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Primary and secondary trimethylsilylmethylstibines. Synthesis, characterization and chemical vapor deposition properties

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Abstract

The primary and secondary trimethylsilylmethylstibines (trimethylsilylmethyl = Me_3SiCH_2–) $(Me_3SiCH_2)SbH_2$ and $(Me_3SiCH_2)_2SbH$ have been synthesized by the reduction of a corresponding dihalo- and monohaloantimony compound, respectively. Trimethylsilylmethylstibine was prepared by the reduction of $(Me_3SiCH_2)SbBr_2$ with lithium aluminum hydride (LAH) in tetraglyme. The primary stibine is highly air-sensitive and exhibits a vapor pressure of 2.0 Torr at 0°C. Bis-(trimethylsilylmethyl)stibine was synthesized by the LAH reduction of either $(Me_3SiCH_2)_2SbBr$ or $(Me_3SiCH_2)_2SbI$ in diethyl ether. The secondary stibine is less sensitive to air than $(Me_3SiCH_2)SbH_2$ but nonetheless decomposes quickly when exposed to air. The detailed synthesis, spectroscopic characterizations and physical properties of both stibines, as well as the preliminary chemical vapor deposition experiments of $(Me_3SiCH_2)SbH_2$, are discussed.

1. Introduction

Antimonide-based semiconductors with low-energy bandgaps have been the subject of considerable interest. There have been a number of reports describing the use of triorganoantimony compounds (R_3Sb) as precursors to grow antimonides by metal organic chemical vapor deposition (MOCVD) [1–3]. In a previous publication, we described the synthesis of the primary and secondary neopentylstibines $(Me_3CCH_2)SbH_2$ and $(Me_3CCH_2)_2SbH$, which represent the first thermally stable (at ambient T) and volatile organoantimony hydrides [4]. However, to our knowledge there have been no reports of primary or secondary stibines being used as precursors for antimonide MOCVD. This is somewhat surprising considering the relative success of t-$BuPH_2$ [5] and $^tBuAsH_2$ [6] as precursors for use in MOCVD growth of InP and GaAs respectively. This may be attributed to the inherent instability and/or lack of volatility of organoantimony hydrides previously reported [7–12]. As part of our continuing studies into organoantimony hydrides, we now wish to report the synthesis of the trimethylsilylmethyl analogs $(Me_3SiCH_2)SbH_2$ and $(Me_3SiCH_2)_2SbH$. We have characterized these compounds by $^1H/^{13}C$ NMR, infrared spectroscopy and elemental analysis. Also, we have conducted a preliminary evaluation of the primary stibine as an MOCVD precursor.

2. Experimental section

2.1. General

The compounds described in this manuscript were synthesized by using a combination of Schlenk and vacuum-line techniques. Although no information exists on the toxicity of these compounds, the parent compound, SbH_3, is very toxic, and its derivatives should be regarded likewise until data are available to indicate otherwise. All glassware used in the synthetic work was washed in 6 M HCl, rinsed with distilled water and oven-dried. It was observed that not employing the acid wash resulted in the partial decomposition of the stibines as evidenced by a darkening on the surface of the glass. Other manipulations were performed in a helium-filled glove box (Vacuum Atmospheres). Diethyl ether and tetraglyme were dried over sodium/benzophenone and distilled prior to use. Deuterated benzene (Aldrich) was dried over Na/K alloy, degassed three times, and vacuum distilled.

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Lithium aluminum hydride (Aldrich) was used as received. Antimony tribromide (Strem) was used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-300 spectrometer at 300.13 and 75.468 MHz respectively. ^{1}H spectra were referenced to the residual protic peak of benzene at 7.15 ppm, while proton decoupled ^{13}C spectra were referenced to the center of the benzene triplet at 128.00 ppm. Vapor pressure measurements were made using a capacitance manometer. Infrared spectra were recorded as either gas phase or neat liquids between potassium bromide plates on a Perkin-Elmer 1430 spectrophotometer. Absorption intensities were determined by the method of Durkin, DeHayes and Glore [13] and are reported with the following abbreviations: w (weak), m (medium), sh (shoulder), s (strong), v (very). Elemental analyses were performed by E & R Microanalytical Laboratories, Corona, New York.

