromatic region)

**Figure 13.** $^{13}$C NMR ($CDCl_3$, 500 MHz, r.t.) spectrum of **10**.

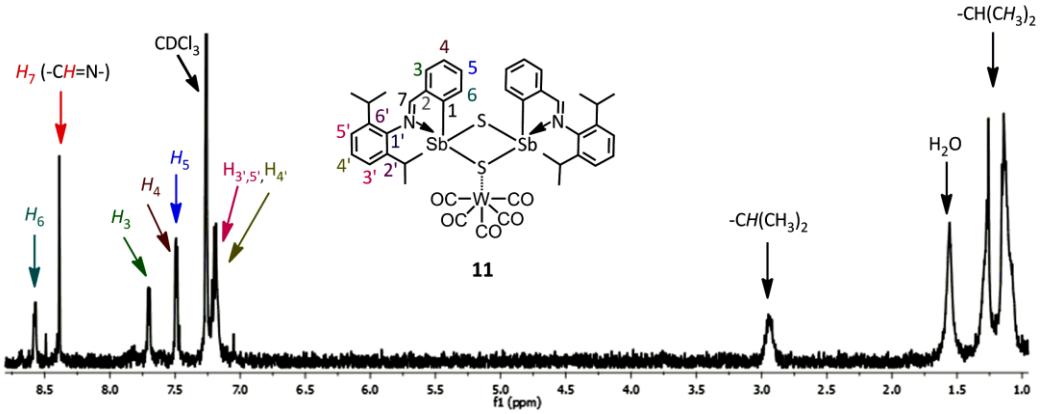



**Figure 14.** $^1$H NMR ($CDCl_3$, 300 MHz, r.t.) spectrum of complex *cis-cyclo*-[$(RSbS)_2W(CO)_5$] (**11**).

The room temperature $^1$H NMR spectrum of **16** (**Figure 17**) shows in the aliphatic region a singlet resonance, corresponding to the methyl protons ($\delta$ 2.07 ppm), and an AB spin system with A at 3.40 and B at 3.95 ppm for the methylene protons. As for the starting material **15**, the presence of only one set of signals indicates the equivalence of the organic ligands in solution due to a fast dynamic behavior.

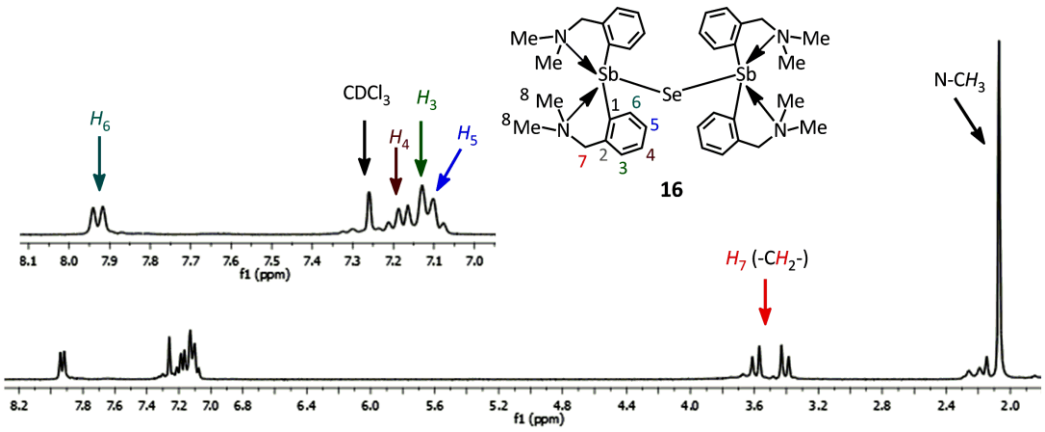



**Figure 17.** $^1$H NMR ($CDCl_3$, 300 MHz, r.t.) spectrum of $(R''_2Sb)_2Se$ (**16**).

The presence of only one singlet resonance in the $^{77}$Se spectrum ($\delta$ –179.89 ppm) (**Figure 19**) is consistent with the presence of one selenium-containing species, *i.e.* the bis(diorganoantimony)selenide **16**, in solution.

The assignment of the resonances in the $^1$H and $^{13}$C NMR spectra of compound **13**, **15** and **16** was based on the bidimensional H-H (COSY) and H-C (HSQC, HMBC) experiments.

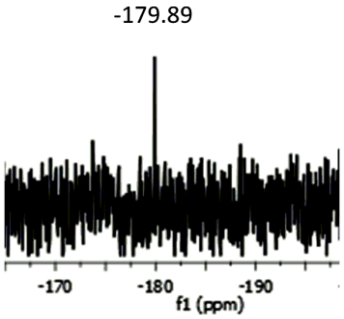



**Figure 19.** $^{77}$Se NMR ($CDCl_3$, 57.26 MHz, r.t.) spectrum of $(R''_2Sb)_2Se$ (**16**)

### *III.B.6. Single–crystal X–ray diffraction studies*

The chalcogenides $[\{2\text{-}((2',6'\text{-}Pr^i_2C_6H_3)N{=}CH)C_6H_4\}_2Sb]_2S$ (**7**), $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Sb]_2O$ (**15**)[63] and $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Sb]_2Se$ (**16**) crystallize in the monoclinic space group *C*2/*c*. A first molecular structure determination of the oxide **15** has been already reported.[76] In all cases the crystals contain discrete molecules, with distances between heavy atoms larger than the sum of the corresponding van der Waals radii.

In the molecule of sulfide **7** (**Figure 20**) only one of the organic groups 2-[(2',6'-$^iPr_2C_6H_3$)N=CH]$C_6H_4$ per metal atom acts as a bidentate chelating ligand, its nitrogen atom being coordinated to antimony *trans* to the Sb(1)-S(1) bond [N(1)-Sb(1)-S(1) 166.14(3)°].

The strength of the nitrogen-antimony interaction *trans* to the chalcogen atom in **7** [Sb(1)-N(1) 2.6162(17) Å] is stronger than in the oxide **15** [Sb(1)-N(1) 2.775(5) Å] or in the selenide **16** [Sb(1)-N(1) 2.8333(36) Å]. The [Sb(1)-N(1) bond distance in **7** is also shorter than in the related sulfide $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Sb]_2S$ [Sb(1)-N(1) 2.855(3) Å].[63]

This contrasts to the situation observed in the molecules of the chalcogenides **15** (**Figure 21**) and **16** (**Figure 22**) in which all the 2-$(Me_2NCH_2)C_6H_4$ groups act as bidentate *C,N*-chelating ligands with intramolecular N→Sb interactions *trans* to the Sb(1)-O(1) and Sb(1)-C(1) bonds [N(1)-Sb(1)-O(1) 161.32(12)°; C(1)-Sb(1)-N(2) 157.85(17)°] (for **15**) and Sb(1)-Se(1) and Sb(1)-C(1) bonds [N(1)-Sb(1)-Se(1) 160.23(8)°; C(1)-Sb(1)-N(2) 163.61(12)°] (for **16**), respectively. The internal N(2)→Sb(1) interactions *trans* to the C(1) atom are considerably longer [Sb(1)-N(2) 3.240(4) Å in **15**;[63] Sb(1)-N(2) 3.0671(42) Å in **16**] than the N(1)→Sb(1) interactions, but however they lie between the sums of the corresponding covalent [$\Sigma r_{cov}$(Sb,N) 2.11 Å] and van der Waals radii [$\Sigma r_{vdW}$(Sb,N) 3.74 Å].[28]

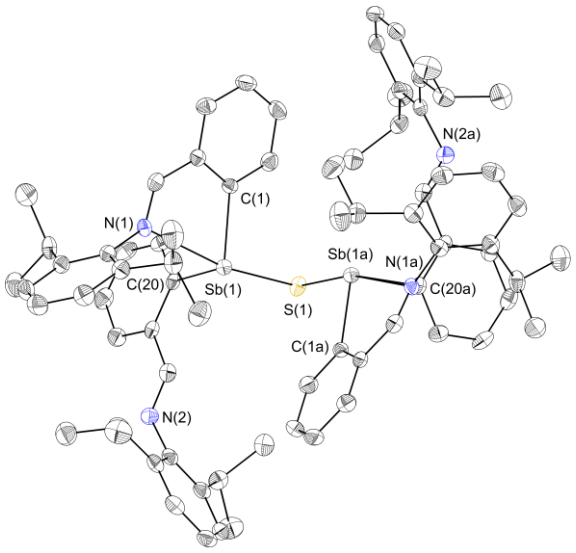



**Figure 20.** ORTEP representation at 50% probability and atom numbering scheme for ($C_{Sb1}$/$C_{Sb1a}$)−**7** isomer [symmetry equivalent atoms (–*x*, *y*, 0.5 – *z*) are labelled with "a"] Hydrogen atoms are omitted for clarity.

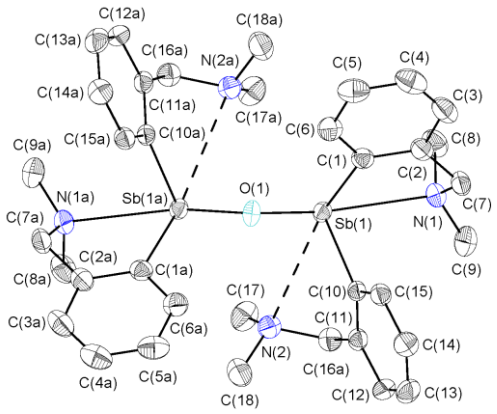



**Figure 21.** ORTEP representation at 30% probability and atom numbering scheme for ($S_{N1}$,$R_{N2}$,$A_{Sb1}$/$S_{N1a}$,$R_{N2a}$,$A_{Sb1a}$)−**15** isomer [symmetry equivalent atoms (–*x*, *y*, 0.5 – *z*) are labelled with"a"]. Hydrogen atoms are omitted for clarity.

In the case of compounds **15** and **16**, if both intramolecular N→Sb interactions per metal are taken into account, the geometry around each antimony atom is distorted square pyramidal [(*C,N*)$_2$SbE core; hypervalent 12-Sb-5 species[70,71]], with the C(10) atom in the apical position and the C(1), the chalcogen and the two nitrogen atoms describing the basal plane.

