Journal of Organometallic Chemistry 693 (2008) 2527–2534

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Syntheses of a stable tristibine and of related antimony compounds with the 2,6-dimesitylphenyl (Dmp) substituent

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ARTICLE INFO

Article history:
Received 27 March 2008
Received in revised form 25 April 2008
Accepted 28 April 2008
Available online 6 May 2008

Keywords:
Antimony
Terphenyl
X-ray structure
Hydride
Hydroxide

ABSTRACT

$DmpSbBr_2$ (Dmp = 2,6-$Mes_2C_6H_3$) (**1**) is obtained by the reaction of DmpMgBr with $SbCl_3$. The reaction of **1** with KI in ethanol gives $DmpSbI_2$ (**2**). Dmp(Ph)SbBr (**3**) is prepared from DmpMgBr and $PhSbCl_2$. Compound **1** or **3** react with $LiAlH_4$ to form $DmpSbH_2$ (**4**) or Dmp(Ph)SbH (**5**). Compound **4** reacts with MeI in presence of DBU to give Dmp(Me)SbH (**6**). $DmpSb(SbMe_2)_2$ (**7**) is obtained from **4** and Me_4Sb_2. Elimination of hydrogen from **6** gives $[Dmp(Me)Sb]_2$ (**8**). Hydrolysis of **3** gives Dmp(Ph)SbOH (**9**). The molecular structures of **1**–**3**, **5**, **8** and **9** were determined by X-ray diffraction on single crystals.

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1. Introduction

The 2,6-dimesitylphenyl (Dmp) and related terphenyl groups (2,6-$Trip_2C_6H_3$, Trip = 2,4,6-$^iPr_3C_6H_2$) were used in antimony chemistry to stabilize the Sb═Sb bond or to protect labile bonds like Sb–H. The stable distibenes: $(RSb)_2$ R = Dmp or 2,6-$Trip_2C_6H_3$ [1], the hydrides $DmpSbH_2$ (**4**) [2], $RSbH_2$ and RSb(Li)H, R = 2,6-$Trip_2C_6H_3$ [3], and their precursors $DmpSbCl_2$ [1,4] and 2,6-$Trip_2C_6H_3SbCl_2$ [1] were obtained. The Dmp group was also used to protect the P_3 unit in $DmpP(PPh_2)_2$ [5].

Our aim was to stabilize *catena*-tristibines of the types I and II (Scheme 1) with the Dmp group. Known *catena*-stibines exist as mixtures of Sb_3 and Sb_4 chains, as components of ring-chain equilibria, or as ligands in transition metal carbonyl complexes [6].

We report here the stepwise syntheses of the type I tristibine, $DmpSb(SbMe_2)_2$ (**7**) and the formation and characterization of precursors of type II tristibines with terminal Dmp(Me)Sb and Dmp(Ph)Sb groups. In this context, we have prepared the compounds $DmpSbX_2$, X = Br (**1**), I (**2**), H (**4**); Dmp(Ph)SbX, X = Br (**3**), H (**5**), OH (**9**); Dmp(Me)SbX, X = H (**6**), Sb(Me)Dmp (**8**). Compound **4** was prepared before by another route [2]. The compounds **3**, **5**, **6** and **9** are of interest as racemic Sb-chiral stibines. A related stibine with a known crystal structure is RR′SbCl [R = 2-$(Me_2NCH_2)C_6H_4$, R′ = $CH(SiMe_3)_2$] [7]. Compound **9** is the first authentic diorganoantimony hydroxide (stibinic acid). Compounds that were called diorganoantimony hydroxides in the older literature were actually oxides. A complex with a diorganoantimony hydroxide ligand was reported recently [8].

2. Results and discussion

$DmpSbBr_2$ (**1**) is obtained by the reaction of DmpMgBr with $SbCl_3$. Due to the presence of bromide in the reaction mixture halide exchange occurs. Reaction of **1** with excess KI in ethanol leads quantitatively to $DmpSbI_2$ (**2**). Compound **1** reacts with $LiAlH_4$ to give $DmpSbH_2$ (**4**) in a similar way like $DmpSbCl_2$ [2]. Reacting **4** with MeI in the presence of DBU in a 1:1:1 molar ratio leads to the selective substitution of one hydrogen atom with formation of light sensitive Dmp(Me)SbH (**6**). Photolysis of a solution of **6** in C_6D_6 in a NMR tube in day light gives the racemic Sb chiral distibine $[Dmp(Me)Sb]_2$ (**8**). Crystals of **8** were obtained by catalytic hydrogen removal in presence of $Cp_2Ti(Me_3SiC)_2$ [9]. The role of group 4 metallocenes as catalysts for the elimination of hydrogen from organoantimony(III) hydrides was reported before [2]. Addition of excess tetramethyldistibine to **4** leads to $DmpSb(SbMe_2)_2$ (**7**). Compound **7** is the first *catena*-tristibine isolated in pure state. Attempts to obtain single crystals of **7** suitable for X-ray diffraction failed. The reaction of DmpMgBr and $PhSbCl_2$ gives Dmp(Ph)SbBr (**3**). Reaction of **3** with $LiAlH_4$ leads to the chiral secondary stibine Dmp(Ph)SbH (**5**). Attempts to obtain the tristibine $DmpSb[Sb(Ph)Dmp]_2$ by UV photolysis of solutions containing stoichiometric mixtures of **4** and **5** were not successful due to the stability of **5** under these conditions. In a serendipitous reaction, when the purification of **3** by column chromatography was intended, the hydroxide Dmp(Ph)SbOH (**9**) was obtained as solid.

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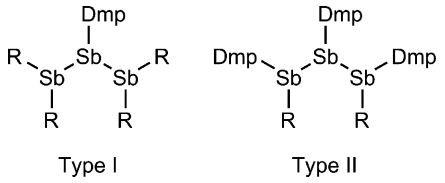
doi:10.1016/j.jorganchem.2008.04.038



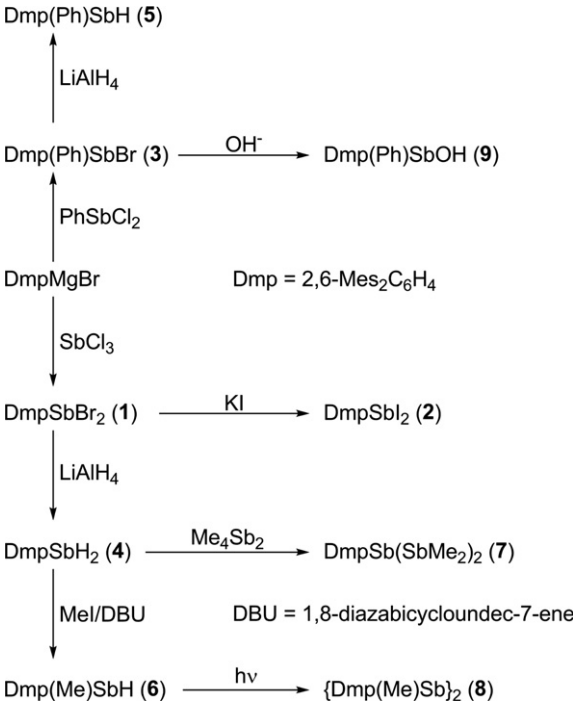
Scheme 1.