2.1.1. Synthesis of (Me$_3$SiCH$_2$)SbBr$_2$ (1)

The synthesis of **1** followed a procedure published by Sowerby and Breunig [14] for the preparation of PhSbBr$_2$. In a typical reaction, 1.00 g (2.61 mmol) of (Me$_3$SiCH$_2$)$_3$Sb [15] was mixed in a flask with 1.89 g (5.22 mmol) of SbBr$_3$ and suspended in an oil bath held at 110°C. Upon melting (approximately 70–80°C), the mixture turned black and solidified. Continued warming to 150°C and heating for 24 h converted the black solid to a yellowish-brown oil. Vacuum distillation of the crude product through a short-path still afforded 2.26 g (78.4% yield) of a slightly greenish-yellow oil. Bp 63–67°C (4.0×10^{-6} Torr). ^{1}H NMR: −0.02 (s, 9H, Sb–CH$_2$–Si–(CH_3)$_3$), 1.46 (s, 2H, Sb–CH_2–Si–(CH$_3$)$_3$). ^{13}C {^{1}H}: 1.23 (s, Sb–CH$_2$–Si–(CH$_3$)$_3$), 26.91 (s, Sb–CH$_2$–Si–(CH$_3$)$_3$). IR (neat): 2950s, 2890m, 1450w, 1405m, 1340m, 1305w, 1260s, 1250vs, 1195vw, 1040m, 1005s, 965m, 850vs, 835vs, 790m, 765s, 755sh, 700s, 650vw, 615w, 600w, 520m, 485vw. Elemental analysis: Calcd. for C$_4$H$_{11}$SiSbBr$_2$: C, 13.03; H, 3.01; Br, 43.34. Found: C, 12.93; H, 3.01; Br, 43.49%.

2.1.2. Synthesis of (Me$_3$SiCH$_2$)SbH$_2$ (2)

To 0.495 g (13.1 mmol) of lithium aluminum hydride suspended in 8 ml of tetraglyme stirred at −25°C, 4.95 g (13.4 mmol) of **1** in 8 ml of tetraglyme at 0°C was added dropwise via cannula. Immediately upon introduction of the dibromide to the LAH solution, a darkening was observed with a small evolution of gas. Addition of the dibromide solution was made over a period of 5–10 min. Following addition, the reaction flask was suspended in an ice bath and evacuated on a high-vacuum line. Volatile materials from the reaction were trapped and fractionated by passing through a −78°C trap and a −196°C trap. The contents of the −78°C trap were examined and found to be a colorless liquid. Transfer of the volatile liquid to a weighed container afforded 1.45 g (51.4% yield) of liquid identified as **2**. ^{1}H NMR: 0.02 (s, 9H, Sb–CH$_2$–Si–(CH_3)$_3$), 0.19 (t, ^{3}J(HH) = 6.3 Hz, 2H, Sb–CH_2–Si–(CH$_3$)$_3$), 1.79 (t, ^{3}J(HH) = 6.3 Hz, 2H, Sb–H_2). ^{13}C {^{1}H}: −0.35 (s, Sb–CH$_2$–Si–(CH$_3$)$_3$), −15.17 (s, Sb–CH$_2$–Si–(CH$_3$)$_3$). IR (gas): 2965s, 2910w, 1865vs, 1415vw, 1385vw, 1370vw, 1300w, 1260s, 1140vw, 1080w, 1030m, 980w, 860vs, 840vs, 775m, 720m, 695w, 660vw, 620vw, 595vw, 545vw, 480w. Elemental analysis: Calcd. for C$_4$H$_{13}$SiSbH$_2$: C, 22.77; H, 6.21; Sb, 57.71. Found: C, 22.45; H, 6.31; Sb, 57.96%.