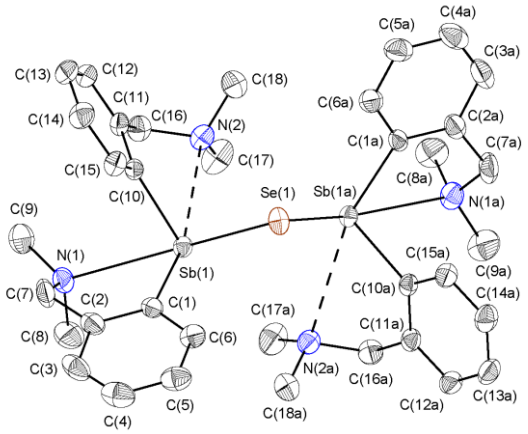



**Figure 22.** ORTEP representation at 30% probability and atom numbering scheme for ($S_{N1}$,$R_{N2}$,$A_{Sb1}$/$S_{N1a}$,$R_{N2a}$,$A_{Sb1a}$)−**16** isomer [symmetry equivalent atoms (*–x*, *y*, 0.5 – *z*) are labelled with "a"]. Hydrogen atoms are omitted for clarity.

The crystals of the cyclic sulfides **8** and **9** consist of a 1:1 racemic mixture of dinuclear units of *trans-cyclo*-($C_{Sb1}$/$A_{Sb1a}$) and *trans-cyclo*-($A_{Sb1}$/$C_{Sb1a}$) isomers. The molecular structures of isomers *trans-cyclo*-($C_{Sb1}$/$A_{Sb1a}$)-**8** and *trans-cyclo*-($C_{Sb1}$/$A_{Sb1a}$)-**9** are depicted in **Figure 23** and **Figure 24**, respectively.

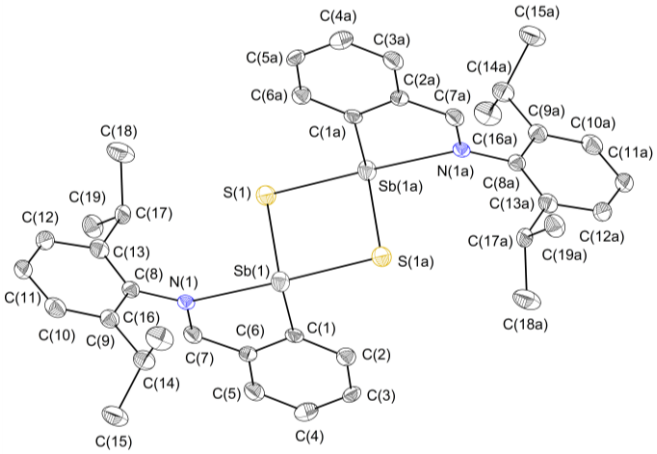



**Figure 23.** ORTEP representation at 50% probability and atom numbering scheme for *trans-cyclo*-($C_{Sb1}$/$A_{Sb1a}$)-**8** isomer [symmetry equivalent atoms (–x, –y, 2 – z) are labelled with "a"]. Hydrogen atoms are omitted for clarity.

Within the $Sb_2S_2$ ring the antimony-sulfur bond distances are different, *i.e.* Sb(1)-S(1a) bond distance [2.527(9) Å in **8** and 2.553(10) Å in **9**] being longer in comparison with the Sb(1)-S(1) bond [2.417(10) Å in **8** and 2.402(9) Å in **9**]. In both compounds there is a strong coordination of the nitrogen from the pendant arm to each antimony atom [Sb(1)-N(1) 2.558(2) Å in **8**, and 2.553(2) Å in **9**] *trans* to a sulfur atom [N(1)-Sb(1)-S(1a) 161.56(6)° in **8**, and 161.88(6)° in **9**]. The resulting $SbC_3N$

ring is basically planar, with deviations less than 0.1 Å for the nitrogen atom from the remaining best $SbC_3$ plane.

The aryl substituents occupy *trans* positions with respect to the central, planar four-membered $Sb_2S_2$ ring, with endocyclic angles on the antimony and sulfur atoms closed to 90° [Sb(1)-S(1)-Sb(1a) 90.92(3) and S(1)-Sb(1)-S(1a) 89.08(3)° for **8**; Sb(1)-S(1)-Sb(1a) 91.31(3) and S(1)-Sb(1)-S(1a) 88.69(3)° for **9**]. The transannular Sb(1)···Sb(1a) non–bonding distances [3.525(4) Å in **8**; 3.530(4) Å in **9**] are almost similar to that found in *trans-cyclo*-[{2-$(Me_2NCH_2)C_6H_4$}SbS]$_2$ [Sb(1)···Sb(1a) 3.549(5) Å].[43]

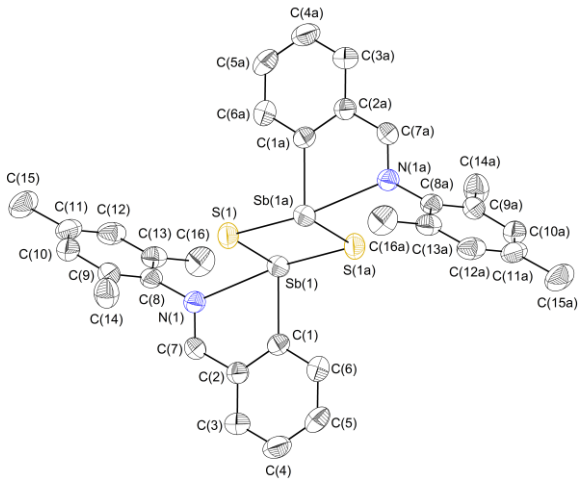



**Figure 24.** ORTEP representation at 50% probability and atom numbering scheme for *trans-cyclo*-($C_{Sb1}$/$A_{Sb1a}$)-**9** isomer [symmetry equivalent atoms (1–x, 1–y, –z) are labelled with "a"]. Hydrogen atoms are omitted for clarity.

## *III.B.7. Conclusions*

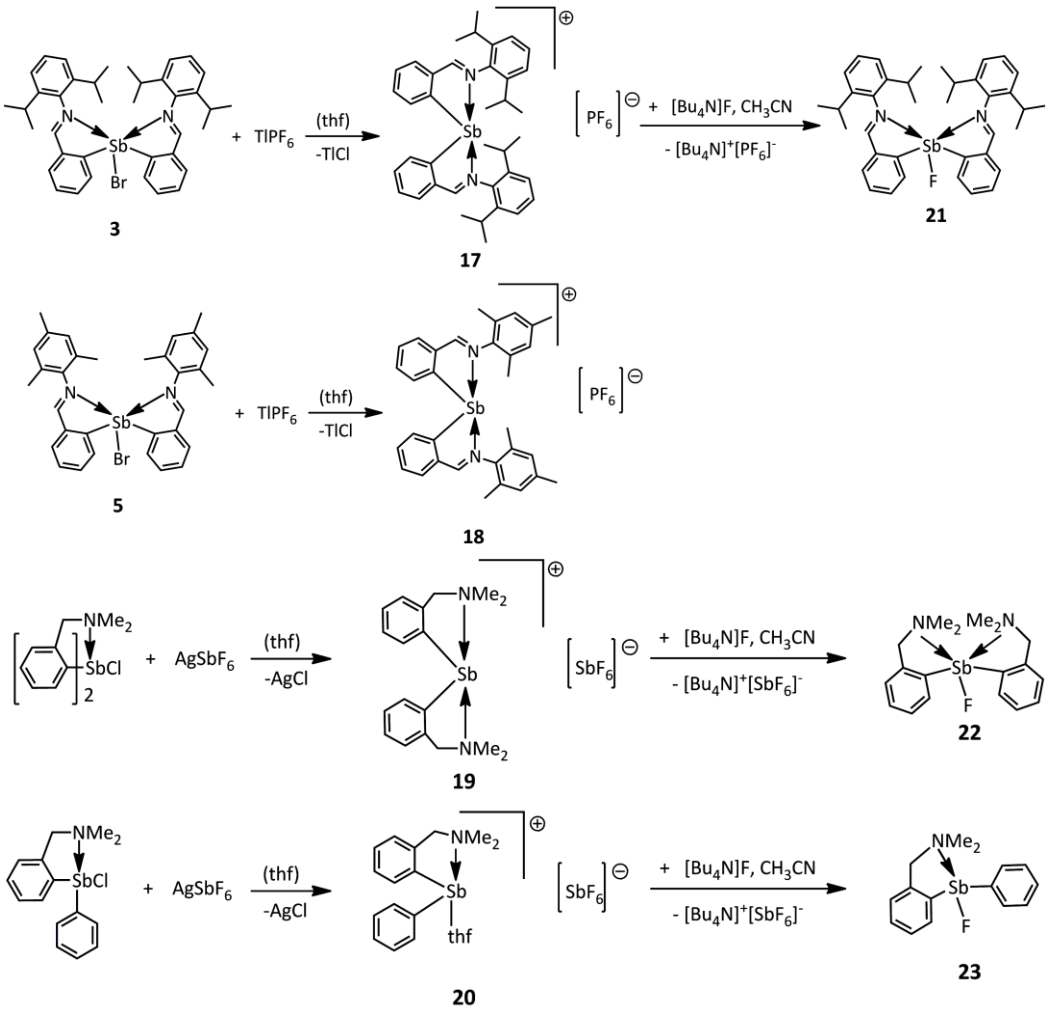
- New organoantimony(III) sulfides, with ligands containing nitrogen atom able to coordinate intramolecularly through N→Sb, and some of their metalcarbonyl complexes were obtained and structurally characterized both in solution and in solid state.
- The intramolecular N→Sb coordination induces chirality at the antimony atom.
- For the chalcogenides **7**, **8** and **13** the presence of the broad pattern of the resonance for methyl protons of the isopropyl groups suggests a fluxional behavior at room temperature in solution, *i.e.* dissociation – re-coordination of the nitrogen to antimony.
- In the case of the oxide **10** and selenide **13** the NMR data are indicative for two sets of signals with an integral ratio of 2:1, suggesting the formation of a trimer, *cis-trans*-$(RSbE)_3$. The presence in solution of both *cis* and *trans* isomers was assumed in the case of disulfides **8** and **9**.