The synthetic pathways leading to **1**–**9** are summarized in Scheme 2.

The compounds **1**–**9** are yellow (**1**–**3**, **7** and **8**) or colourless (**4**–**6** and **9**) solids, soluble in aromatic solvents and little soluble in aliphatic solvents with exception of the hydrides **4**–**6**. Solutions of **1**–**6**, **8** and **9** are air sensitive. The thermal stability of the hydride **5**, which does not decompose at 3×10^{-2} mbar at 200 °C is remarkable. The analogous stibine Ph_2SbH decomposes above 20 °C [10].

Compounds **1**–**9** were characterized by mass spectrometry, ^1H, ^{13}C, HSQC, HMBC, COSY (**6**) NMR spectroscopy, infrared spectroscopy (**5**, **6** and **9**) and elemental analyses (**1**–**3** and **9**). Mass spectra of **1**–**3**, **6**, **7** and **9** contain molecular ions. The composition of **3** was also confirmed by HRMS. The molecular ion of the tristibine **7** found in the EI-MS and the theoretical isotopic distributions are shown in Fig. 1.

The ^1H NMR spectra of **1**–**7** show characteristic signals for the Dmp group and for the hydrogen atoms bonded to antimony where the case. The signal assignment was performed using HSQC and HMBC spectra. The ^1H NMR spectra of the compounds of the type $DmpSbX_2$ X = Br (**1**), I (**2**), H (**4**), $SbMe_2$ (**7**) contain two signals, the spectra of **3**, **6**, **8** and **9** three signals for the mesityl methyl groups. In the ^1H NMR spectrum of **5** there are only two signals for the methyl groups visible due to overlapping of signals. These findings indicate that the rotation of the *m*-terphenyl substituents around the Sb–C_{ipso} bond is hindered in the Dmp(R)SbX type compounds **3**, **5**, **6**, **8** and **9** where three methyl signals occur, whereas free rotation is observed for the $DmpSbX_2$ type compounds **1**, **2**, **4** and **7** where the *ortho* methyl groups are equivalent. In **6** the $SbCH_3$ protons are coupled with the Sb*H* proton and a doublet and a quadruplet signal appear in the spectrum. The coupling is observed also in the COSY spectrum of the compound. The ^1H NMR spectrum of the tristibine **7** is depicted in Fig. 2. It shows the pattern for the Dmp group and two characteristic signals for the diastereotopic methyl groups directly attached to peripheric antimony atoms. In the HMBC spectrum of **7** a three bond correlation between the hydrogen atoms of the methyl group and the carbon atoms of the other methyl group attached to the same antimony atom is observed. The ^{13}C NMR spectrum of **7** shows as well two signals for the methyl groups bonded to antimony. The ^1H NMR spectra of **8** show the presence of only one diastereomeric form, assigned on the basis of the X-ray diffraction results, as *R*,*R* and *S*,*S* form.



Scheme 2.

The IR spectra of **5** and **6** in Nujol display characteristic signals at 1883 and 1870 cm^{-1} for the SbH stretching vibration.

The molecular structures of **1**–**3**, **5**, **8** and **9** were determined by single crystal X-ray diffraction. The antimony atoms in all the structures have pyramidal geometries with unexceptional bond lengths and angles. In the typical way for terphenyl substituents the flanking mesityl groups are orientated perpendicular to the plane of the central phenyl ring and close contacts between the antimony centres and the carbon atoms of the mesityl ring result. These contacts are partially imposed by the geometry of the terphenyl substituent but they depend also in a significant way on the nature of the inorganic substituents at the antimony centres.

Particularly close intramolecular contacts comparable with the well known π interactions in Menshutkin complexes between arenes and antimony trihalides [11] exist in the organoantimony dihalides **1** and **2**, which crystallize with 4 (**1**) or 2 (**2**) different monomeric molecules in the asymmetric unit. The only other known example of an organoantimony dihalide that crystallizes as monomer is $2,6\text{-}Trip_2C_6H_3SbCl_2$ [1]. $DmpSbCl_2$, the dichloride analogue of **1** forms dimers with chlorine bridges in the solid state [4]. Solid phenyl- or methylantimony dihalides are polymeric [12,13]. Representative molecular structures of **1** and **2** are shown in Figs. 3 and 4.

Under the influence of the intra molecular contacts the antimony halogen bonds in **1** and **2** are not much shorter than in the corresponding methyl- or phenylantimony dihalides where intermolecular interactions are important (Sb–Br, **1**: 2.5124(15), 2.5164(15); $MeSbBr_2$: 2.564(3), 2.583(3) [13], $PhSbBr_2$: 2.526(1), 2.563(1) Å [12]. Sb–I, **2**: 2.7049(14), 2.7019(11); $MeSbI_2$: 2.799(2), 2.761(2) [14], $PhSbI_2$: 2.753(1), 2.738(1) Å [12]). The intramolecular interactions between the SbX_2 unit and the opposite mesityl groups in **1** and **2** lead to a bending of the Dmp groups which can be quantified by the difference between the bonding angles at the C_{ipso} atom of the central phenyl group. The found values are 22.6°, 22.2°, 21.5° and 20.5° for **1** and 21.7° and 22.2° for **2**. These values are close to the reported values for $DmpSbCl_2$ (20.9° and 20.3°) [4] and $2,6\text{-}Trip_2C_6H_3SbCl_2$ (22.5°) [1].

Compound **3** crystallizes as a mixture of *R* and *S* isomers in a ratio of 1:1 in the *C*2/*c* space group with eight molecules per unit cell. The molecular structure of (*S*)-**3** is shown in Fig. 5.

The antimony bromine bond length (2.5264(15) Å) in **3** is similar to the one found in Ph_2SbBr (2.553(1) Å [15]). The direction of Sb–Br bond is almost perpendicular to the plane of the central phenyl group of Dmp substituent.

Crystals of **5** contain pairs of enantiomers which are symmetry related, with respect to the inversion centres of the space group. Between the molecules there is a contact with a Sb···Sb distance of 3.941(2) Å, which is close to $\sum_{rvdw}$(Sb,Sb) = 4.0 Å [16]. The structure of two associated molecules of **5** is shown in Fig. 6.