2.1.3. Synthesis of (Me$_3$SiCH$_2$)$_2$SbBr (3)

To 1.00 g (2.61 mmol) of (Me$_3$SiCH$_2$)$_3$Sb, 0.47 g (1.30 mmol) of SbBr$_3$ was added. The two white solids were heated to 125°C where they melted to form a black liquid. After 10 min at this temperature the black liquid solidified. Continued heating at this temperature for 16 h gave rise to a green oil. The resulting oil was then transferred and distilled through a short-path still to afford 1.09 g (2.89 mmol, 74.2% yield) of a greenish-yellow oil. Bp 45–48°C (1×10^{-5} Torr). ^{1}H NMR: 0.07 (s, 9H, Sb–CH$_2$–Si–(CH_3)$_3$), 1.12 (broad, 2H, Sb–CH_2–Si–(CH$_3$)$_3$). ^{13}C {^{1}H}: 1.16 (s, Sb–CH$_2$–Si–(CH$_3$)$_3$), 15.58 (s, Sb–CH$_2$–Si–(CH$_3$)$_3$). IR (neat): 2950vs, 2890m, 1445w, 1405m, 1345m, 1300w, 1260vs, 1250vs, 1020m, 995s, 960m, 840vs, 760vs, 705vs, 690sh, 605w, 515m. Elemental analysis: Calcd. for C$_8$H$_{22}$Si$_2$SbBr: C, 25.55; H, 5.90; Br, 21.25. Found: C, 25.55; H, 5.18; Br, 21.63%.

2.1.4. Synthesis of (Me$_3$SiCH$_2$)$_2$SbH (4)

The preparation of **4** was accomplished by the reduction of (Me$_3$SiCH$_2$)$_2$SbI or (Me$_3$SiCH$_2$)$_2$SbBr. The synthesis of (Me$_3$SiCH$_2$)$_2$SbI has been previously reported [15]. To 0.084 g (2.22 mmol) of LAH suspended in 5 ml of diethyl ether at −50°C, 0.937 g (2.22 mmol) of (Me$_3$SiCH$_2$)$_2$SbI in 10 ml of diethyl ether was added slowly with stirring. The mixture was held at −50°C for 2 h followed by gradual warming to ambient temperature. Following stirring overnight, the diethyl ether was removed *in vacuo* at −20°C (0.01 Torr) to leave a colorless liquid and an off-white solid. The residue was extracted with pentane and transferred to another vessel. Concentration of the solution at 0.01 Torr afforded 0.300 g (45.5% yield) of a colorless liquid. In an analogous manner using **3**, following removal of the diethyl ether, the remaining residue was transferred to a short-path still and distilled under dynamic vacuum (5×10^{-6} Torr) at ambient temperature. This procedure afforded a higher yield of 53.4% of **4**. ^{1}H NMR: 0.07 (s, 18H, Sb–CH$_2$–Si–(CH_3)$_3$), 0.33

(m, ^2J(HH) = 12.9 Hz, ^3J(HH) = 7.8 Hz, 2H, Sb–CH_2–Si–$(CH_3)_3$), 0.62 (m, ^2J(HH) = 12.9 Hz, ^3J(HH) = 4.6 Hz, 2H, Sb–CH_2–Si–$(CH_3)_3$), 2.38 (triplet of triplets, ^3J(HH) = 4.6 Hz and 7.8 Hz, 1H, Sb–H). ^{13}C {^{1}H}: 0.34 (s, Sb–CH_2–Si–$(CH_3)_3$), −5.03 (s, Sb–CH_2–Si–$(CH_3)_3$). IR (neat): 2955s, 2895m, 2800vw, 1835m, 1450w, 1405m, 1395vw, 1360w, 1300w, 1260s, 1250vs, 1015m, 1000m, 965w, 855vs, 835vs, 760m, 710s, 690m, 635vw, 610vw, 540vw, 510m. Elemental analysis: Calcd. for $C_8H_{23}Si_2SbH$: C, 32.33; H, 7.80; Sb, 40.97. Found: C, 31.82; H, 7.21; Sb, 40.07%.