## III.C. Ionic organoantimony(III) derivatives containing ligands with pendant arms and their corresponding fluorides

### III.C.2. Preparation

The monobromides $R_2SbBr$ (**3**) and $R'_2SbBr$ (**5**) [R = 2-{(2',6'-$Pr^i_2C_6H_3$)N=CH}$C_6H_4$; R' = 2-{(2',4',6'-$Me_3C_6H_2$)N=CH}$C_6H_4$] reacts with Tl[$PF_6$] in THF, at room temperature, to give the cationic diorganoantimony species [{2-((2',6'-$Pr^i_2C_6H_3$)N=CH)$C_6H_4$}$_2$Sb]$^+$[$PF_6$]$^-$ (**17**) and [{2-((2',4',6'-$Me_3C_6H_2$)N=CH)$C_6H_4$}Sb]$^+$[$PF_6$]$^-$ (**18**) compounds. Also the monochlorides R''$_2$SbCl and R''PhSbCl [R'' = 2-($Me_2NCH_2$)$C_6H_4$] were reacted with Ag[$SbF_6$] to give [{2-($Me_2NCH_2$)$C_6H_4$}$_2$Sb]$^+$[$SbF_6$]$^-$ (**19**) and [{2-($Me_2NCH_2$)$C_6H_4$}PhSb]$^+$[$SbF_6$]$^-$ (**20**) as shown in **Scheme 5**. The diorganoantimony(III) cation [{2-($Me_2NCH_2$)$C_6H_4$}$_2$Sb]$^+$ has already been reported.[82]

The treatment of the ionic compounds **17**, **19** and **20** with [$Bu_4N$]F·3$H_2O$ in acetonitrile, at room temperature, leads to the formation of the corresponding organoantimony(III) fluorides, [2-{(2',6'-$Pr^i_2C_6H_3$)N=CH}$C_6H_4$]$_2$SbF (**21**), [2-($Me_2NCH_2$)$C_6H_4$]$_2$SbF (**22**) and [2-($Me_2NCH_2$)$C_6H_4$]PhSbF (**23**).




**Scheme 5.** Preparation of ionic organoantimony(III) complexes and their corresponding fluorides.

### III.C.5. NMR spectroscopy

The solution behavior of the ionic organoantimony(III) compounds **17**, **18**, **20**, and the fluorides **21–23** was investigated by NMR spectroscopy.

The $^{1}$H NMR spectrum of compound **17** (**Figure 26**), measured in $CDCl_3$, at room temperature, exhibits in the aliphatic region four doublet resonances for the methyl protons of the isopropyl groups ($\delta$ 1.17, 1.38, 1.42, 1.51 ppm) and two heptet resonances for the methine protons of the isopropyl groups ($\delta$ 3.03 and 3.29 ppm). This is consistent with non-equivalent isopropyl groups and diastereotopic behavior. The aromatic region shows the expected resonances for the aromatic protons and contains only one singlet resonance corresponding to the iminic protons, –C*H*=N–, which is significantly downfield shifted ($\delta$ 8.93 ppm).

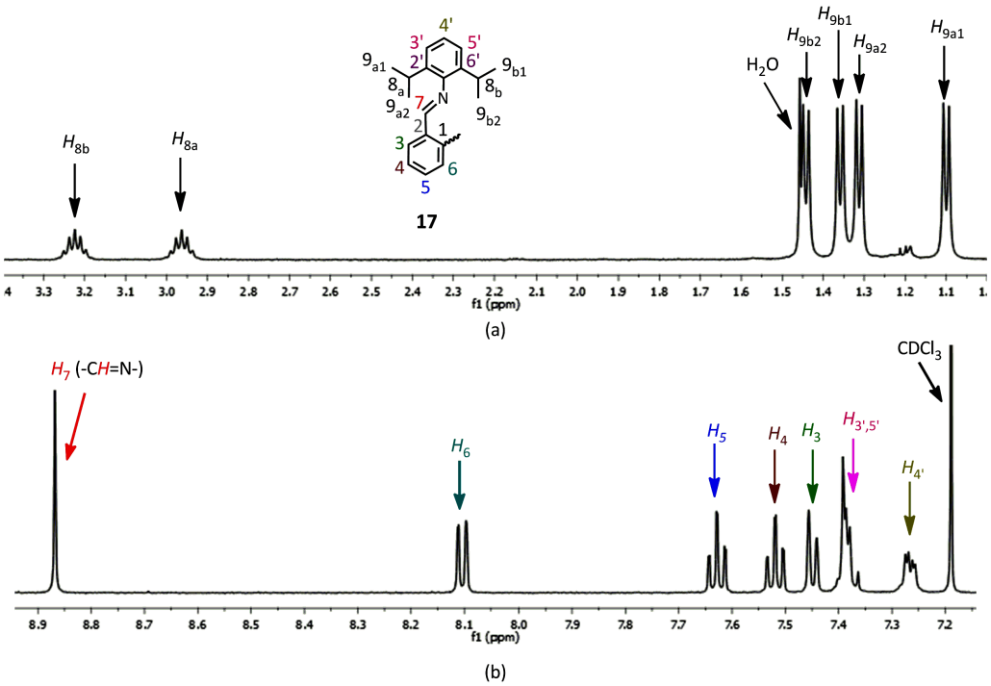



**Figure 26.** $^{1}$H NMR ($CDCl_3$, 500 MHz, r.t.) spectrum of complex **17**: aliphatic part (a) and aromatic part (b).

The $^{1}$H NMR spectrum of **18** displays in the aliphatic region two singlet resonances corresponding to the protons of the methyl groups placed in *orto* ($\delta$ 2.44 ppm) and *para* ($\delta$ 2.37 ppm) position of the mesityl moiety. Also the aromatic region of the spectrum contains the expected resonances for the aromatic protons. The most downfield shift was observed for the resonance corresponding to the iminic proton –C*H*=N– ($\delta$ 8.93 ppm

The $^{31}$P NMR spectra (**Figure 28**) of the ionic compounds described here exhibits a heptet resonance centered at $\delta$ –144.29 ppm ($^{1}J_{P,F}$ = 713.3 Hz) for **17**, and $\delta$ –144.32 ppm ($^{1}J_{P,F}$ = 713.0 Hz) for **18**, due to phosphorus-fluorine spin coupling.

In the $^{19}$F NMR spectra of compound **17** and **18** (**Figure 29**) the equivalence of the six fluorine atoms and their coupling with the phosphorous results in a doublet signal at $\delta$ –72.97 ppm ($^{1}J_{F,P}$ = 713.0 Hz) for **17**, and $\delta$ –72.80 ppm ($^{1}J_{F,P}$ = 713.1 Hz) for **18**.

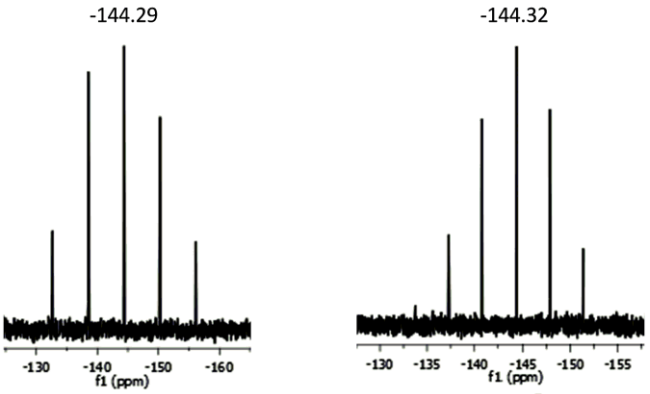



**Figure 28.** $^{31}P$ NMR spectra ($CDCl_3$, 202 MHz, r.t.) of complexes **17** (left) and **18** (right).

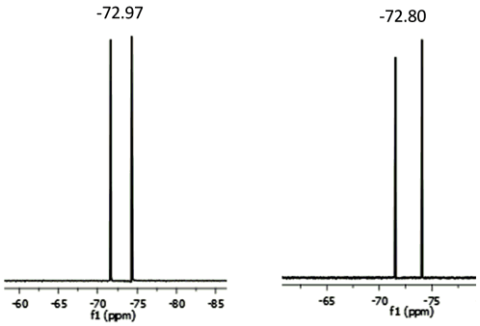



**Figure 29.** $^{19}F$ NMR spectra ($CDCl_3$, 282.2 MHz, r.t.) of complexes **17** (left) and **18** (right)

The room temperature $^{1}H$ NMR spectrum of compound **20** [**Figure 30** (a)] contains two singlets resonances for the protons of the methyl groups ($\delta$ 2.52 and 2.81 ppm) and an AB spin system with A at 3.96 and B at 4.05 ppm for the methylene protons. This is consistent with the coordination of nitrogen to antimony. in solution as observed in the solid state (see subsequent discussion). The presence of two multiplets resonances which belongs to the protons of an (THF) group indicates that a molecule of THF is coordinated to the antimony atom. The $^{13}C$ NMR spectrum of **20** [**Figure 30** (b)] shows the expected number of signals for the carbons in the aliphatic and aromatic region, *i.e.* three carbon resonances which belong to the methyl (two signals) and methylene (one signal) groups and ten singlet resonances for the aromatic carbons. The $^{19}F$ spectrum of the ionic compound **20** consists of a sharp singlet resonance at $\delta$ –125.00 ppm.

