Two Stable Hydrides of Antimony: $RSbH_2$ and R(H)Sb−Sb(H)R (R = $(Me_3Si)_2CH$)

Gábor Balázs, Hans Joachim Breunig,* Enno Lork, and Werner Offermann

Fachbereich 2 (Chemie) der Universität Bremen, D-28334 Bremen, Germany

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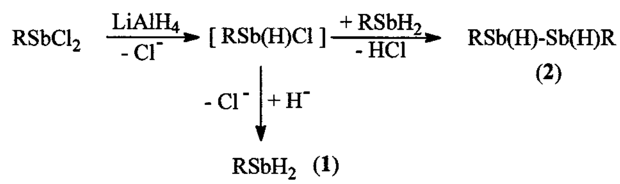
*Summary: $RSbH_2$ (**1**) and R(H)Sb−Sb(H)R (**2**) (R = $(Me_3Si)_2CH$) are formed in good yield by reactions of $RSbCl_2$ with $LiAlH_4$. The crystal structure of **2** consists of molecules in the meso form.*

Hydrides of main group 15 elements are important compounds, which are frequently used as reducing agents or as precursors for electronic materials. In the case of hydrides of the heavier group 15 elements the characterization and the application of the compounds are limited by their low thermal stability. Many hydrides of antimony, e.g., the monostibanes SbH_3,[1] $RSbH_2$ (R = CH_3, C_6H_5), and R_2SbH (R = CH_3, C_2H_5)[2] or the distibane Sb_2H_4,[3] decompose in minutes or hours at room temperature with autocatalysis to form dihydrogen and antimony or organoantimony compounds with Sb−Sb bonds. This instability is probably not a consequence of unusually weak antimony−hydrogen bonds (E_{Sb-H} = 255 kJ mol^{-1},[4] E_{Sb-C} = 215 kJ mol^{-1} [5]) but may be due to insufficient steric protection.

With this explanation, it is easy to understand that secondary stibanes are generally more stable than the corresponding primary stibanes and that the stability is increased by bulky substituents. Under the protection of the isobutyl group, the secondary stibane R_2SbH is stable for several weeks and the primary stibane $RSbH_2$ (R = $(CH_3)_2CHCH_2$) is stable for several days at room temperature.[6] Two antimony hydrides have been characterized by X-ray crystallography: Mes_2SbH (Mes = 2,4,6-$(CH_3)_3C_6H_2$)[7] and $ArSbH_2$ (Ar = 2,6-[2,4,6-triisopropylphenyl]$_2C_6H_3$),[8] a compound stable to 200 °C.

We report here on $RSbH_2$ (**1**; R = $(Me_3Si)_2CH$), a primary stibane which is stable to 100 °C, and R(H)-Sb−Sb(H)R (**2**; R = $(Me_3Si)_2CH$), the first organodistibane with Sb−H bonds. Both antimony hydrides are protected by the bulky bis(trimethylsilyl)methyl group. The monostibane **1** is formed in 69% yield when a solution of $RSbCl_2$ in Et_2O is added to $LiAlH_4$ at −60 °C.[9] **1** is a colorless, air-sensitive liquid which can be distilled without decomposition at reduced pressure and is stable in a sealed tube at room temperature for weeks. At −28 °C the stability is unlimited. The reaction with air gives RH and other products. Heating to 110−120 °C leads to decomposition with formation of cyclo-R_4Sb_4. The identity of **1** is proven by the molecular ion in the mass spectrum. The signal for the Sb−H valence vibration appears at 1860 cm^{-1} in the infrared spectrum. The ^{1}H NMR spectrum shows a singlet for the CH_3 group, a triplet for the CH protons, and a doublet for the SbH_2 group. The novel distibane **2** is formed from the same reagents as **1**; the sequence of addition is, however, reversed. Adding $LiAlH_4$ to $RSbCl_2$ in Et_2O at −78 °C gives **2** in 93% yield[10] as a yellow, crystalline compound, which is very soluble in hydrocarbons. The yellow solutions are stable under an argon atmosphere for several days at ambient temperature, and even chromatographic methods of separation can be applied. Crystals of **2** are stable at room temperature for a long time. Intermediates in the formation of **2** were not identified. A possible intermediate is the mixed compound RSb(H)Cl, which may be formed in the presence of excess $RSbCl_2$ and may react with $RSbH_2$ with elimination of HCl to give **2**. HCl possibly is removed by reaction with $LiAlH_4$ with formation of H_2 (Scheme 1).