The value for Sb–H bond length of 1.59(7) Å in the structure of **5** is similar to the Sb–H distance determined by X-ray diffraction of

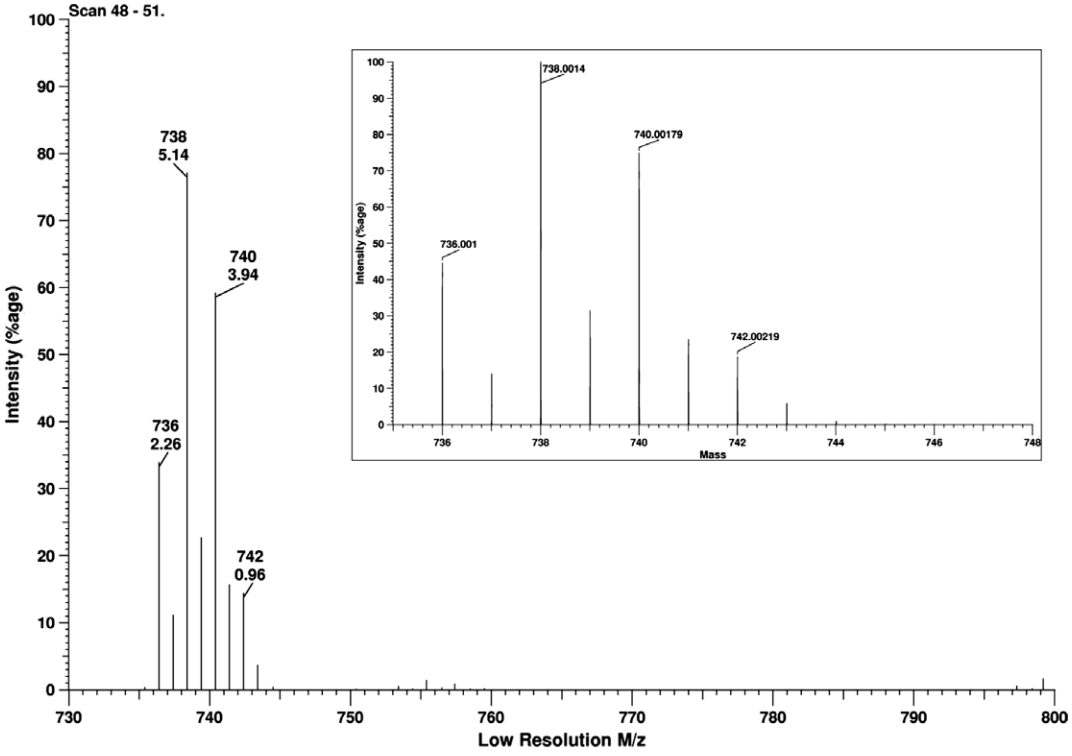


Fig. 1. Measured (down left) and calculated (up right) isotopic pattern of $[C_{28}H_{37}Sb_3]^+$ ($[DmpSb(SbMe_2)_2]^+$) (**7**).

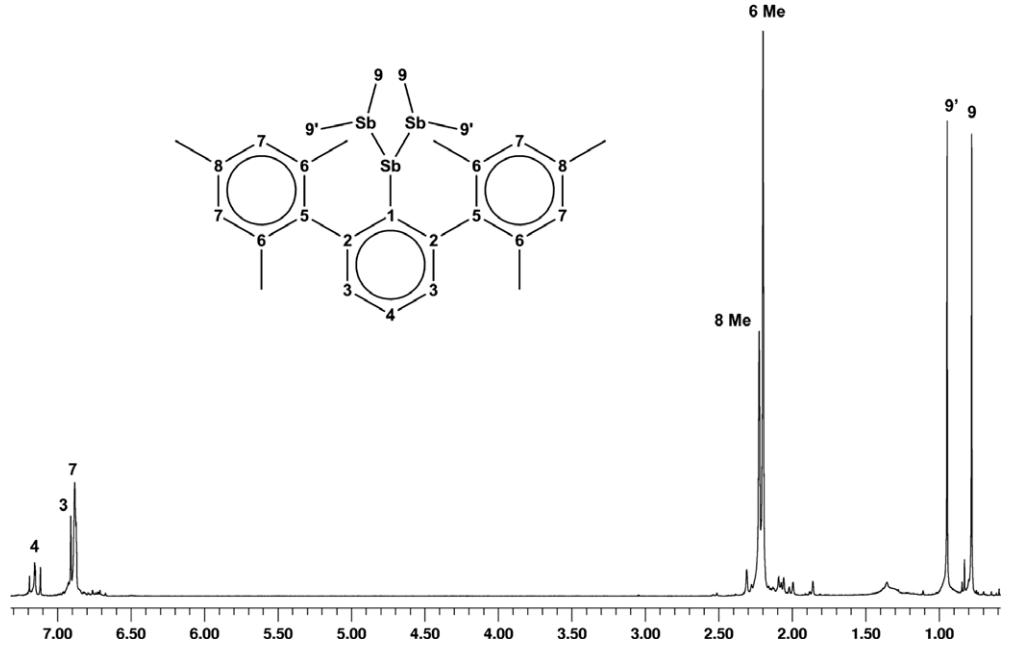


Fig. 2. ^1H NMR spectrum of $DmpSb(SbMe_2)_2$ (**7**).

$\{(Me_3Si)_2CH_2SbH\}_2$ (1.58(3) Å) [17]. The distibine **8** crystallized as 1:1 solvate with C_6D_6. The crystals contain the *R*,*R* and *S*,*S* isomers in a 1:1 ratio. The structure of the *R*,*R* isomer of **8** is shown in Fig. 7.

The Sb–Sb bond length in **8** is 2.8371(7) Å, almost the same as in $\{(Me_3Si)_2CH(H)Sb\}_2$ (2.8304(8) Å) [17]. Compound **8** adopts a close to antiperiplanar conformation with the torsion angle between Dmp groups of 155.30(15)°.

Crystals of **9** contain the *R* and *S* isomers in the 1:1 molar ratio. Two molecules are associated to dimers as shown in Fig. 8.

Between the dimers there are loose Sb···O contacts (3.520(7), 3.377(11) Å) close to $\sum_{rvdW}(Sb,O) = 3.52$ Å [16]. The Sb–O bond lengths are in the range of the analogous values encountered oxides of the type $(R_2Sb)_2O$ [18].