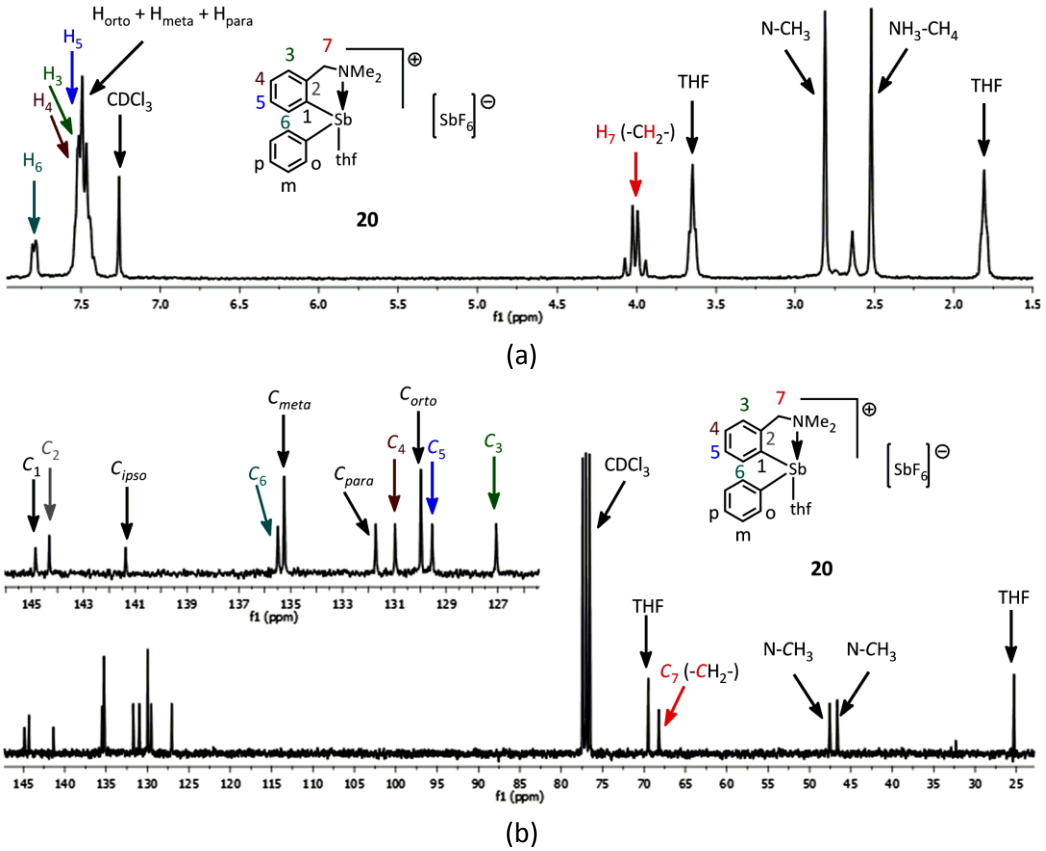



**Figure 30.** (a) $^{1}$H NMR, and (b) $^{13}$C NMR ($CDCl_3$, 300 MHz, r.t.) spectra of **20**.

The aliphatic region of the $^{1}$H NMR spectrum (in $CDCl_3$) of fluoride **22** shows a singlet resonance for the $NMe_2$ protons ($\delta$ 2.21 ppm) and an AB spin system with A at $\delta$ 3.50 and B at $\delta$ 3.69 ppm, for the $CH_2$ protons. The aromatic region exhibits the resonances expected for the aromatic protons (**Figure 32**). The $^{13}$C NMR spectrum contains all the expected singlet resonances, *i.e.* two singlet resonances which were assigned for the aliphatic carbons and six singlet resonances which were assigned to the aromatic carbons. The coupling of the fluorine with $C_6$ results in a doublet signal at $\delta$ 135.08 ($^{3}J_{CF}$ = 3.9 Hz).

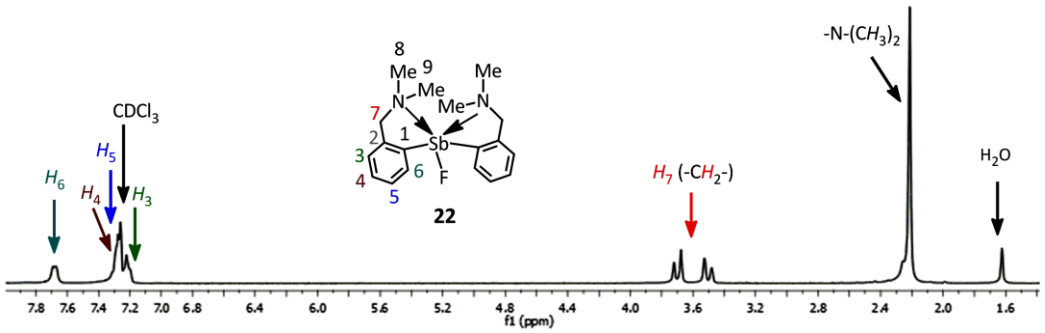
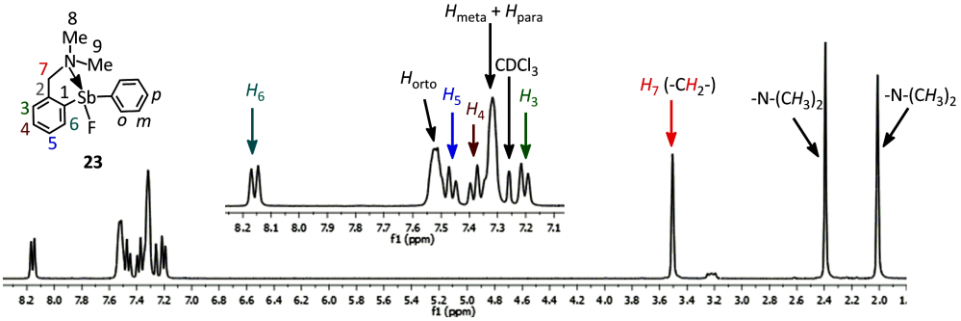



**Figure 32.** $^{1}$H NMR ($CDCl_3$, 300 MHz, r.t.) spectrum of $R''_2SbF$ (**22**).

The $^{1}$H NMR spectrum of the fluoride **23** [**Figure 33** (a)] at room temperature exhibits in the aliphatic region two sharp singlet resonances which were assigned to the non-equivalent $NMe_2$ protons ($\delta$ 2.01 and 2.39 ppm) and a sharp singlet for the $CH_2$ protons ($\delta$ 3.50 ppm). The aromatic region showed the expected resonances corresponding to the $C_6H_4$ and pheny protons, respectively.




(a)

**Figure 33.** $^{1}$H (a) and $^{13}$C (b) NMR ($CDCl_3$, 300 MHz, r.t.) spectra of R''PhSbF (**23**).

The $^{13}$C NMR spectrum for the fluoride **23** shows all the expected carbon resonances for the both aliphatic and aromatic carbons. In the case of $C_1$ ($\delta$ 148.14 ppm, $^{2}J_{CF}$ = 7.7 Hz) and $C_6$ ($\delta$ 135.07 ppm, $^{3}J_{CF}$ = 6.9 Hz) from the pendant arm-containing organic ligand and also for the $C_{ipso}$ (δ 146.92ppm, $^{2}J_{CF}$ = 10.1 Hz) of the phenyl ring doublet resonances were observed due to carbon-fluorine spin coupling.

The $^{19}$F spectra of fluorides **22** and **23** consist of a sharp singlet resonance at δ –176.90 ppm for **22**, and $\delta$ –169.17 ppm for **23**.

### *III.C.6. Single–crystal X–ray diffraction studies*

Single crystal, suitable for X-ray crystallography, were obtained by slow diffusion of *n*-hexane into solution of $CH_2Cl_2$ (3:1 v/v) at −28 °C for [{2-((2',6'-$Pr^{i}_2C_6H_3$)N=CH)$C_6H_4$}$_2$Sb]$^+$[$PF_6$]$^-$ (**17**), and by slow evaporation of a chloroform solution of [{2-((2',4',6'-$Me_3C_6H_2$)N=CH)$C_6H_4$}Sb]$^+$[$PF_6$]$^-$ (**18**). The ionic compounds **17** and **18** crystallize in the monoclinic space group $P2_1/c$ and triclinic *P*-1 space group, respectively. The crystals contain the corresponding diorganoantimony(III) cations and hexafluorophosphate anions. The structures of compounds **17** and **18** are depicated in **Figure 35** and **Figure 36**, respectively.

In the cation both nitrogen atoms are coordinated to antimony, in an almost *trans* arrangement [N(1)-Sb(1)-N(2) 159.69(11)° for **17**; 155.02(16)° for **18**] with nitrogen-antimony bond distances [N(1)-Sb(1) 2.351(3) Å for **17**; 2.365(4) Å for **18**, and N(2)-Sb(1) 2.365(3) Å for **17**; 2.394(4) Å for **18**] shorter than those found in the related derivative [2-{($Me_2NCH_2$)$C_6H_4$}$_2$Sb]$^+$[$PF_6$]$^-$ [Sb-N 2.414(4) Å][82] or in the bromide precursor [2-{(2',6'-$^{i}Pr_2C_6H_3$)N=CH}$C_6H_4$]$_2$SbBr (**3**) [Sb-N 2.498(4) / 2.996(7) Å], due to the more electrophilic nature of the antimony in the cation.

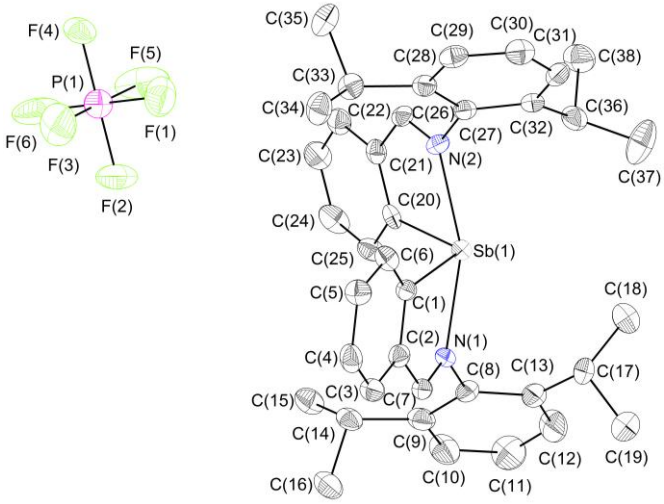



**Figure 35.** ORTEP representation at 50% probability and atom numbering scheme for $\Lambda_{Sb}$-**17** isomer. Hydrogen atoms are omitted for clarity.

The coordination geometry at antimony is *pseudo*-trigonal bipyramidal with the two *ipso* carbon atoms placed in equatorial positions; [C(1)-Sb(1)-C(20) 105.00(14)° for **17**, and C(1)-Sb(1)-C(17) 102.8(2)° for **18**].

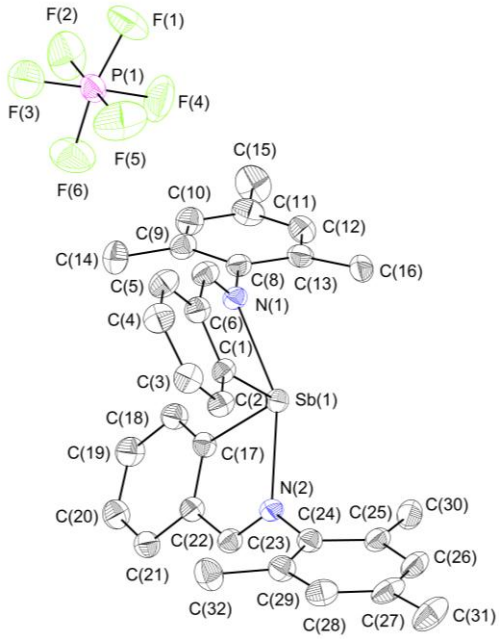



**Figure 36.** ORTEP representation at 50% probability and atom numbering scheme for $\Delta_{Sb}$-**18** isomer. Hydrogen atoms are omitted for clarity.