Scheme 1



2 was characterized by observation of the molecular ion in the mass spectrum as well. The signal for the Sb−H valence vibration appears at 1849 cm^{-1}. Particularly informative are the ^{1}H and ^{13}C NMR spectra, as

* To whom correspondence should be addressed. E-mail: breunig@chemie.uni-bremen.de. Fax: 49-421-2184042.

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(9) Synthesis of **1**: 4.349 g (12.367 mmol) of $(Me_3Si)_2SbCl_2$ in 50 mL of diethyl ether was added dropwise to 0.52 g (13.75 mmol) of $LiAlH_4$ in 50 mL of diethyl ether at −60 °C. The mixture was warmed and filtered through a D4 frit covered with Kieselguhr. Removal of the solvent at 20 mbar and distillation at 1 mbar, bp 39−41 °C, gave 2.418 g (69%) of **1** as a colorless liquid. ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ −0.21 (t, $^3J_{HH}$ = 5.86 Hz, $^2J_{SiH}$ = 8.7 Hz, 1H; CH) 0.097 (s, $^2J_{SiH}$ = 6.3 Hz, $^1J_{CH}$ = 118.6 Hz, 18H; CH_3) 2.12 (d, $^3J_{HH}$ = 5.86 Hz, $^2J_{SiH}$ = 4.7 Hz, 2H; SbH_2). ^{13}C NMR (200 MHz, C_6D_6, 25 °C, TMS): δ −8.52 (s; CH) 1.6 (s, $^1J_{SiC}$ = 50.9 Hz; CH_3). IR (Et_2O): ν 1860 cm^{-1} (Sb−H). MS (70 eV): *m/z* (%) 282 (25) [M$^+$], 267 (55) [M$^+$ − CH_3]. Anal. Calcd for $C_7H_{21}SbSi_2$: C, 29.69; H, 7.48. Found: C, 29.70; H, 7.40.

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recorded in C_6D_6 or $C_6D_5CD_3$ solution. Because of the chirality of the antimony centers there are two possible isomers of **2**, the *meso* and the *d,l* forms, which are distinguishable by ^{1}H NMR spectroscopy. Diastereotopic effects should lead to two singlets for the trimethylsilyl groups of both forms and signals of an AA′XX′ spin system for the CH and SbH protons in the ^{1}H NMR spectrum. The experimental spectrum of a solution of pure crystals of **2** at ambient temperature in C_6D_6 is complex. Regions for the Me_3Si, CH, and SbH groups are clearly distinguishable. The most intense signals are assigned to both isomers of **2** by low-temperature measurements. At room temperature the protons of the diastereotopic Me_3Si groups of the *meso* form are accidentally isochronic. Cooling to 0 °C abolishes the accidental isochrony, and the two expected singlet signals appear also for the Me_3Si groups of the *meso* form. An inspection of the intensities of the signals in the ^{1}H NMR spectrum of **2** reveals that the molar ratio of the *d,l* and *meso* forms is 2:1. This result is confirmed by the observation of the intensities of the signals of the AA′XX′ spin systems of the CH and SbH groups, for both isomers. The lesser proportion of the *meso* form can be explained on the basis of a higher reactivity of this species. The additional lines in the ^{1}H NMR spectrum of **2** are assigned to **1** and to the oligostibanes R(H)SbSb(R)Sb(H)R and R(H)SbSb(R)Sb(R)Sb(H)R, because the Sb−H protons of the latter interact only with one C−H proton and there are no interactions with other Sb−H protons. These additional signals also are observed, when crystals of **2** are dissolved in $C_6D_5CD_3$ at −80 °C and when the NMR experiment is performed at this temperature. Fragment ion peaks due to R(H)SbSb(R)Sb(H)R appear also in the mass spectrum of **2**. The findings from ^{13}C NMR spectroscopy are in accordance with the ^{1}H NMR spectra.

The structure of **2** in the crystal form was investigated by single-crystal X-ray diffractometry.[11] The structure consists of partially disordered distibane molecules. Ninety percent of the molecules were completely characterized as the *meso* form in the antiperiplanar conformation (Figure 1).