2.2. *Chemical vapor deposition experiments*

Silicon or gallium arsenide (100) wafers with a thickness of 0.4 mm were cut into pieces ranging from 10 to 20 mm per side. The pieces were degreased with detergent, washed with distilled water, isopropyl alcohol, boiling trichloroethylene, isopropyl alcohol, and blown dry with a stream of nitrogen. The piece of cleaned wafer (polished side up) was placed on a static, graphite susceptor within an atmospheric pressure, vertical growth, Pyrex reactor. A smaller piece of substrate (polished side down) was placed on top of the clean wafer to serve as a mask. The vertical reactor contained three separate inlets arranged in a triangular fashion with spacing between the inlets of approximately one inch. For all CVD growth runs, the graphite susceptor was positioned about 2.5 inches below the inlets and inductively heated to 350–450°C with an RF source operating between 250–800 kHz. Using CAJON Ultra-Torr fittings and stainless steel flexible tubing, two glass bubblers (one containing trimethylindium—Alfa, electronic grade—and the other containing $(Me_3SiCH_2)SbH_2$) were connected to two of the reactor inlets. The third inlet was connected to a hydrogen flow source (push gas). Flows through both bubblers and the push gas were controlled with calibrated flowmeters. The hydrogen carrier and push gas was reagent grade and passed through a molecular sieve cartridge. Gas flows for the antimony source, trimethylindium and push gas ranged from 50–150 standard cm^3 per minute (sccm), 25–50 sccm, 0.5–2.0 l/min respectively depending on conditions of the specific growth run. During growth runs, trimethylindium was maintained at ambient temperature (23–24°C) and $(Me_3SiCH_2)SbH_2$ was held at 0°C. Following the termination of the growth run, the susceptor was heated for an additional 3–5 min with purging after stopping the source flows; purging was then continued as the system was allowed to cool to ambient temperature. The substrate was then removed from the reactor and characterized. A total of eight individual growth runs was made for $(Me_3SiCH_2)SbH_2$.

2.3. *Characterization of thin films*

The thin films grown by chemical vapor deposition experiments were characterized by Auger electron spectroscopy (AES) and X-ray diffraction (XRD). The Auger spectra were obtained on a Physical Electronics Industries Model 10-155 equipped with a cylindrical mirror analyzer. Spectra of as-mounted films were recorded, followed by sputtering with Ar^+ ions for two minutes at a pressure of 5×10^{-5} Torr with a beam energy of 700 eV and a beam current of 16 μA to remove adsorbed carbon and oxygen from the surface of the film. Data from the sputtered samples are reported here. A reference spectra for InSb was obtained on a piece of molecular beam epitaxy (MBE) grown InSb (bulk mobility 2×10^5 cm^2/V s) and gave an In/Sb ratio of 1.13. X-ray diffraction patterns were obtained on a Philips 12045 Theta-Two Theta diffractometer equipped with Cu Kα radiation.

3. Results and discussion

We have prepared the trimethylsilylmethylstibines in yields of 51 and 53%, as shown in eqn. (1).

$$(Me_3SiCH_2)_ySbBr_{3-y} + LiAlH_4 \xrightarrow{\text{solvent}} (Me_3SiCH_2)_ySbH_{3-y} \quad (1)$$