The molecular structure of the chiral diorganoantimony(III) fluoride [2-($Me_2NCH_2$)$C_6H_4$]PhSbF (**23**) was also determined by single-crystal X−ray diffraction studies and shows that a monomer is formed (**Figure 39**).

The nitrogen atom of the pendant arm is strongly coordinated to the antimony atom, *trans* to the halogen atom [N(1)−Sb(1)−F(1) 161.48(9)°]. The value of the intramolecular interaction [Sb(1)−N(1) 2.526(3) Å] distance lie between the sums of the respective covalent [$\Sigma r_{cov}$(Sb,N) 2.11 Å] and van der Waals radii [$\Sigma r_{vdW}$(Sb,N) 3.74 Å][28] and is longer than the Sb(1)−N(1) bond distances found in the related halides [2-($Me_2NCH_2$)$C_6H_4$]PhSbX [Sb(1)−N(1) 2.453(4) Å (X = Cl); 2.443(4) Å (X = Br); 2.425(3) Å (X = I)].[62]

The geometry around antimony atom is distorted *pseudo*−trigonal bipyramidal, (*C,N*)SbCX core, with the two carbon atoms placed in equatorial positions, while the halogen and the nitrogen atoms are situated in the axial positions. The compound can be described as a hypervalent 10-Sb-4 species.[70,71]

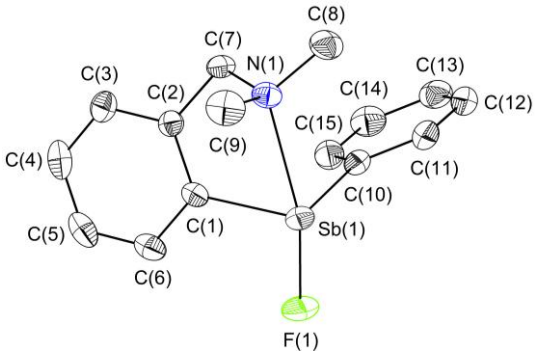



**Figure 39.** ORTEP representation at 30% probability and atom numbering scheme for ($R_N$,$A_{Sb}$)-**23** isomer. Hydrogen atoms are omitted for clarity.

As a consequence of the non-planar chelate $SbC_3N$ ring and due to the chirality induced at the antimony centre, the compound **23** crystallizes as a racemate, *i.e.* 1:1 mixture of ($R_N$,$A_{Sb}$) and ($S_N$,$C_{Sb}$) isomers.

## *III.C.7. Conclusions*

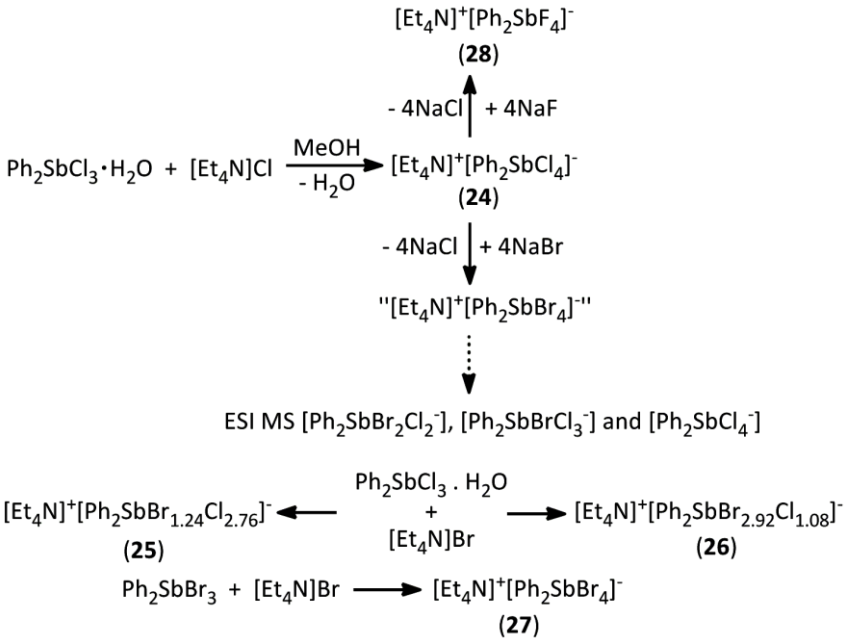
- A new method for the preparation of diorganoantimony(III) fluorides was established. It is based on ionic derivatives, *i.e.* diorganoantimony(III) cations stabilized by intramolecular N→Sb interactions.
- The diorganoantimony(III) cations exhibit helical chirality, due to the intramolecular N→Sb interactions.
- The intramolecular N→Sb interactions induce chirality at the metal centre in the monofluorides **21**–**23**.
- For the chiral fluorides the presence of the intramolecular N→Sb interaction in solution, at room temperature, was proved by NMR studies.

## III.D. Ionic organoantimony(V) derivatives (Ammonium diphenyltetrahaloantimonates)

### III.D.2. Preparation

Compound $[Et_4N]^+[Ph_2SbCl_4]^-$ (**24**) was synthesized by reacting diphenylantimony trichloride with $[Et_4N]Cl$, in methanol. When the reaction between onium bromides and $Ph_2SbCl_3$ is performed in acetonitrile, mixtures of chloro/bromo derivatives are obtained. These mixtures are obtained due to scrambling of halogens. From such mixtures of compounds crystals of $[Et_4N]^+[Ph_2SbBr_{1.24}Cl_{2.76}]^-$ (**25**) and $[Et_4N]^+[Ph_2SbBr_{2.92}Cl_{1.08}]^-$ (**26**) were isolated. Attempts to complete the exchange of halogen by reacting the crude $[Et_4N]^+[Ph_2SbBr_nCl_{4-n}]^-$ (n = 0 – 4) with NaBr had failed. The pure $[Et_4N]^+[Ph_2SbBr_4]^-$ (**27**) was synthesised by the reaction of $[Et_4N]Br$ with $Ph_2SbBr_3$, in acetonitrile.[107]

However, the full exchange of halogen was achieved when $[Et_4N]^+[Ph_2SbCl_4]^-$ (**24**) was reacted with NaF and the tetrafluoroantimonate $[Et_4N]^+[Ph_2SbF_4]^-$ (**28**) was obtained. The reactions between $Et_4ECl$ and $R_2SbCl_3$ are straight forward with the transfer of the chloride ion from the ammonium compound to the Lewis acidic diorganoantimony(V) trichloride (**Scheme 6**).[107]




**Schema 6.** Preparation of ionic organoantimony(V) compounds.

The pure tetrahaloantimonates **24**, **27** and **28** were isolated as air stable, colorless crystalline solids which are thermally stable and melt without decomposition. Due to their ionic nature the compounds were soluble in DMSO and in solid state they are stable to hydrolysis and oxidation. All compounds were characterized by spectroscopic methods (NMR, MS) and the crystal and molecular structures were determined by single-crystal X-ray diffraction studies.

### III.D.3. Mass spectrometry

Mass spectra obtained with the electrospray ionization technique (ESI) show the cation and the anion for these compounds. In the ESI(+) mass spectra of compounds **24–28** was observed the peak which corresponds to the molecular cation [$Et_4N^+$] (*m/z* 130). In the ESI(-) mass spectra of compounds **24**, **27** and **28** could be observed the corresponding anions at the value (*m/z* 417) assigned to the [$Ph_2SbCl_4^-$] (for **24**), (*m/z* 595) assigned to the [$Ph_2SbBr_4^-$] (for **27**) and (*m/z* 351) assigned to the [$Ph_2SbF_4^-$] (for **28**). For the crude product isolated from the reaction of $Et_4NBr$ with $Ph_2SbCl_3{\cdot}H_2O$ the ESI(-) MS data are consistent with mixture of chloro / bromo derivatives, several anions being observed, *e.g.* [$Ph_2SbBr_2Cl_2^-$], [$Ph_2SbBrCl_3^-$] and [$Ph_2SbCl_4^-$].

### III.D.4. NMR spectroscopy

The $^1$H- and $^{13}$C-NMR spectra of **24–28** and the $^{19}$F-NMR spectrum of **28** were obtained from solutions in DMSO, at room temperature. They show the expected signals for the respective nuclei of the cations and anions, according to the *trans*-$R_2SbCl_4$ model for the anions, which implies equivalence of the R groups. The $^{14}$N isotope has a quadrupole nucleus with I = 1.[108] As a result there are three spin states for this nucleus and the coupling with $^{14}$N will split a signal of another atom into a triplet.[109] The $^1$H NMR spectra of all onium salts show in the aliphatic region a triplet of triplets (**Figure 40**) resonance which corresponds to the methyl protons of the ethyl group ($\delta$ 1.13 ppm, $^3J_{NH}$ = 1.8 Hz for **24**; $\delta$ 1.14 ppm, $^3J_{NH}$ = 1.7 Hz for **27**; $\delta$ 1.11 ppm, $^3J_{NH}$ = 1.5 Hz for **28**) and a quartet resonance which corresponds to the methylene protons of the ethyl group ($\delta$ 3.15 ppm, $^3J_{NH}$ = 7.1 Hz for **24**; $\delta$ 3.20 ppm, $^3J_{NH}$ = 7.3 Hz for **27**; $\delta$ 3.14 ppm, $^3J_{NH}$ = 7.2 Hz for **28**). The aromatic region of the $^1$H NMR spectrum exhibits the expected number and pattern of resonances.