3. Conclusion

The present results illustrate the role of terphenyl substituents in stabilising unusual organoantimony compounds. With sterical

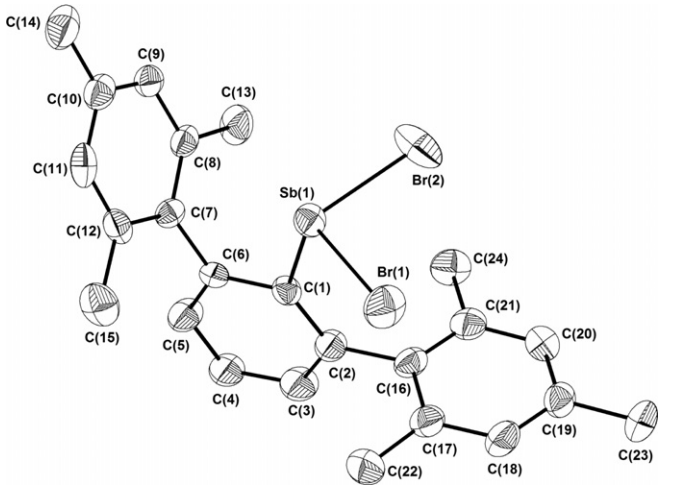


Fig. 3. Thermal ellipsoid representation (50%) of one molecule of $DmpSbBr_2$ (**1**). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Sb(1)–C(1) 2.174(9), Sb(1)–Br(1) 2.5124(15), Sb(1)–Br(2) 2.5164(15), C(1)–Sb(1)–Br(1) 101.7(2), C(1)–Sb(1)–Br(2) 99.8(2), Br(1)–Sb(1)–Br(2) 97.05(5).

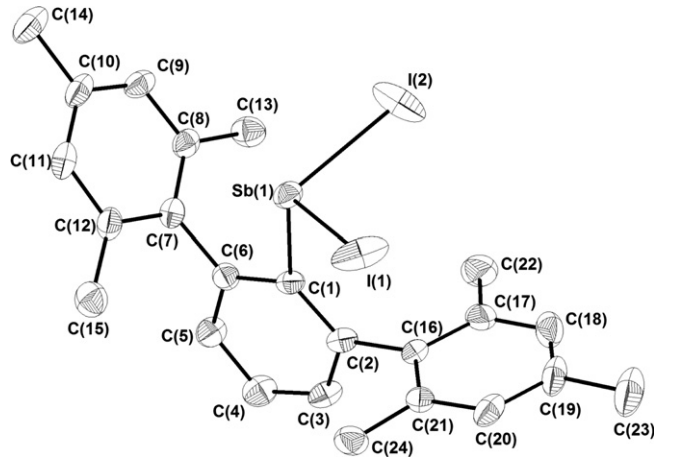


Fig. 4. Thermal ellipsoid representation (30%) of one molecule of $DmpSbI_2$ (**2**). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Sb(1)–C(1) 2.176(7), Sb(1)–I(1) 2.7049(14), Sb(1)–I(2) 2.7019(11), C(1)–Sb(1)–I(1) 105.5(2), C(1)–Sb(1)–I(2) 102.36(19), I(1)–Sb(1)–I(2) 97.21(4).

protection by the Dmp group a *catena*-tristibine, racemic Sb-chiral secondary stibines and distibines as well as a diorganoantimony hydroxide were obtained. All these new products are promising starting materials for further work in the syntheses and characterisation of *catena*-stibines, Sb-chiral stibines and other useful organoantimony compounds.

4. Experimental

The reactions and manipulations of the air sensitive compounds were performed in an atmosphere of argon using modified Schlenk techniques. All solvents were dried and freshly distilled. $SbCl_3$ and $BiCl_3$ were sublimed prior to use. The syntheses of DmpMgBr and $DmpSbH_2$ were reported before [2,19]. NMR spectra were recorded in C_6D_6 on Bruker DPX-200 and NB-360 spectrometers. Mass spectra were recorded on Finnigan MAT 95 (EI, FD, HRMS), Finnigan MAT 8200 (EI, CI). The pattern of antimony containing ions was compared with theoretical values calculated using *MASPECII*. The

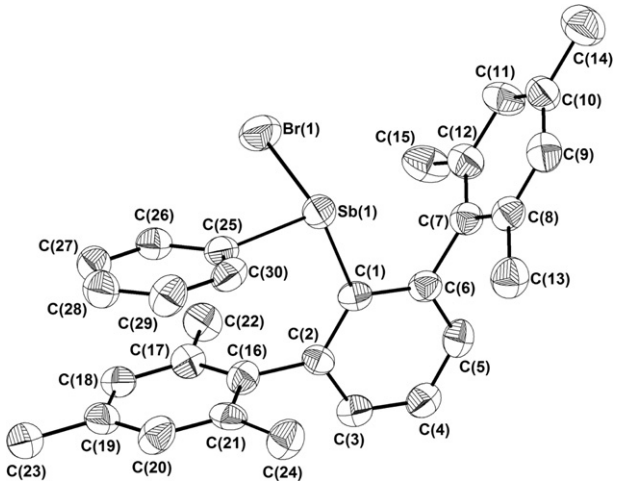


Fig. 5. Thermal ellipsoid representation (40%) of (*S*)-Dmp(Ph)SbBr (**3**). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Br(1)–Sb(1) 2.5264(15), C(1)–Sb(1) 2.190(9), C(25)–Sb(1) 2.149(9), C(1)–Sb(1)–Br(1) 97.8(2), C(25)–Sb(1)–C(1) 105.0(3), C(25)–Sb(1)–Br(1) 96.1(3), C(2)–C(1)–Sb(1)–Br(1) 92.3(8).

C and H elemental analyses were performed by Mikroanalytisches Laboratorium Beller-Matthies in Göttingen, Germany.

4.1. Synthesis of $DmpSbBr_2$ (**1**)

A solution of DmpMgBr was added dropwise to a solution of 4.56 g (20 mmol) $SbCl_3$ in 20 ml THF. The reaction mixture was stirred for 16 h at room temperature. The solvent mixture was removed under reduced pressure and the product extracted with 200 ml toluene. Single crystals suitable for X-ray diffraction were obtained from petroleum ether solutions at 7 °C. Yield: 3.57 g (30%), m.p. 75–76 °C. ^{1}H NMR (200.1 MHz): δ 2.11 (s, 12H, *o*-CH_3), 2.14 (s, 6H, *p*-CH_3), 6.79 (m, 4H, *m*-Mes), 6.84 (d, 2H, *m*-C$_6H_3$, $^3J_{HH}$ = 7.1 Hz), 7.11 (dd, 1H, *m*-C$_6H_3$, $^3J_{HH}$ = 7.1 Hz). ^{13}C NMR (50.3 MHz, C_6D_6): δ 21.3 (*p*-CH_3), 21.7 (*o*-CH_3), 128.9 (*m*-Mes), 130.2 (*m*-C_6H_3), 132.0 (*p*-C_6H_3), 136.5 (*i*-Mes), 137.1 (*o*-Mes), 138.6 (*p*-Mes), 144.6 (*i*-C_6H_3), 148.6 (*o*-C_6H_3). MS (EI, 70 eV) *m*/*z* (relative intensity %): 592 (6.4) $[M]^+$, 513 (55.4) $[M-Br]^+$, 312 $[Dmp-H]^+$. Anal. Calc. for $C_{24}H_{25}SbBr_2$ (595.01): C, 48.45; H, 4.23. Found: C, 48.55; H, 4.50%.