For $y = 2$, solvent = Et_2O, −50°C
For $y = 1$, solvent = tetraglyme, −25°C

The primary and secondary trimethylsilylmethylstibines are both colorless, volatile liquids at room temperature. Vapor pressure measurements using a capacitance manometer indicate that the primary stibine exhibits a vapor pressure of 2.0 Torr at 0°C, while the secondary stibine is substantially less volatile (will move very slowly under dynamic vacuum (10^{-6} Torr) at ambient temperature). In addition to their volatility, both species are rapidly oxidized to white solids in the presence of air. They also exhibit good solubility in typical organic solvents such as hydrocarbons and ethers. Like their neopentyl counterparts, these compounds exhibit reasonable thermal stability. Under identical conditions (*i.e.*, H_2 atmosphere, ambient T and unexposed to light) trimethylsilylmethylstibine is more stable than neopentylstibine, showing no signs of decomposition over a period of three months (the neopentyl stibine has been shown to be stable for at least two months). For the case of the secondary stibines, the opposite is observed with bis(neopentyl)-stibine exhibiting better thermal stability than bis-(trimethylsilylmethyl)stibine. The decomposition product, obtained from trimethylsilylmethylstibine after standing for months, has been isolated and characterized by ^{1}H/^{13}C NMR spectroscopy. Based on a comparison of the NMR spectra for this compound with those reported by Wells *et al.* [16] for $(Me_3SiCH_2)As)_5$, we believe that the decomposition product is $(Me_3SiCH_2)Sb)_5$. The ^1H NMR spectrum of the antimony compound consists of three singlets (0.17, 0.18 and 0.20 ppm) with an intensity ratio of 2:1:2 corresponding to three distinct methyl hydrogens and a complex region for the methylene hydrogens made up of two AB patterns (1.44 and 1.68 ppm, $^2J(HH) = 15.0$ Hz; 1.52 and 1.58 ppm, $^2J(HH) = 12.9$ Hz) as well as a singlet at 1.37 ppm. The ^{13}C NMR spectrum is also consistent with the pentameric formulation in that there are three methyl resonances (0.60, 0.75 and 1.03 ppm) and three methylene resonances (−5.4, −7.0 and −7.5 ppm). Thus, the oligomeric nature of the antimony compound is supported by the complicated spectral patterns (2 AB patterns, *etc.*), magnitude of $^1H-^1H$ coupling constants, and chemical shift correlations between a number of related trimethylsilylmethyl derivatives of arsenic and antimony. Spectra involving tetrameric or hexameric species of this nature would give rise to different number of resonances as well as coupling constants of significantly different magnitudes.

Both $(Me_3SiCH_2)SbH_2$ and $(Me_3SiCH_2)_2SbH$ have been characterized by infrared spectroscopy and $^1H/^{13}C$ NMR. The infrared spectra of the two hydrides are dominated by a very intense absorption associated with the Sb–H stretch. In the case of $(Me_3SiCH_2)SbH_2$, the band is centered at 1865 cm^{-1} and for $(Me_3SiCH_2)_2SbH$, it is observed at 1835 cm^{-1}. This agrees quite favorably with the neopentylstibines $(Me_3CCH_2)SbH_2$ and $(Me_3CCH_2)_2SbH$ which exhibit stretches at 1870 and 1840 cm^{-1}, respectively. Characterization of the two trimethylsilylmethylstibines by $^1H/^{13}C$ NMR show results similar to those obtained for the neopentyl system. The only difference between the two systems occurs in the secondary stibines. In the case of $(Me_3CCH_2)_2SbH$, the methylene hydrogens show equivalent coupling to the antimony hydrogen thus giving rise to an AA'BB' pattern in which $J(AX) = J(BX)$. However, for $(Me_3SiCH_2)_2SbH$, the coupling of H_A and H_B to the antimony hydrogen (H_X) is significantly different (4.6 and 7.8 Hz). This difference is manifested by the Sb–H resonance becoming a triplet of triplets (see Fig. 1) rather than a simple quintet. We attribute this to a possible structural difference between the neopentyl and trimethylsilylmethyl derivatives, the neopentyl compound being more pyramidal than the trimethylsilylmethyl compound as evidenced by our structural results involving trineopentyl- and tris-(trimethylsilylmethyl)stibine [15]. Consequently, the methylene hydrogens in the trimethylsilylmethyl system possess markedly different dihedral angles with respect to the antimony hydrogen (time-averaged on the NMR timescale) and thus the two different coupling constants.