In the NMR spectra of some quaternary ammonium compounds, including a series of heterocyclic cations, spin-spin coupling between $^{14}$N and $^{13}$C nuclei was also observed. The $^1J_{NC}$ values are found in the range 2.2–3.4 Hz.[110] The $^{13}$C resonance of the carbon bonded to nitrogen in [$Et_4N]^+$ ions appears as a well resolved triplet signal due to the coupling with the $^{14}$N nucleus. The aliphatic region exhibit a singlet resonance for the methyl carbons and a triplet resonance of the methylene carbons ($\delta$ 51.28 ppm, $^1J_{NC}$ = 2.9 Hz for **24**; $\delta$ 51.29 ppm, $^1J_{NC}$ = 3.0 Hz for **27**; $\delta$ 51.30 ppm, $^1J_{NC}$ = 3.0 Hz for **28**), see **Figure 41**. The aromatic region shows all the expected resonances for the phenyl carbons.

The $^{19}$F spectrum of fluoride **28** consists of a sharp singlet resonance at δ –103.16 ppm for the [$Ph_2SbF_4]^-$ anion.

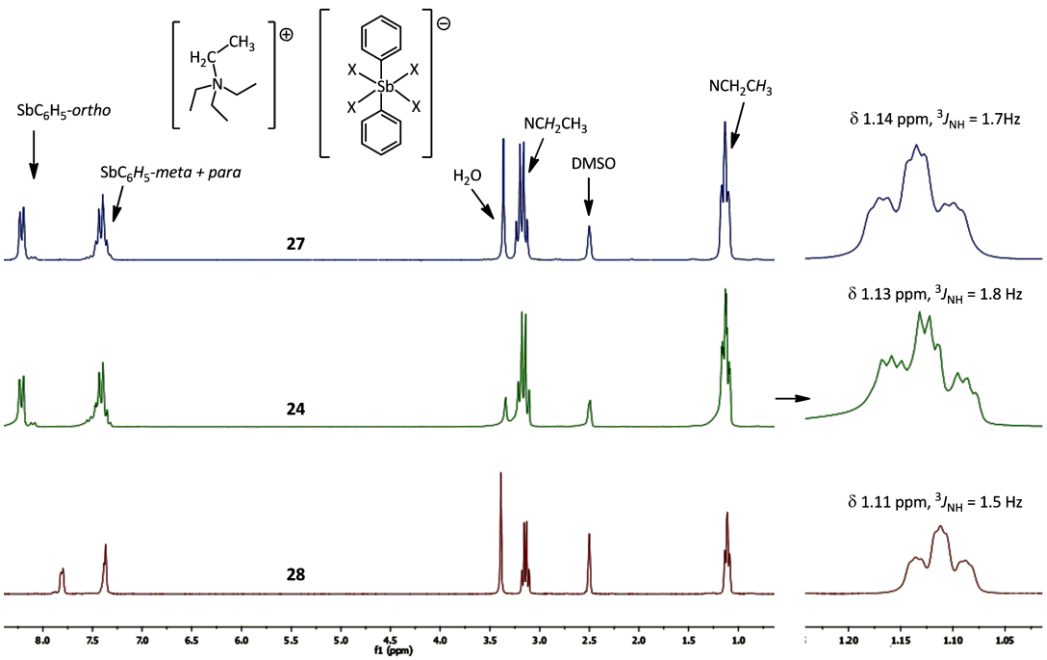



**Figure 40.** $^{1}$H NMR (DMSO, 200 MHz, r.t.) spectra of $[Et_4N]^+[Ph_2SbF_4]^-$ (**28**), $[Et_4N]^+[Ph_2SbCl_4]^-$ (**24**) and $[Et_4N]^+[Ph_2SbBr_4]^-$ (**27**).

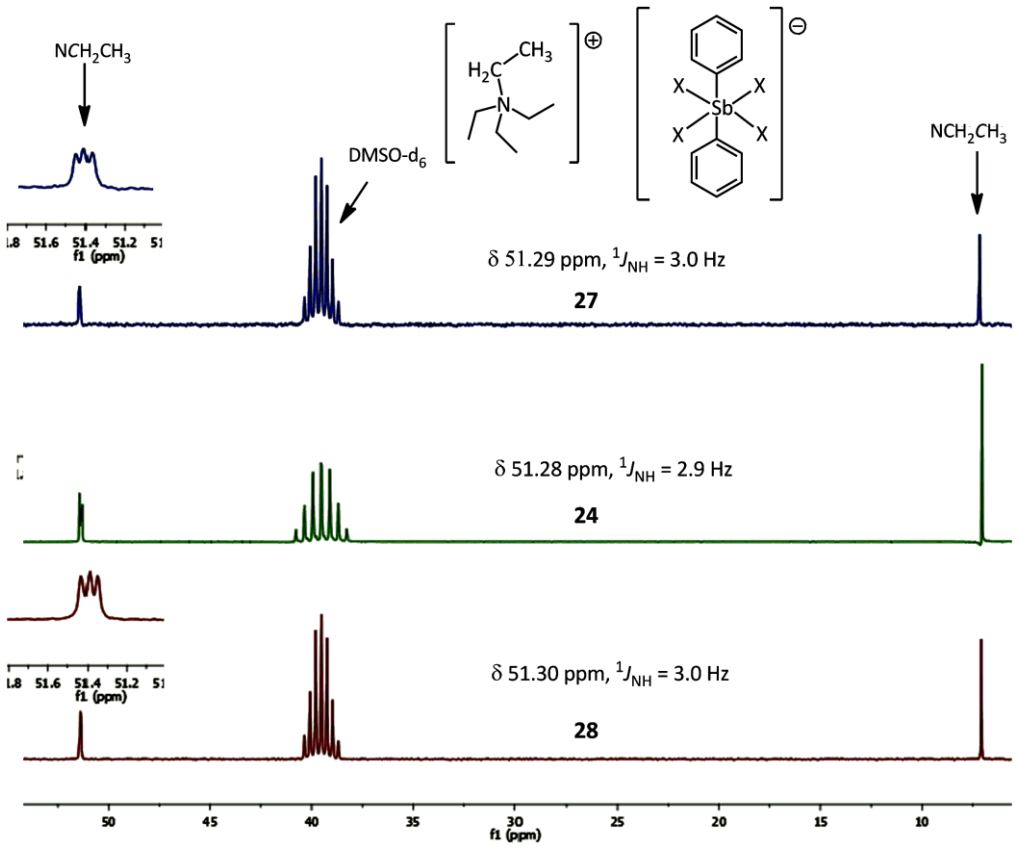



**Figure 41.** $^{13}$C NMR (DMSO, 200 MHz, r.t.) spectra (aliphatic region) of $[Et_4N]^+[Ph_2SbF_4]^-$ (**28**), $[Et_4N]^+[Ph_2SbCl_4]^-$ (**24**) and $[Et_4N]^+[Ph_2SbBr_4]^-$ (**27**).

### *III.D.5. Single–crystal X–ray diffraction studies*

Single crystals suitable for X-ray diffraction studies were obtained from acetonitrile solutions by slow evaporation, at room temperature, in an open atmosphere, for compounds **24**–**28**.

As representative examples the structures of $[Et_4N]^+[Ph_2SbCl_4]^-$ (**24**) and $[Et_4N]^+[Ph_2SbF_4]^-$ (**28**) are depicted in **Figures 43** and **45**. The relevant interatomic distances and angles are listed in **Table 10** (for compounds **25** and **26**). For the mixed-halogen compounds, *i.e.* $[Et_4N]^+[Ph_2SbBr_{1.24}Cl_{2.76}]^-$ (**25**) and $[Et_4N]^+[Ph_2SbBr_{2.92}Cl_{1.08}]^-$ (**26**), there was disorder involving the bromine or chlorine atoms. The best solution was obtained with Br/Cl occupancy of 0.31/0.69 for **25** and 0.73/0.27 for **26**, respectively. Disorder phenomena were also observed for the $[Et_4N]^+$ cation in the corresponding salts **24**–**28**.

All the salts are composed of tetrahedral onium cations and octahedral anions. In all cases, regardless the nature of the halogen, the phenyl groups in the $[R_2SbX_4]^-$ anions are placed in *trans* positions. The major difference in the anions containing phenyl groups is concerned to the relative orientation of the two aromatic rings. In all compounds the phenyl rings are basically bisecting the X–Sb–X angles of the square planar $SbX_4$ plane. For compounds **24**–**28**, which contain the $[Et_4N]^+$ countercation, the phenyl rings are orthogonal.

Crystals of **24** belong to the monoclinic space group *C*2/*c*. In the tetrachloroantimonate **24** (**Figure 43**) described here the Sb–Cl bond distances are in the range 2.456(1)–2.503(3) Å, being of intermediate length between terminal and bridging antimony–halogen bonds in the dimers $(Ph_2SbCl_3)_2$ [2.346(4), 2.388(4) Å vs. 2.620(4), 2.839(4) Å][111] or $(Me_2SbCl_3)_2$ [2.353(2), 2.356(2) Å vs. 2.798(2), 2.801(2) Å][112] and of same magnitude as found for the equatorial Sb–Cl bonds in *trans* to each other in the monomer $Ph_2SbCl_3{\cdot}H_2O$ [2.462(2) Å].[113]

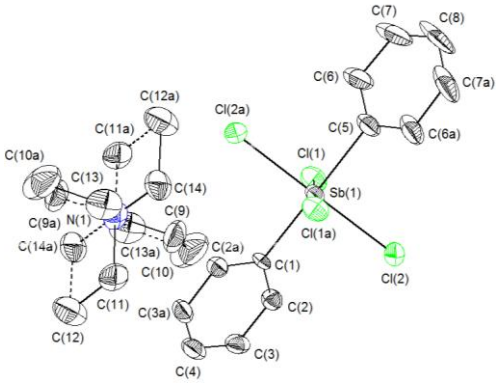



**Figure 43.** ORTEP-like representation at 30% probability and atom numbering scheme for **24** [symmetry equivalent positions (–x, 1 – y, 1 – z) and (– x, y, 0.5 – z) are labelled with "a" for the anion and cation]. Hydrogen atoms are omitted for clarity.