4.2. Synthesis of $DmpSbI_2$ (**2**)

A mixture of 1.64 g (2.75 mmol) **1** and 1.11 g (3.34 mmol) KI were stirred in 60 ml EtOH for 3 days at room temperature. The solvent was removed under reduced pressure and the solid extracted with 60 ml benzene. Yield: 1.8 g (94%), m.p. 115–116 °C. ^{1}H NMR (200.1 MHz): δ 2.13 (s, 12H, *o*-CH_3), 2.16 (s, 6H, *p*-CH_3), 6.80 (s, 2H, *m*-Mes), 6.84 (d, 2H, *m*-C$_6H_3$), 7.14 (dd, 1H, *p*-C$_6H_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 21.4 (*p*-CH_3), 22.1 (*o*-CH_3), 129.2 (*m*-Mes), 129.7 (*m*-C_6H_3), 131.8 (*p*-C_6H_3), 133.7 (*i*-C_6H_3), 137.1 (*o*-Mes), 137.2 (*i*-Mes), 138.6 (*p*-Mes), 148.8 (*o*-C_6H_3). MS (EI, 70 eV): 561 (100) $[M-I]^+$; (CI, positive): 706 (100) $[M+NH_4]^+$, 561 (47.2) $[M-I]^+$.

4.3. Synthesis of Dmp(Ph)SbBr (**3**)

A solution of DmpMgBr was added dropwise to a solution 5.4 g (20 mmol) $PhSbCl_2$ in 30 ml THF. After 16 h of stirring the solvent was removed at reduced pressure. The product was extracted with 50 ml toluene. Crystals suitable for X-ray diffraction were obtained by cooling a benzene solution to −10 °C. Yield: 4.1 g (35%), m.p.

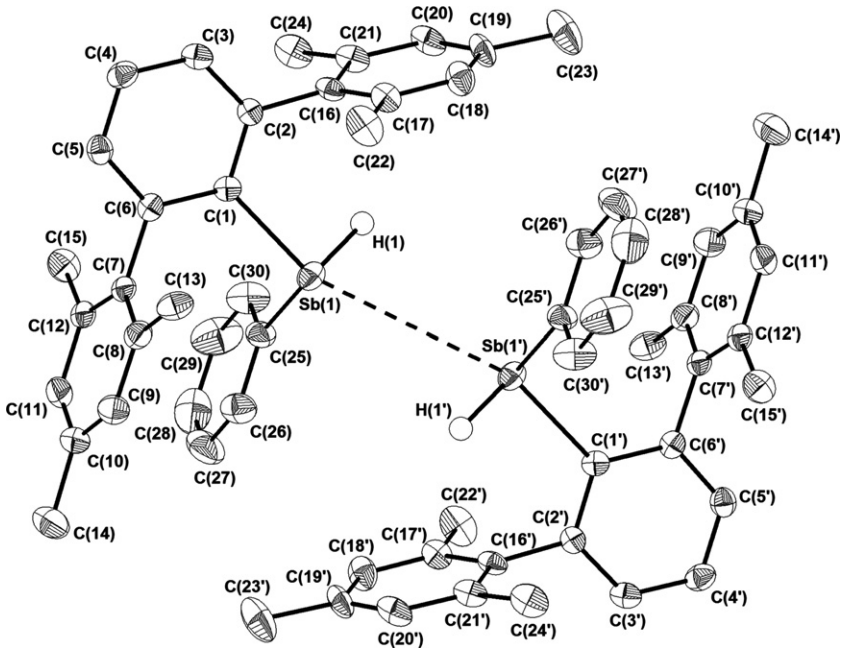


Fig. 6. Thermal ellipsoid representation (30%) of dimeric units in the structure Dmp(Ph)SbH (**5**). The carbon bonded hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Sb(1)–H(1) 1.59(7), Sb(1)–C(1) 2.165(7), Sb(1)–C(25) 2.148(9), Sb(1)···Sb(1′) 3.941(2), C(1)–Sb(1)–C(25) 102.1(3), C(1)–Sb(1)–H(1) 95(2), C(25)–Sb(1)–H(1) 93(2); C(2)–C(1)–Sb(1)–C(25) 127.4(6)°.

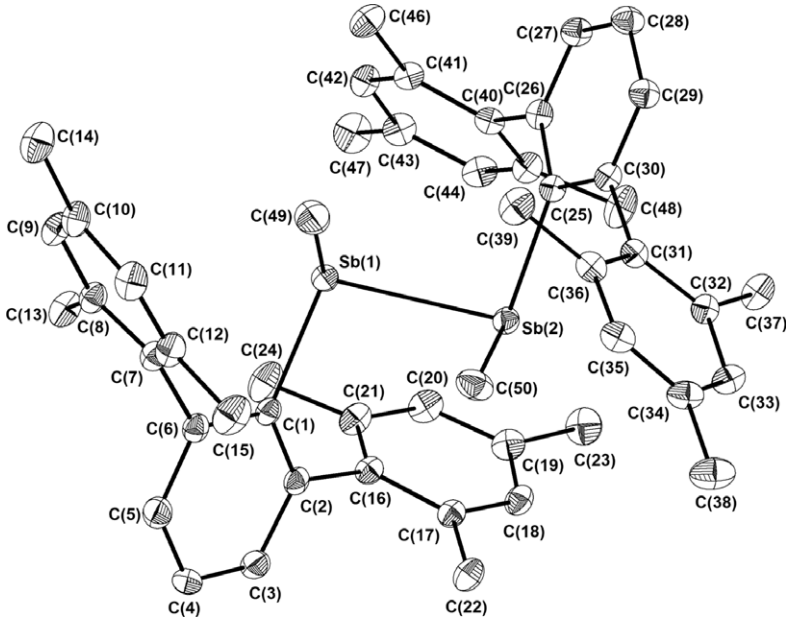


Fig. 7. Thermal ellipsoid representation (30%) of (*R*,*R*)-{2,6-$Mes_2C_6H_3$(Me)Sb}$_2$ (**8**). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Sb(1)–Sb(2) 2.8371(7), C(1)–Sb(1) 2.200(4), C(25)–Sb(2) 2.198(4), C(49)–Sb(1) 2.179(5), C(50)–Sb(2) 2.170(5), C(1)–Sb(1)–C(49) 103.21(17), C(1)–Sb(1)–Sb(2) 98.09(10), C(49)–Sb(1)–Sb(2) 91.50(14), C(25)–Sb(2)–C(50) 102.89(17), C(25)–Sb(2)–Sb(1) 98.47(10), C(50)–Sb(2)–Sb(1) 92.25(13), C(1)–Sb(1)–Sb(2)–C(25) 155.30(15), C(49)–Sb(1)–Sb(2)–C(50) 51.65(19), C(1)–Sb(1)–Sb(2)–C(50) 51.91(17), C(49)–Sb(1)–Sb(2)–C(25) 51.74(17).

