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Synthesis and ^{121}Sb Mössbauer Study of a Number of Organoantimony(III) Compounds Containing Antimony–Main Group V Element Bonds

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Abstract

The synthesis of organoantimony(III) compounds of the type $R_2SbMR'_2$ in which R,R′ = Et or Ph and M = N, P or As has been investigated. Diphenylaminodiethylstibine and diphenylaminodiphenylstibine were successfully synthesized. Attempts to prepare phosphinostibines and arsinostibines of the type $R_2Sb{-}MR'_2$ (M = P, As) failed and resulted in the formation of the corresponding diphosphines, diarsines, and distibines Only in the case of the synthesis of $Ph_2AsSbPh_2$ was an analytically pure product obtained. A series of antimony(III) compounds containing antimony–main group V element bonds has been investigated by ^{121}Sb Mössbauer spectroscopy. The near consistency in the isomer shift (−4.0 to −4.6 mm/s relative to InSb) implies almost no change in the s-character in the total antimony–ligand bonds. Variation in the values of the quadrupole coupling constant and the asymmetry factor are discussed in terms of structure and/or changes in the p-character of the antimony–ligand bonds.

Introduction

A great deal has been reported in the literature on the synthesis, bonding, and structure of a variety of compounds in which there are examples of antimony being bonded to numerous different kinds of ligands, but so far little information is available on organoantimony(III) compounds in which a substituent group is bound to antimony by a Vth main group element.

Aminoorganostibines have been known since 1970, when Meinema and Noltes [1] reported on the synthesis of compounds of the type $R_nSb(NEt_2)_{3-n}$ (R = Me, Et, n-Pr, n-Bu and Ph; n = 1, 2). The corresponding dimethylaminodimethylstibine has been reported by Koketsu *et al.* [2]. Recently the synthesis of diphenylphosphino- and diphenylarsinodiphenylstibine has been reported by Kuhn and Winter [3]. The tetraorganodistibines, R_2SbSbR_2 (R = Me [4], Et [4], Ph [5], $R_2 = (CH_2)_4$ [6], $(CH_2)_5$ [6]), have been prepared by the reaction of the corresponding diorganostibylsodium derivatives with 1,2-dihaloethane.

In the present paper we report on studies aimed at the synthesis of a complete series of organoantimony(III) compounds of the type $R_2SbMR'_2$, in which R,R′ = Et or Ph and M = N, P, or As, and an investigation of these compounds with ^{121}Sb Mössbauer spectroscopy [7]. This is a continuation of our recent studies of organoantimony bonded to chlorine [8], oxygen [9], and sulfur [10]. For the antimony(III) complexes we have studied, the most frequently used model for understanding these species has been a trigonal structure, containing three ligands, and a charge density representing the 'lone pair' electrons which are directed in space from the antimony in the opposite direction of the bonds to the three ligands. The charge density of the 'lone pair' electrons has been the primary contribution to the values of the quadrupole coupling constants for most Sb(III) compounds. In our studies of organoantimony(III) complexes, the ^{121}Sb Mössbauer isomer shift [10] (δ) values (relative to the InSb standard) range from −8 to 0 mm/s. This span of δs is indicative of the variety of differences in the bonding between antimony and its ligands (*i.e.*, the bond characteristics are very much ligand dependent).

Experimental

All synthetic operations were performed under oxygen-free nitrogen. Et_2PH was purchased from

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Alfa; Ph_2PH (boiling point (b.p.) 90–95 °C/0.5 mm Hg) and Ph_2AsH (b.p. 96–98 °C/0.2 mm Hg) were prepared from Ph_3P and Ph_3As by the procedure reported for Ph_2PH [11]. Analytical data were provided by the Section Elemental Analysis of the Institute of Applied Chemistry TNO, Utrecht, The Netherlands.

Diethylaminoorganostibines

R_2SbNEt_2 (R = Et, Ph) and $RSb(NEt_2)_2$ (R = Me, Ph) have been prepared according to a procedure described in the literature [1].