Crystals of **28** belong to the monoclinic space group $P2_1/n$. In compound $[Et_4N]^+[Ph_2SbF_4]^-$ (**28**) phenyl rings are slightly deviated from coplanarity (dihedral angle 11.3°) comparable with the

related $[Me_4Sb]^+[Ph_2SbCl_4]^-$, in which the phenyls rings are coplanar.[107] The Sb–F bond lengths in **28** [1.957(2), 1.960(3) Å] are slightly shorter than in the monomeric $Me_3SbF_2$ [1.993(4), 2.004(4) Å].[90]

The values of the Sb–C bond lengths in the $[R_2SbX_4]^-$ anions are comparable with the values found in the related starting materials, *i.e.* $(Ph_2SbCl_3)_2$ [2.125(9) Å][111], $Ph_2SbCl_3{\cdot}H_2O$ [2.1218(8) Å][113] or $Ph_2SbBr_3$ [2.149(12) Å].[114]

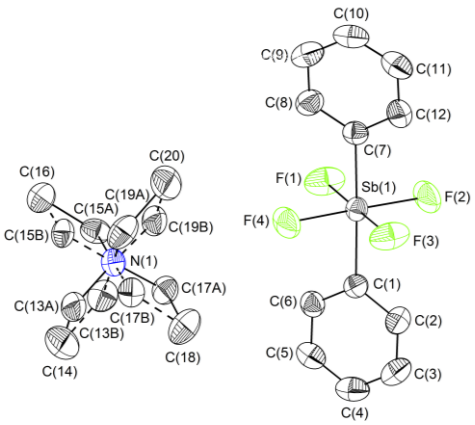



**Figure 45.** ORTEP-like representation at 30% probability and atom numbering scheme for **28**.Hydrogen atoms are omitted for clarity.

**Tabel 10.** Selected interatomic distances (Å) and angles (°) in compounds $[Et_4N]^+[Ph_2SbBr_{1.24}Cl_{2.76}]^-$ (**25**) and $[Et_4N]^+[Ph_2SbBr_{2.92}Cl_{1.08}]^-$ (**26**).

| **25** | | **26** | |
|---|---|---|---|
| Sb(1)-C(1) | 2.139(10) | Sb(1)-C(1) | 2.143(9) |
| Sb(1)-C(5) | 2.124(15) | Sb(1)-C(5) | 2.152(7) |
| Sb(1)–X(1)[a] | 2.5498(15) | Sb(1)-X(1)[b] | 2.6164(7) |
| C(1)–Sb(1)–C(5) | 180.000(2) | C(1)–Sb(1)–C(5) | 180.000(1) |
| C(1)–Sb(1)–X(1) | 89.78(3) | C(1)–Sb(1)–X(1) | 90.170(15) |
| C(5)–Sb(1)–X(1) | 90.22(3) | C(5)–Sb(1)–X(1) | 89.830(15) |
| X(1)–Sb(1)–X(1b) | 179.56(7) | X(1)–Sb(1)–X(1b) | 179.66(3) |
| X(1)–Sb(1)–X(1a) | 90.04(7) | X(1)–Sb(1)–X(1a) | 90.20(3) |
| X(1)–Sb(1)–X(1c) | 89.96(7) | X(1)–Sb(1)–X(1c) | 89.80(3) |

[a] X(1) is Br(1)/Cl(1) in the ratio 0.31/0.69.

[b] X(1) is Br(1)/Cl(1) in the ratio 0.73/0.27.

## *III.D.6. Conclusions*

- The onium diorganotetrafluoro–, –chloro- and –bromoantimonates reported here represent a large family of easily accessible, stable organoantimony(V) compounds.

- The ionic nature and the almost uniform structure of the tetrahedral cations and the octahedral antimony(V) anions with the organic groups in *trans* positions are clearly demonstrated.
- Applications of this class of compounds in organoantimony syntheses, *e.g.* the preparation of stibinic acids have a long tradition. The antimonates are certainly useful for the formation of salts with a variety of inorganic or organic cations.

**References:**


1. http://www.feenindia.com/symbol.htm
2. R. E. Krebs in The History and Use of Our Earth's Chemical Elements: A Reference Guide, Greenwood, 2nd edn., 2006, pp 219.
3. T. Thomson in *The History of Chemistry*, London, 1830**,** Vol. 1, pp.74.
4. V. Biringuccio in *The Pirotechnia*, Dover Publications, 1990, pp.201.
5. http://www.muzeuminbm.ro/exponate.php
6. M. M. Kumbar in *Chemistry in a Day of Student's Life*, iUniverse, 2003, pp. 179.
7. C. Yu Wagn in *Antimony*, Charles Griffin and Co. Ltd, 1919, pp. 10.
8. http://tw.strahlen.org/fotoatlas1/antimony foto.html
9. G. S. Brady, H. R. Clauser, J. A. Vaccari in *Materials Handbook*, McGraw Hill Professional, 2002, pp. 74.
10. M. J. Aroney, I. E. Buys, M. S. Davies, T. W. Hambley, *J. Chem. Soc., Dalton Trans*., **1994**, 2827.
11. A. M. Hill, N. J. Holmes, A. R. J. Genge, W. Levason, M. Webster, S. Rutschow, *J. Chem. Soc., Dalton Trans*., **1998**, 825.
12. H. J. Breunig, T. Borrmann, E. Lork, C. I. Raț, *J. Organomet. Chem*., **2007**, *692*, 2593.
13. H. J. Breunig , E. Lork, C. I. Raț, R. P. Wagner, *J. Organomet. Chem*., **2007**, *692*, 3430.
14. H. J. Breunig, T. Borrmann , E. Lork, O. Moldovan , C. I. Raț, R. P. Wagner, *J. Organomet. Chem*., **2009**, *694*, 427.
15. W. Levason, M. L. Matthews, G. Reid, M. Webster, *Dalton Trans*., **2004**, 51.
16. W. Kutzelnigg, *Angew. Chem. Int. Ed. Engl.*, **1984**, *23*, 272.
17. N. R. Champness, W. Levason, *Coord. Chem. Rev.*, **1994**, *133*, 115.
18 E. W. Abel, I. S. Butler, J. G. Reid, *J. Chem. Soc.*, **1963**, 2068.
19. M. D. Brown, W. Levason, J. M. Manning, G. Reid, *J. Organomet. Chem*., **2005**, *690*, 1540.
20. E. Shewchuk, S. B. Wild, *J. Organomet. Chem*., **1977**, *128*, 115.
21. T. Fukumoto, Y. Matsumura, R. Okawara, *Inorg. Nucl. Chem. Lett*., **1973**, *9*, 711.
22. L. R. Martin, F. W. B. Einstein and R. K. Pomeroy, *Inorg. Chem.*, **1985**, *24*, 2777.
23. J. Chatt and F. A. Hart, *J. Chem. Soc.*, **1960**, 1378.
24. A. M. Hill, W. Levason, M. Webster, I. Albers, *Organometallics*, **1997**, *16*, 5641.
25. A. F. Chiffey, J. Evans, W. Levason, M. Webster, *Organometallics*, **1996**, *15*, 1280.
26. W. Buchner, W. A. Schenk, *Inorg. Chem*., **1984**, *23*, 132.
27. (a) D. J. Thornhill, A. R. Manning, *J. Chem. Soc., Dalton Trans*., **1973**, 2086; (b) J. Ellermann, *J. Organomet. Chem*., **1975**, *94*, 201.

28. J. Emsley, *Die Elemente*, Walter de Gruyter, Berlin, **1994**.
29 (a) N. J. Holmes, W. Levason and M. Webster, *J. Chem. Soc., Dalton Trans.*, **1997**, 4223; (b) G. Becker, O. Mundt, M. Sachs, H. J. Breunig, E. Lork, J. Probst, A. Silvestru, *Z. Anorg. Allg. Chem.*, **2001**, *627*, 699.
30. (a) H. Schmidt, *Liebigs Ann. Chem.*, **1920**, *421*, 174. (b) M. Wieber, *Gmelin Handbook of Inorganic Chemistry*, Sb Organoantimony Compounds, Part 2; Springer-Verlag: Berlin, **1981**. (c) H. J. Breunig, R. Rösler, *Coord. Chem. Rev.*, **1997**, *163*, 33. (d) H. J. Breunig, R. Rösler, *Chem. Soc. Rev.*, **2000**, *6*, 403.
31. H. J. Breunig, I. Ghesner, E. Lork, *Organometallics*, **2001**, *20,* 1360.
32. M. Baudler, G. Reuschenbach, D. Koch, B. Carlsohn, *Chem. Ber*., **1980**, *113*, 1264.
33. E. Urnezius, K.-Ch. Lam, A.L. Rheingold, J. D. Protasiewicz, *J. Organomet. Chem*., **2001**, *630*, 193.
34. G. Johannes, O. Stelzer, E. Unger, *Chem. Ber*., **1975**, *108*, 1259.
35. O. Stelzer, E. Unger, V. Wray, *Chem. Ber*., **1977**, *110*, 3430.
36. H. J. Breunig, I. Ghesner, M. E. Ghesner, E. Lork, *J. Organomet. Chem*., **2003**, *677*, 15.
37. H. J. Breunig, W. Fichtner, *Z. Anorg. Allg. Chem.*, **1979**, *454*, 167.
38. I.-P Lorenz, S. Rudolph, H. Piotrowski, K. Polborn, *Eur. J. Inorg. Chem.*, **2005**, 82.
39. H. J. Breunig, E. Lork, O. Moldovan, C. I. Raț, *Z. Anorg. Allg. Chem*., **2010**, *636*, 1090
40. H. J. Breunig, E. Lork, O. Moldovan, C. I. Raț, U. Rosenthal, C. Silvestru, *Dalton Trans.,* **2009**, 5065.
41. H. J. Breunig, I. Ghesner, E. Lork, *Appl. Organomet. Chem.*, **2002**, *16*, 547.
42. H. J. Breunig, I. Ghesner, E. Lork, *J. Organomet.Chem.,* **2002**, *664*, 130.
43. L. M. Opriş, A. Silvestru, C. Silvestru, H. J. Breunig, E. Lork, *Dalton Trans.,* **2004**, 3575.
44. H. J. Breunig, W. Fichtner, T. P. Knobloch, *Z. Anorg. Allg. Chem*., **1981**, *477*, 126.
45. A. F. Clifford, A. K. Mukherjee, *Inorg. Synth*., **1966**, *8*, 185.
46. H. J. Breunig, M. Jönsson, R. Rösler, E. Lork, *Z. Anorg. Allg. Chem.,* **1999**, *625*, 2120**.**
47. E. J. Corey, J. C. Bailar, *J. Am. Chem. Soc*., **1959**, *81*, 2620.
48. H. J. Breunig, E. Lork, R. Rösler, G. Becker, O. Mundt, W. Schwarz, *Z. Anorg*. *Allg*. *Chem*., **2000**, *626*, 1595.
49. G. Balázs, H. J. Breunig, E. Lork, S. A. Mason, *Organometallics*, **2003**, *22*, 576.
50. L. Balázs, H. J. Breunig, E. Lork, C. Silvestru, *Eur. J. Inorg. Chem.*, **2003**, *7*, 1361.
51. G. Huttner, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme, Stuttgart, **1990**.
52. J. von Seyerl, G. Huttner, *Angew. Chem.*, **1978**, *90*, 911; J. von Seyerl, G. Huttner, *Angew. Chem. Int. Ed. Engl.*, **1978**, *17*, 843.
53. U. Weber, L. Zsolnai, G. Huttner, *J. Organomet. Chem.*, **1984**, *260*, 281.
54. A. H. Cowley, N. C. Norman, M. Pakulsky, *J. Am. Chem. Soc.*, **1984**, *106*, 6844.
55. A. M. Arif, A. H. Cowley, N. C. Norman, M. Pakulsky, *J. Am. Chem. Soc.*, **1985**, *107*, 1062.
56. A. H. Cowley, N. C. Norman, M. Pakulsky, D. L. Bricker, D. H. Russell, *J. Am. Chem. Soc.*, **1985**, *107*, 8211.
57. M. Arif, A. H. Cowley, N. C. Norman, M. Pakulsky, *Inorg. Chem.*, **1986**, *25*, 4836.
58. G. Balazs, H. J. Breunig, E. Lork, *Z. Anorg. Allg. Chem.*, **2003**, *629*, 1937.
59. H. J. Breunig, J. Pawlik, *Z. Anorg. Allg. Chem*., **1995**, *621*, 817.