137–138 °C. ^{1}H NMR (360.1 MHz, C_6D_6): δ 2.01, 2.06 (s, 12H, *o*-CH_3), 2.15 (s, 6H, *p*-CH_3), 6.60, 6.76 (m, 2H, *m*-Mes), 6.86 (d, 2H, *m*-C_6H_3), 6.87 (m, 1H, *p*-Ph), 6.91 (m, 2H, *m*-Ph), 7.13 (dd, 1H, *p*-C_6H_3), 7.19 (m, 2H, *o*-Ph). ^{13}C NMR (90 MHz, C_6D_6): δ 21.2 (*p*-CH_3), 21.5, 21.7 (*o*-CH_3), 128.3 (*m*-Ph), 128.4 (*p*-Ph), 128.8 (*m*-Mes), 129.7 (*m*-C_6H_3), 130.9 (*p*-C_6H_3), 134.6 (*o*-Ph), 136.4, 136.5 (*o*-Mes), 137.6 (*p*-Mes), 138.8 (*i*-Mes), 141.0 (*i*-Ph), 141.8 (*i*-C_6H_3), 149.3 (*o*-C_6H_3). MS (EI, 70 eV) *m*/*z* (relative intensity %): 590 (22.7) $[M]^+$, 511 (45.0) $[M-Br]^+$, 312 (38.9) $[Dmp-H]^+$. HRMS (EI, 70 eV) *m*/*z*: Calc. for $[M]^+$ $C_{30}H_{30}{}^{79}Br^{121}Sb$, 590.05691; found, 590.05691. Anal. Calc. for $C_{30}H_{30}BrSb$ (592.22): C, 60.84; H, 5.11. Found: C, 60.69; H, 5.30%.

4.4. Synthesis of $DmpSbH_2$ (**4**)

A suspension of 3.3 g (5.5 mmol) $DmpSbBr_2$ in 100 ml Et_2O was added over a suspension of 2.1 g (55.3 mmol) $LiAlH_4$ in 50 ml Et_2O. After 2 h of stirring the solvent was removed under reduced pres-

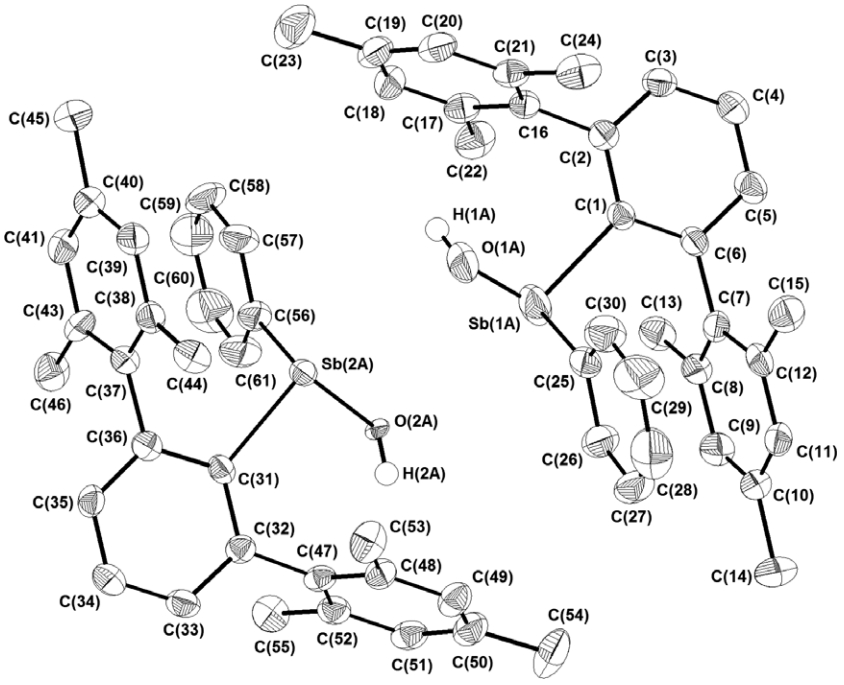


Fig. 8. Thermal ellipsoid representation (30%) of dimeric units in the structure of Dmp(Ph)SbOH (**9**). The carbon bonded hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Sb(1A)–O(1A) 1.814(13), Sb(2A)–O(2A) 2.065(5), C(1)–Sb(1A) 2.167(5), C(25)–Sb(1A) 2.217(6), C(31)–Sb(2A) 2.176(5), C(56)–Sb(2A) 2.175(6), C(1)–Sb(1A)–C(25) 100.1(2), C(1)–Sb(1A)–O(1A) 104.5(4), C(25)–Sb(1A)–O(1A) 88.0(5), C(31)–Sb(2A)–C(56) 100.4(2), C(31)–Sb(2A)–O(2A) 95.9(2), C(56)–Sb(2A)–O(2A) 86.0(2); C(6)–C(1)–Sb(1A)–C(25) 69.2(4), C(36)–C(31)–Sb(2A)–C(56) 69.9(4).

sure. Extraction with 300 ml hexane followed by solvent removal under reduced pressure afforded $DmpSbH_2$ [2]. Yield: 1.99 g (83%). ^{1}H NMR (200.1 MHz, C_6D_6): δ 2.09 (s, 12H, *o*-CH_3), 2.19 (s, 6H, *p*-CH_3), 2.81 (s, 2H, SbH_2), 6.86 (s, 4H, *m*-Mes), 6.98 (d, 2H, *m*-C_6H_3), 7.20 (t, 1H, *p*-C_6H_3).

4.5. Synthesis of Dmp(Ph)SbH (**5**)

A suspension of 1.0 g (1.69 mmol) Dmp(Ph)SbBr in diethyl ether was added dropwise to 0.2 g (5 mmol) $LiAlH_4$ in diethyl ether cooled to −50 °C. After 2 h stirring the solvent was removed in vacuum and the solid was extracted with hexane. The removal of the solvent afforded solid **5**. Yield: 0.5 g (60%). ^{1}H NMR (200.1 MHz): δ 1.82 (s, 6H, *o*-CH_3), 2.22 (s, 12H, *o*- and *p*-CH_3), 5.09 (s, 1H, Sb*H*), 6.72, 6.90 (s, 4H, *m*-Mes), 6.91 (m, 2H, *m*-Ph), 6.96 (d, 2H, *m*-C_6H_3), 6.98 (m, 1H, *p*-Ph), 7.18 (t, 1H, *p*-C_6H_3), 7.21 (m, 2H, *o*-Ph). ^{13}C NMR (50.3 MHz): δ 21.2 (*o*-CH_3), 21.57, 21.61 (*o*- and *p*-CH_3), 128.5 (*p*-Ph), 128.6 (*m*-C_6H_3), 128.7 (*m*-Ph), 129.2, 129.3 (*m*-Mes), 129.7 (*p*-C_6H_3), 133.3 (*i*-Ph), 135.6, 137.0 (*o*-CH_3), 137.3 (*o*- and *p*-CH_3), 139.7 (*i*-C_6H_3), 140.0 (*o*-Ph), 142.3 (*i*-Mes), 149.5 (*o*-C_6H_3). MS (FD, positive): 314 (11.7) $[DmpH]^+$, 434 (91.4) $[DmpSb]^+$, 511 (16.6) $[Dmp(Ph)Sb]^+$, 528 (60.4) $[Dmp(Ph)SbOH]^+$. IR (nujol, cm^{-1}): 1883 (ν_{SbH}).