Diphenylaminodiethylstibine

Et_2SbNEt_2 (3.3 g, 13.1 mmol) and Ph_2NH (2.2 g, 13.0 mmol) were heated together at 100 °C for a period of 3 h. During this process Et_2NH was distilled from the reaction mixture. Subsequently, Et_2SbNPh_2 (2.7 g, 61%). b.p. 130–135 °C/0.1 mm Hg was obtained as a pale yellow liquid. *Anal.* Calc. for $C_{16}H_{20}NSb$: Sb, 34.96; N, 4.02. Found: Sb, 34.6; N, 4.2%.

Diphenylaminodiphenylstibine

Ph_2SbNEt_2 (1.3 g, 3.7 mmol) and Ph_2NH (0.6 g, 3.6 mmol) were heated together at reduced pressure (40 mm Hg) at 140 °C for a period of 4 h. Diethylamine was evaporated from the reaction mixture. Subsequently a yellow solid was isolated, which was recrystallized from a benzene/pentane mixture to give Ph_2SbNPh_2 (0.6 g, 37%) melting point (m.p.) 79–81 °C. *Anal.* Calc. for $C_{24}H_{20}NSb$: Sb, 27.41; N, 3.15. Found: Sb, 27.6; N, 3.1%.

Attempted Preparation of Diethylphosphinodiphenylstibine

Diethylphosphine (3.0 ml) was syringed into a solution of Ph_2SbNEt_2 (0.8 g, 2.3 mmol) in pentane (10 ml). The mixture was stirred magnetically. After 60 min $Ph_2SbSbPh_2$ (0.32 g, 50%), m.p. 123–124 °C (literature [5], 125 °C) had deposited as a yellow crystalline solid. *Anal.* Calc. for $C_{24}H_{20}Sb_2$: Sb, 44.11. Found: Sb, 44.2%.

Attempted Preparation of Diphenylphosphinodiethylstibine

Diphenylphosphine (0.9 g, 4.8 mmol) was added to a solution of Et_2SbNEt_2 (1.2 g, 4.8 mmol) in pentane (5 ml). After 45 min Ph_2PPPh_2 (0.48 g, 54%), m.p. 121–123 °C (literature [12] 120.5 °C) had deposited as a colourless solid. *Anal.* Calc. for $C_{24}H_{20}P_2$: P, 16.73. Found: P, 16.9%.

-n-BuLi (1.26 molar) in hexane (35 ml) was added to a solution of Ph_2PH (8.2 g, 44.1 mmol) in THF (75 ml) to give a red-coloured solution of Ph_2PLi. This was added dropwise to a stirred solution of Et_2SbBr [13] (11.4 g, 44 mmol) in THF (25 ml). The red colour disappeared instantaneously. Evaporation of the solvents resulted in the isolation of a mixture of a yellow liquid and a colourless solid. Recrystallization of the solid from benzene/methanol gave Ph_2PPPh_2 (2.8 g, 34%), m.p. 115–117 °C.

Attempted Preparation of Diphenylphosphinodiphenylstibine

Reactions of Ph_2SbNEt_2 (0.8–1.6 g) and Ph_2PH (0.5–0.9 g) in a 1/1 molar ratio in pentane (10–100 ml) resulted in the deposition of a pale yellow crystalline solid (0.5–1.3 g). It was either analyzed as such or after recrystallization from a benzene/pentane mixture. C, H analytical data of the various products suggested that mixtures of $Ph_2SbSbPh_2$ and Ph_2PPPh_2 had been isolated. *Anal.* Calc. for $C_{24}H_{20}Sb_2$: C, 52.23; H, 3.63. Calc. for $C_{24}H_{20}P_2$ C, 77.75; H, 5.40. Found: C, 56.3–61.2; H, 3.8–5.0%.

Attempted Preparation of Diphenylarsinodiethylstibine

Addition of Ph_2AsH (1.3 g, 5.7 mmol) to a solution of Et_2SbNEt_2 (2.0 g, 7.9 mmol) in hexane (20 ml) resulted in the isolation of $Ph_2AsAsPh_2$ (0.95 g, 73%), m.p. 127–128 °C (literature [14] 128–129 °C) which had deposited from the reaction mixture as a colourless solid. *Anal.* Calc. for $C_{24}H_{20}As_2$: As 32.69. Found: As, 33.0%.