60. C. J. Carmalt, A. H. Cowley, R. Culp, R. A. Jones, S. Kamepalli, N. C. Norman, *Inorg. Chem.,* **1997**, *36*, 2770.
61. L. M. Opriş, A. Silvestru, C. Silvestru, H. J. Breunig, E. Lork, *Dalton Trans.,* **2003**, 4367.
62. D. Copolovici, V. R. Bojan, C. I. Raț, A. Silvestru, H. J. Breunig, C. Silvestru, *Dalton Trans.*, **2010**, *39*, 6410.
63. L. M. Opriş, A. M. Preda, R. A. Varga, H. J. Breunig, C. Silvestru, *Eur. J. Inorg. Chem.,* **2009**, 1187.
64. T. Tokunaga, H. Seki, S. Yasuike, M. Ikoma, J. Kurita, K. Yamaguchi, *Tetrahedron Lett.,* **2000**, *41*, 1031.
65. T. Tokunaga, H. Seki, S. Yasuike, M. Ikoma, J. Kurita, K. Yamaguchi, *Tetrahedron,* **2000**, *56*, 8833.
66. H. J. Breunig, I. Ghesner, M. E. Ghesner, E. Lork, *Inorg.Chem.,* **2003**, *42*, 1751.
67. L. Dostal, R. Jambor, A. Ruzicka, Petr Simon, *Eur. J. Inorg. Chem.,* **2011**, 2380.
68. C. Comsa, Studies of the Chemistry of Organotin compounds containing Metal-Chalcogen Bonds, Ph.D. Thesis, Babes-Bolyai University, Cluj-Napoca, **2009**.
69. N. G. Connelly, T. Damhus, R. M. Hartshorn, A. T. Hutton (Eds.), *Nomenclature of Inorganic Chemistry–IUPAC Recommendations 2005*, RSC Publishing, Cambridge, 2005.
70. K. Akiba (Ed.), *Chemistry of Hypervalent Compounds*, Wiley-VCH, New York, **1999**.
71. The *N*-X-*L* nomenclature system has been described previously: *N* valence shell electrons about a central atom X with *L* ligands: C. W. Perkins, J. C. Martin, A. J. Arduengo III, W. Lau, A. Alegria, K. Kochi, *J. Am. Chem. Soc.,* **1980**, *102*, 7753.
72. J. Hasenbäumer, *Ber. Deut. Chem. Ges*., **1898**, *31*, 2910.
73. M. A. Mohammed, K. H. Ebert, H. J. Breunig, *Z. Naturforsch*., **1996**, *51b*, 149.
74. L. Dostal, R. Jambor, A. Ruzicka, J. Holecek, *Organometallics*, **2008**, *27*, 2169.
75. L. Dostal, R. Jambor, A. Ruzicka, A. Lycka, J. Brus, F. de Proft, *Organometallics*, **2008**, *27*, 6059.
76. L. M. Opris, New Organoantimony Compounds with Intramolecular N→Sb Coordination, Ph. D. Thesis, Babes-Bolyai University, Cluj-Napoca, **2006**.
77. H. J. Breunig, T. Krüger, E. Lork, *J. Organomet. Chem.,* **2002**, *648*, 209.
78. J. Rigauy, S. P. Klesney (Eds.), *Nomenclature of Organic Chemistry – The Blue Book*, Pergamon Press, Oxford, **1979**.
79. A. Neuhaus, G. Frenzen, J. Pebler, K. Dehnicke, *Z. Anorg. Allg. Chem.,* **1992**, *618*, 93.
80. F. Huber, H. Preut, G. Alonzo, N. Bertazzi, *Inorg. Chim. Acta,* **1985**, *102*, 181.
81. G. R. Willey, M. P. Spry, M. G. Drew, *Polyhedron*, **1996**, *15*, 4497.
82. C. J. Carmalt, D. Walsh, A. H. Cowley,N. C. Norman, *Organometallics*, **1997**, *16,* 3597.
83. Y. Mourad, Y. Mugnier, H. J. Breunig, M. Ates, *J. Organomet.Chem*., **1990**, *388*, C9.
84. L. Dostal, R. Jambor, A. Ruzicka, R. Jirasko, I. Cisarova, J. Holecek, *J. Fluorine Chem.,* **2008**, *129*, 167.
85. S. P. Bone, D. B. Sowerby, *J. Chem. Soc. Dalton Trans.,* **1979***,* 1430.
86. K. Ohkata, S. Takemoto, M. Ohnishi, K. Akiba, *Tetrahedron Lett*., **1989**, *30*, 4841.
87. S. P. Bone, M. J. Begley, D. B. Sowerby, *J. Chem. Soc. Dalton Trans.,* **1992***,* 2085.
88. M. J. Begley, S. P. Bone, D. B. Sowerby, *J. Organomet.Chem*., **1979**, *165*, C47
89. P. J. Cox, R. A. Howie, J. N. Low, J. L. Wardell, *Inorg. Chem. Commun*., **1998**, *1*, 463.
90. W. Schwarz, H. J. Guder, *Z. Anorg. Allg. Chem*., **1978**, *444*, 105.

91. A. Herzog, F. Q. Lin, H. W. Roesky, A. Demsar, K. Keller, M. Noltemeyer, F. Pauer, *Organometallics*, **1994**, *13*, 1251.
92. J. Bares, P. Novak, M. Nadvornik, R. Jambor, T. Lebl, I. Cisarova, A. Ruzicka, J. Holecek, *Organometallics*, **2004**, *23*, 2967.
93. P. Novak, J. Brus, I. Cisarova ,A. Ruzicka, J. Holecek, *J. Fluorine Chem*., **2005**, *126*, 1531.
94. P. Novak, Z. Padelkova, I. Cisarova, L. Kolarova, A. Ruzicka, J. Holecek, *Appl. Organomet. Chem*., **2006**, *20*, 226.
95. P. Svec, P. Novak, M. Nadvornik, Z. Pade Lkova ,I. Cisarova ,A. Ruzicka, J. Holecek*, J. Fluorine Chem*., **2007**, *128*, 1390.
96. (b) H. Schmidt, *Liebigs Ann. Chem*., **1922**, *429*, 123.
97. M. Mirbach, M. Wieber, Gmelin Handbook of Inorganic Chemistry, Sb Organoantimony Compounds, Part 5, Springer-Verlag, Berlin, **1990**.
98. S. Samaan, in: H. Kropf (Ed.), *Methoden der organischen Chemie (Houben-Weyl)*, *vol. 13*, Metallorganische Verbindungen, Thieme, Stuttgart, **1978**.
99. G. O. Doak, L. D. Freedman, S. M. Efland, *J. Am. Chem. Soc*., **1952**, 74830.
100. N. Bertazzi, T. C. Gibb, N. N. Greenwood, *J. Chem. Soc., Dalton Trans*., **1976**, 1153.
101. N. Bertazzi, *Atti Accad. Sci. Lett*., Arti Palermo I, **1973**, *33*, 483.
102. N. Bertazzi, *J. Organomet. Chem*., **1976**, *110*, 175.
103. M. Nunn, M. J. Begley, D. B. Sowerby, I. Haiduc, *Polyhedron*, **1996**, *15*, 3167.
104. E. G. Zaitseva, S. V. Medvedov, L. A. Aslanov, Zh. Strukt. Khim. *J. Struct. Chem*., **1990**, *31*, 133.
105. P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed*., **2000**, *39*, 3772.
106. R. Bentley, T. G. Chasteen, *Microbiol. Mol. Biol. Rev*., **2002**, *66*, 250.
107. H. J. Breunig, T. Koehne, O. Moldovan, A. M. Preda, A. Silvestru, C. Silvestru, R. A. Varga, L. F. Piedra-Garza, U. Kortz, *J. Organomet. Chem*., **2010**, *695*, 1307.
108. J. Mason, in J. Mason (Ed.), *Multinuclear NMR*, Plenum Press, New York, **1987**, 335; *Chem. Rev*., **1981**, *81*, 205.
109. K. M. Harmon, T. E. Nelson and M. S. Janos, *Journal of Molecular Structure*, **1989**, *213*, 185.
110. M. J. Taylor, D. J. Calvert, C. M. Hobbis, *Magnetic Resonance in Chemistry*, **1988**, *Vol 26*, 619.
111. J. Bordner, G. O. Doak, J. R. Peters Jr., *J. Am. Chem. Soc*., **1974**, *96*, 6763.
112. W. Schwarz, H. J. Guder, *Z. Naturforsch*., **1978**, *33b*, 485.
113. T. T. Bamgboye, M. J. Begley, D. B. Sowerby, *J. Organomet. Chem*., **1989**, *362*, 77.
114. S. P. Bone, D. B. Sowerby, *J. Chem. Soc., Dalton Trans*., **1979**, 718.