4.6. Synthesis of Dmp(Me)SbH (**6**)

A slurry of 0.35 g (2.5 mmol) MeI and 0.38 g (2.5 mmol) DBU in 50 ml Et_2O was added dropwise to solution of 1.1 g (2.5 mmol) $DmpSbH_2$ in 50 ml Et_2O at −50 °C. The reaction mixture was stirred for 1 h at −50 °C and then was allowed to warm gradually to room temperature. The solvent was removed in vacuum and the solid was extracted with 200 ml hexane. After the removal of the hexane **6** remained. Yield: 1.1 g (90%). ^{1}H NMR (200.1 MHz, C_6D_6): δ 0.45 (d, 3H, Sb–CH_3, $^3J_{HH}$ = 6 Hz), 2.07 (s, 6H, *o*-CH_3), 2.18, 2.19 (s, 12H, *o*-CH_3), 3.31 (q, 1H, Sb*H*, $^3J_{HH}$ = 6 Hz), 6.84, 6.87 (d, 4H, *m*-Mes), 6.97 (d, 2H, *m*-C_6H_3, $^3J_{HH}$ = 7.4 Hz), 7.21 (t, 1H, *p*-C_6H_3, $^3J_{HH}$ = 7.4 Hz). ^{13}C NMR (90 MHz, C_6D_6): δ −11.5 ($SbCH_3$), 21.5 (*o*- and *p*-CH_3), 128.3 (*m*-C_6H_3), 129.3, 129.6 (*m*-Mes), 129.9 (*p*-C_6H_3), 135.9, 136.5 (*o*-Mes), 137.3 (*p*-Mes), 138.1 (*i*-C_6H_3), 149.7 (*o*-C_6H_3). MS (EI, 70 eV): 450 (49.4) $[M]^+$, 435 (100) [M−Me], 314 (77.5) $[Dmp+H]^+$. IR (nujol, cm^{-1}): 1870 (ν_{SbH}).

4.7. Synthesis of $DmpSb(SbMe_2)_2$ (**7**)

0.85 g (2.8 mmol) Me_4Sb_2 were added via syringe over 0.61 g (1.4 mmol) $DmpSbH_2$. The reagents were allowed to react at room temperature for 1 h. The reaction mixture was heated gradually under reduced pressure up to 90 °C to remove traces of Me_4Sb_2 and **7** remained. Yield: 0.8 g (77%). ^{1}H NMR (200.1 MHz, C_6D_6): δ 0.78 (s, 6H, Sb–CH_3), 0.95 (s, 6H, Sb–CH_3), 2.20 (s, 12H, *o*-CH_3), 2.23 (s, 6H, *m*-CH_3), 6.87–6.91 (m, 6H, *m*-Mes and *m*-C_6H_3), 7.16 (dd, 1H, *p*-C_6H_3). ^{13}C NMR (50.3 MHz, C_6D_6): δ −6.5, −6.9 (Sb–CH_3), 21.2 (*p*-CH_3), 22.3 (*o*-CH_3), 128.2 (*m*-C_6H_3), 128.8 (*p*-C_6H_3), 129.1 (*m*-Mes), 134.5 (*i*-C_6H_3), 136.0 (*o*-Mes), 137.2 (*p*-Mes), 142.9 (*i*-Mes), 150.2 (*o*-C_6H_3). MS (EI, 70 eV): 989 (3.0) $[Dmp_2Sb_3]^+$, 868 (3.0) $[Dmp_2Sb_2]^+$, 736 (3.0) $[M]^+$, 585 (7.1) [M−Sb−3Me]$^+$, 555 (2.8) $[DmpSb_3]^+$, 449 (64.2) $[Dmp(Me)Sb]^+$, 434 (81.4) $[DmpSb]^+$, 419 (2.1) $[DmpSb]^+$, 151 (77.9) $[Me_2Sb]^+$.

4.8. Formation of $\{Dmp(Me)Sb\}_2$ (**8**)

Exposure of a 2% solution of **6** in C_6D_6 to day light gives **8**. Yield: 49%. ^{1}H NMR (360.1 MHz, C_6D_6): δ 0.49 (s, 6H, Sb–CH_3), 2.03, 2.07 (s, 6H, *o*-CH_3), 2.20 (s, 12H, *p*-CH_3), 6.77 (d, 4H, *m*-C*H*), 6.80 (s, 8H, *m*-Mes), 7.06 (s, 2H, *p*-C_6H_3). ^{13}C NMR (50.3 MHz, C_6D_6): δ −7.6 (Sb–CH_3), 21.2 (*p*-CH_3), 21.8, 21.9 (*o*-CH_3), 128.3 (*p*-C_6H_3), 128.7 (*m*-C_6H_3), 128.9 (*m*-Mes), 136.1, 136.4 (*o*-CH_3), 136.7 (*p*-Mes), 137.3 (*i*-C_6H_3), 141.7 (*i*-Mes), 149.6 (*o*-C_6H_3).

Crystals of **8** · C_6D_6 were grown from a 5% solution of $DmpSbH_2$ and $Cp_2Ti[C_2(Me_3Si)_2]$ in a NMR tube.