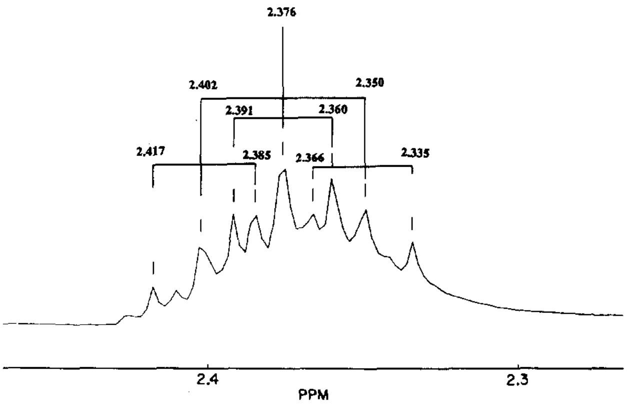

Fig. 1. Complex multiplet for Sb–H resonance of $(Me_3SiCH_2)_2SbH$ as observed by ^1H NMR.

In addition to the spectral characterization of these compounds, we have explored the utility of $(Me_3SiCH_2)SbH_2$ as a potential MOCVD precursor. As noted above, $(Me_3SiCH_2)_2SbH$ was considerably less volatile than the primary stibine; therefore, due to its low volatility it was not considered as an attractive CVD precursor and was not used in any deposition experiments. Specifically, we have explored the reaction of $(Me_3SiCH_2)SbH_2$ with trimethylindium to achieve the deposition of an indium antimonide film using a very simple, atmospheric, vertical, Pyrex reactor. Our goal has been to demonstrate the ability to deposit InSb and to identify gross impurities associated with these films.

Typical conditions for film depositions employed a V/III ratio of approximately 6–9 and were examined over the temperature range of 350–450°C. At 350°C using a V/III ratio of approximately 7.2, we obtained virtually no film growth over the period of one hour. Increasing the temperature by increments of 25°C did not result in significant growth until the temperature reached 450°C. This was somewhat surprising since we had demonstrated InSb growth at 350°C using $(Me_3CCH_2)SbH_2$ in previous studies. The film was

TABLE 1.

Two-Theta (degrees)	d-values (Å)	Identification and intensity
23.70	3.751	InSb [a] (111) 100%
39.30	2.291	InSb (220) 40%
46.50	1.951	InSb (311) 22%
56.75	1.621	InSb (400) 4%
62.50	1.485	InSb (331) 3%

[a] See ref. 17.

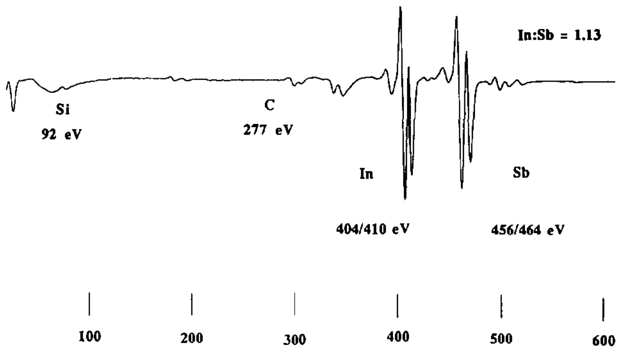

Fig. 2. Auger spectrum of InSb film employing trimethylindium and $(Me_3SiCH_2)SbH_2$ as precursors.

characterized by XRD and AES. X-ray diffraction showed only the presence of peaks associated with polycrystalline InSb, with no preferred orientation. A listing of Two-Theta values, d values and relative intensities is given in Table 1. Examination of the Ar^+ sputtered film by AES showed the presence of In (404/410 eV) and Sb (456/464 eV) in the ratio of 1.13 which was in good agreement with the value obtained for a piece of MBE grown InSb. Furthermore, no gross silicon (92 eV), carbon (277 eV) or oxygen (510 eV) impurities (all less than the detection limit of AES or 1%—see Fig. 2) were observed. Although a broadened feature is observed in the 90–100 eV range of the AES spectrum, this feature is consistent with our reference sample and believed to be characteristic of InSb.

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