Preparation of Diphenylarsinodiphenylstibine

Addition of Ph_2AsH (2.2 g, 9.5 mmol) to a solution of Ph_2SbNEt_2 (3.3 g, 9.5 mmol) in pentane (10 ml) resulted in the gradual deposition of a yellowish solid, which was recrystallized from a benzene/pentane 3/2 mixture to give a product which analyzed for $Ph_2AsSbPh_2$ (2.9 g, 60%), m.p. 114–116 °C. *Anal.* Calc. for $C_{24}H_{20}AsSb$: C, 57.06; H, 3.99; As + Sb, 38.97. Found: C, 57.4; H, 3.9; As + Sb, 38.7%.

Preparation of Tetraorganodistibines

Tetraorganodistibines, R_2SbSbR_2 (R = Me [4], Ph [5], $(CH_2)_4$ [6], $(CH_2)_5$ [6]), have been prepared following the procedures described in the literature.

^{121}Sb Mössbauer Spectra

A $Ni_{21}{}^{121m}Sn_2B_6$ source was used for obtaining the ^{121}Sb Mössbauer spectra with both the source and absorber cooled to 4.2 K. All spectral data were fitted to theoretical line shapes using transmission integral analysis. Figure 1 shows the spectra of three of the samples in this investigation. The data for all the samples studied are listed in Table I. All isomer shifts are given relative to an InSb absorber at 4.2 K. Additional experimental details and information on the data analysis are given in a previous paper [10].

TABLE I. ^{121}Sb Mössbauer Parameters for Organoantimony(III) Compounds Containing Antimony–Main Group V Element Bond. All Data Taken at 4.2 K

Compounds	δ^a (mm/s) (±0.2)	e^2qQ/h (mm/s) (±1.0)	η^a (+0.2)
$(CH_2)_4SbSb(CH_2)_4$	-4.5	+16.2	0.9
$(CH_2)_5SbSb(CH_2)_5$	-4.4	+16.4	0.4
$Me_2SbSbMe_2$	-4.0	+13.1	0.0
$Ph_2SbSbPh_2$	-4.5	+13.6	0.4
$Ph_2SbAsPh_2$	-4.6	+14.0	0.3
Et_2SbNEt_2	-4.0	+19.6	0.8
Ph_2SbNEt_2	-4.1	+18.5	0.5
Ph_2SbNPh_2	-4.5	+19.9	0.8
Et_2SbNPh_2	-4.4	+20.4	1.0
$PhSb(NEt_2)_2$	-4.3	+21.6	0.1
$MeSb(NEt_2)_2$	-4.3	+20.7	0.4

^{a}Relative to InSb.