Table 1
X-ray diffraction data and structure refinement for **1**–**3**, **5**, **8** and **9**

	1	**2**	**3**	**5**	**8** · C_6D_6	**9**
Empirical formula	$C_{24}H_{25}Br_2Sb$	$C_{24}H_{25}I_2Sb$	$C_{30}H_{30}BrSb$	$C_{30}H_{31}Sb$	$C_{56}H_{56}D_6Sb_2$	$C_{30}H_{31}OSb$
Formula weight	595.01	688.99	592.20	513.30	984.59	529.30
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$	$P\bar{1}$	P/c
a (Å)	17.175(9)	16.577(3)	39.259(8)	8.760(4)	12.127(5)	8.9514(18)
b (Å)	30.507(10)	16.578(4)	8.6597(17)	22.311(5)	14.102(3)	22.293(5)
c (Å)	17.895(5)	18.086(7)	15.444(3)	12.631(3)	15.315(4)	12.636(3)
α (°)	90	90	90	90	102.370(10)	90
β (°)	90.68(3)	103.94(2)	91.90(3)	91.54(4)	109.43(2)	91.00(3)
γ (°)	90	90	90	90	98.43(2)	90
Volume (Å^3)	9376(6)	4824(2)	5247.7(18)	2467.8(14)	2344.1(12)	2521.1(9)
Z	16	8	8	4	2	4
Calculated density (Mg/m^3)	1.686	1.897	1.499	1.382	1.386	1.394
Absorption coefficient (mm^{-1})	4.593	3.710	2.589	1.132	1.188	1.113
F(000)	4640	2608	2368	1048	1000	1080
Crystal size (mm^3)	0.7 × 0.5 × 0.3	0.9 × 0.3 × 0.3	0.5 × 0.4 × 0.3	0.9 × 0.3 × 0.1	0.6 × 0.4 × 0.2	0.5 × 0.4 × 0.3
θ range for data collection (°)	2.13–25.01	2.53–27.51	2.41–24.99	2.94–25.01	2.64–27.50	2.44–26.08
Index ranges (h,k,l)	−19/20, −11/36, ±21	−21/14, −9/21, ±23	±46, ±10, ±18	−8/10, −26/14, ±15	±15, ±17, ±19	±11, ±27, ±15
Reflections collected/unique [$R_{(int)}$]	19040/16282 [0.0707]	13249/11074 [0.0381]	16992/4260 [0.089.6]	5616/4331 [0.0457]	12341/10636 [0.0275]	25385/9531 [0.0622]
Completeness to θ [θ] (%)	98.4 [25.01]	99.7 [27.51]	92.3 [24.99]	99.6 [25.01]	98.8 [27.50]	96.0 [26.08]
Maximum and minimum transmission	0.3395 and 0.1413	0.4024 and 0.1351	0.5105 and 0.3576	0.8952 and 0.4290	0.7971 and 0.5359	0.7312 and 0.6060
Data/restraints/parameters	16282/0/998	11074/0/499	4260/0/304	4331/0/290	10636/0/547	9531/14/616
Goodness-of-fit on F^2	1.013	1.066	1.081	0.956	1.020	0.949
Final R indices ($I > 2\sigma(I)$) (R_1, wR_2)	0.0624, 0.1346	0.0699, 0.1839	0.0658, 0.1734	0.0662, 0.1427	0.0453, 0.1006	0.0389, 0.0832
R indices (all data) (R_1, wR_2)	0.1199, 0.1611	0.0973, 0.1988	0.1025, 0.1877	0.1303, 0.1653	0.0691, 0.1103	0.0585, 0.0906
Largest difference peak and hole (e · Å^{-3})	0.948 and −1.079	3.381 and −3.197	2.790 and −1.067	0.803 and −1.674	0.801 and −1.131	0.428 and −0.541

4.9. Synthesis of Dmp(Ph)SbOH (**9**)

14.6 g (20 mmol) **3** in 50 ml toluene were flushed over a chromatography column (19 cm × 2.5 cm, Al_2O_3, activity level 2). Two fractions of 50 and 100 ml were eluted with toluene. Removal of the solvent from the second fraction gave crystals of **9**. Yield: 2.0 g (19.3%), m.p. 161–164 °C. ^{1}H NMR (360.1 MHz): δ 1.91, 2.15 (s, 12H, *o*-CH_3), 2.13 (s, 6H, *p*-CH_3), 6.70, 6.79 (m, 4H, *m*-Mes), 6.85 (s, 2H, *m*-C$_6H_3$), 7.03 (m, 1H, *p*-Ph), 7.05 (m, 2H, *m*-Ph), 7.15 (t, 1H, *p*-C$_6H_3$), 7.24 (m, 2H, *o*-Ph). ^{13}C NMR (50.3 MHz, C_6D_6): δ 21.11 (*p*-CH_3), 21.11, 21.37 (*o*-CH_3), 128.89, 129.08 (*m*-Mes), 129.60 (*m*-C_6H_3), 129.60 (*p*-C_6H_3), 133.79 (*o*-Ph), 136.51, 136.89 (*o*-Mes), 137.60 (*p*-Mes), 138.29 (*i*-Mes), 146.50 (*i*-C_6H_3), 147.55 (*o*-C_6H_3). MS (CI, positive): 528 (52.7) [M]$^+$, 511 (100) [M−OH]$^+$, 314 (40.9) [Dmp+H]$^+$, 78 (9.1) [Ph+H]$^+$. MS (CI, negative): 527 (11.7) [M−H]$^-$, 511 (14.0) [M−OH]$^-$, 214 (100) [PhSbO]$^-$. Anal. Calc. for $C_{30}H_{31}OSb$ (529.32): C, 68.07; H, 5.90. Found C, 67.91; H, 6.10%.

4.10. X-ray structure determinations

The data for X-ray structure analysis were collected on a Siemens P4 four-circle (**1**, **2**, **5**, **7**) or STOE-IPDS (**3**, **9**) diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). For this purpose the crystals were attached with Kel-F oil to a glass fibre and cooled in a nitrogen stream to 173 K. The structures were solved by Patterson methods [20], or direct methods [21]. All non-hydrogen atoms were refined with anisotropic thermal parameters. For structure solving and refinement the software package WINGX was used [22]. The drawings were created using Diamond. The hydrogen atoms were calculated in riding positions. The hydrogen atom directly attached to antimony in **5** was refined isotropically without any constraints. The structure of **9** was solved and refined in the space group P/c although the systematic absences indicate that $P2_1/c$ is the correct space group. However, the final structure factors are considerably better for the solution obtained in the P/c space group (R_1 = 0.0389, wR_2 = 0.0832 (P/c) vs. R_1 = 0.1258, wR_2 = 0.2428 ($P2_1/c$)). In both solutions with different space groups there is a disorder involving the antimony atoms and the hydroxyl groups. In the P/c space group the antimony atoms of the two crystallographically independent molecules can be located on two positions and were refined using free variables. They belong to the two isomers (*R* and *S*). The oxygen atoms suffer the same type of disorder and they were refined in an analogous way. The oxygen atoms O1B O2B were constrained to be isotropic (see Table 1).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for financial support. We thank Dipl. Ing. J. Stelten for the 2D NMR spectra acquisition and analysis and Dr. T.Dülcks and Dipl. Ing. D. Kemken for the mass spectra measurements.

Appendix A. Supplementary material

CCDC 678179, 678177, 678175, 678178, 678174 and 678176 contain the supplementary crystallographic data for **1**, **2**, **3**, **5**, **8** and **9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.038.

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