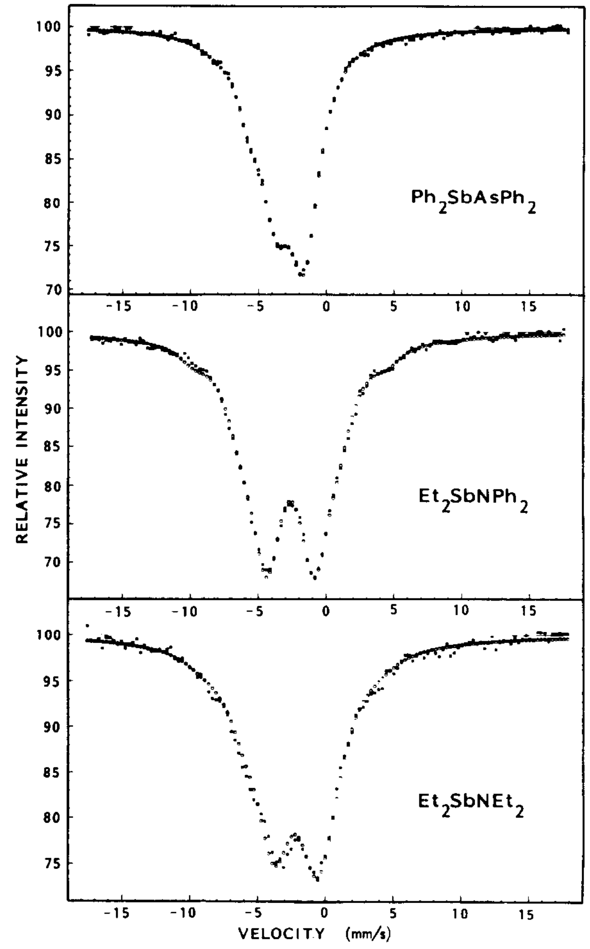

Fig. 1. ^{121}Sb Mössbauer spectra at 4.2 K of $Ph_2SbAsPh_2$, Et_2SbNPh_2, and Et_2SbNEt_2. (■) Measured intensities; (○), intensies calculated with parameters given in Table I.

Results and Discussion

Synthesis

Attempts have been made to synthesize a series of organoantimony(III) compounds of the type $R_2SbMR'_2$ (R,R' = Et, Ph; M = N, P, As). To that purpose diethylaminodiethylstibine [1] and diethylaminodiphenylstibine [1] have been applied as starting materials. Treatment of these compounds with diphenylamine at 100 °C results in the occurrence of a transamination reaction (eqn. (1), R' = Ph, M = N) and the isolation of the corresponding diphenylaminodiorganostibines.

$$R_2SbNEt_2 + HMR'_2 \longrightarrow R_2SbMR'_2 + HNEt_2 \qquad (1)$$

(R = Et, Ph, R' = Ph, M = N)

Similar reactions with diethylphosphine, diphenylphosphine and diphenylarsine, however, take a different course (eqn. (2)) leading to the formation of the corresponding diphosphines, diarsines and distibines.

$$2R_2SbNEt_2 + 2HMR'_2 \longrightarrow$$

$$R'_2MMR'_2 + R_2SbSbR + 2HNEt_2 \qquad (2)$$

(R = Et, Ph; R' = Et, Ph; M = P)
(R = Et, R' = Ph, M = As)

Only for the synthesis of $Ph_2AsSbPh_2$ (eqn. (1) R,R' = Ph; M = As), a product has been obtained which analyzed for the desired compound. It cannot be fully excluded that a 1/1 molar mixture of tetraphenyldiarsine and distibine has been isolated.

An attempt to prepare diphenylphosphinodiethylstibine by the reaction of diphenylphosphinolithium with bromodiethylstibine also did not result in the isolation of the desired product. Again a mixture of the corresponding diphosphine and distibine had been formed.

$$2Ph_2PLi + 2Et_2SbBr \longrightarrow$$

$$Ph_2PPPh_2 + Et_2SbSbEt_2 + 2LiBr \qquad (3)$$

Our results and conclusions differ from those presented by Kuhn and Winter [3]. They reported the isolation of Ph_2PSbPh_2 and $Ph_2AsSbPh_2$. In the case of $Ph_2P{-}SbPh_2$, the inconsistency of the elemental analysis of several preparations points to the presence of a mixture of Ph_3PPPh_2 and $Ph_2SbSbPh_2$ in our experiments. For $Ph_2AsSbPh_2$, we have isolated a pale yellow crystalline compound in contrast to the dark-brown solid they reported.

^{121}Sb-Mössbauer Spectroscopy

One of the more striking results noted from the Mössbauer parameters for the series under investigation is the constancy in the isomer shift. These values are all within the narrow range of −4.0 to −4.6 mm/s. This is interpreted to mean that the s-character of the antimony–ligand bond in the various antimony–main group V compounds studied here remains essentially constant regardless of whether the bonds formed are Sb–Sb, Sb–As or Sb–N.

The positive value for e^2qQ/h and the magnitude of the values in the eleven compounds studied are indicative of lone pair electrons that are composed of a considerable amount of p-character. These values are consistent with values known for a number of simple SbA_3 compounds (See Table II). Structural data are available for the compounds listed in Table II, and generally the ASbA bond angle is close to 95°. For any particular compound, usually all three trigonal bond angles are approximately the same. As we have shown in an earlier paper [8] the main contribution to the value of the quadrupole coupling constant is the p-character of the lone pair. This describes the cases of R_2SbSbR_2 (where $R_2 = Me_2$, Ph_2, $(CH_2)_4$, and $(CH_2)_5$). In the case of $(CH_2)_4SbSb(CH_2)_4$ the asymmetry parameter [9] is not close to 0.0 but is 0.9. We interpret this as having to do with the bond angles Specifically, the CSbC bond angle is likely to be different from the two CSbSb bond angles, while in the other complexes these three bond angles are approximately the same. It is probable that the CSbC bond angle is less than 90°. This is predicted when considering the $(CH_2)_4$ ring with normal C–C and Sb–C bond distances. Also the X-ray structure of $(CH_2)_4SbMeCl_2$ containing a five-membered ring of antimony and four carbons has recently been completed [19]. In this particular case the antimony is in an oxidation state of five and the structure is a distorted trigonal bipyramid (tbp). The expected angle of CSbC based on tbp would be 120°, but the angle determined is 90.4°. Without any strain on the ring, the preferred angle would be less than 80°

TABLE II. ^{121}Sb Mössbauer Isomer Shifts and Quadrupole Coupling Constants Data for SbX_3 Compounds

Compounds	δ^a (mm/s)	e^2qQ/h (mm/s)	Reference
$SbCl_3$	−5.9	13.2	10
$SbBr_3$	−5.9	10.7	10
SbI_3	−7.7	–	10
$SbMe_3$	0.0	15.2	15
$SbPh_3$	−0.7	16.2	16
Sb_2O_3	−3.3	18.2	17
Sb_2S_3	−5.7	–	18

^{a}Relative to InSb.

X-ray structure data is available for the $Ph_2SbSbPh_2$ compound. Specifically, the C_1SbC_2, C_1SbSb, and C_2SbSb bond angles are 94.4°, 96.5° and 93.8°, respectively [20]. This corraborates the interpretation of the Mössbauer parameters in terms of the structure, but there is a difference in bonding descriptions. Von Deuten and Rehder in describing the $Ph_2SbSbPh_2$ structure from the X-ray data [20] interpret that since the bond angles (94.4°, 96.5° and 93.8°) are close to 90°, this indicates the lone pair is primarily s-character. But, this is in contrast to the values of the quadrupole coupling constants interpreted as resulting from the p-character of the lone pair, not the s-character. Extended Hückel calculations show lone pair p-character in the $Me_xSbCl_{(3-x)}$ trigonal series [8] for bond angles in the range of 90–100°. The X-ray structure of a slightly distorted distibine has recently been reported by Ashe *et al.* [21] for 2,2′,5,5′-tetra-methyldistibolyl. In their paper they interpreted as Von Deuten and Rehder did, that the bond angles C_5SbC_2, C_5SbSb', and C_2SbSb' (respectively 81.5, 92.9 and 91.4°) indicate that the lone pair is essentially s-hybridized, not p. More recently, though, an Extended Hückel calculation has been completed on this compound by Hughbanks *et al.* [22]. Their results are that the lone pair indeed has considerable p-character.

The $Ph_2SbAsPh_2$ compound has Mössbauer parameters that are experimentally identical to those for $Ph_2SbSbPh_2$. One can conclude that the molecular structure and bonding are quite similar for these two compounds.

For the two compounds $RSb(NEt_2)_2$ (R = Me, Ph), the asymmetry parameter is close to zero: consequently, the antimony trigonal structure contains quite similar bond angles and bond characters. The quadrupole coupling constants are approximately a third larger than for most cases in Table II and for those compounds discussed so far. This larger value can be explained by an increase in the p-character of the lone pair in comparison with the other compounds. Consequently, the nitrogens are promoting electrons into the lone pair p-orbital.

The four compounds that make up the R_2SbNR_2 (R = Et, Ph) series all have $\eta > 0.5$ and slightly larger e^2qQ/h values compared to the Sb–Sb and Sb–As compounds. The isomer shifts do not differ from others in this investigation. The η value can be explained if there is a p-character difference in the Sb–C and Sb–N bonds. This would also explain the slightly larger quadrupole coupling constant. The constancy in isomer shift is identifying a constancy in s-character of the bonds and lone pair orbitals.

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