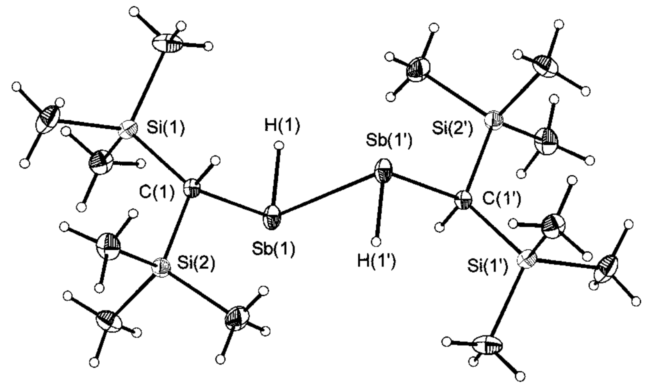

Figure 1. Structure of **2** in the crystal form. The atoms are drawn with 50% probability ellipsoids, except for the hydrogen atoms. Selected bond lengths (Å) and angles (deg): Sb(1)−Sb(1′) = 2.8304(8), Sb(1)−C(1) = 2.195(2), Sb(1)−H(1) = 1.58(3), C(1)−Sb(1)−Sb(1′) = 95.42(6), C(1)−Sb(1)−H(1) = 102.1(13), Sb(1′)−Sb(1)−H(1) = 88.8(12).

The hydrogen atoms of the remaining 10% of the molecules were not located. The Sb−Sb bond length in **2** is 2.8304(8) Å. This value is slightly smaller than those for distibanes with four organic groups (Me_4Sb_2, 2.84 Å,[12] 2.86 Å;[13] Ph_4Sb_2, 2.837 Å).[14] It lies in the usual range for Sb−Sb single bonds (R_4Sb_8, R = $(Me_3Si)_2CH$, Sb−Sb = 2.784(4)−2.852(5) Å).[15] The Sb−Sb double bonds in distibenes RSb═SbR (R = 2,4,6-$[(Me_3Si)_2CH]_3$-C_6H_2), 2.642(1) Å;[16] R = 2,6-$Mes_2C_6H_3$, 2.6558(5) Å)[17] are considerably shorter. The Sb−Sb−C angles in **2** (95.42(6)°) and the Sb−C bond lengths (2.195(2) Å) are not unusual. The Sb−H distances of the *meso* form of **2** were determined as 1.58(3) Å.[18] The average Sb−H distances of $ArSbH_2$ (Ar = 2,6-(2,4,6-triisopropylphenyl)$_2C_6H_3$) are 1.67 Å.[8] The molecules of **2** reside on a crystallographically effective center of inversion. Therefore, despite the disorder, there is only one independent distance for both Sb−C and Sb−H. Residual electron density at a distance of 0.54 Å from Sb was refined as 10% disorder of the antimony atoms.

In the crystal of **2** the molecules are associated in zigzag chains through weak intermolecular contacts between the antimony atoms (Figure 2). The intermolecular Sb···Sb distance is 4.209(14) Å. This value is only slightly shorter than the sum of van der Waals radii of two antimony atoms (4.40 Å). The Sb−Sb···Sb angles are 135.51°. An almost straight chain (Sb−Sb···Sb = 178.80°) with a short intermolecular distance (Sb···Sb = 3.709(1) Å)[13] was observed in the case of the red crystals of $Me_2SbSbMe_2$. Zigzag chains similar to those in **2** occur in the crystal of Ph_4Sb_2 (Sb···Sb = 4.289(18) Å; Sb−Sb···Sb = 108.21(1)°).[14] Both distibanes

(10) Synthesis of **2**: 0.67 g (17.67 mmol) of $LiAlH_4$ was added to a solution of 5.655 g (16.077 mmol) of $RSbCl_2$ in 50 mL of diethyl ether at −78 °C. The mixture was warmed to room temperature, stirred for 1 h, and filtered through a D4 frit covered with Kieselguhr. The resulting yellow solution was reduced to 10 mL. After several hours at −28 °C 4.226 g (93%) of yellow crystals of **2** (mp 69−70 °C) formed. ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 0.176 (s, $^2J_{SiH}$ = 6.3 Hz, $^1J_{CH}$ = 119.2 Hz, 18H; CH_3(a) *d,l*), 0.185 (s, $^2J_{SiH}$ = 6.3 Hz, $^1J_{CH}$ = 119.6 Hz, 18H; CH_3 *meso*), 0.191 (s, $^2J_{SiH}$ = 6.7 Hz, $^1J_{CH}$ = 119.7 Hz, 18H; CH_3(b) *d,l*), 0.47 (2H; CH *d,l*), 0.494 (1H; CH *meso*), 1.676 (2H; SbH *d,l*), 2.357 (1H; SbH *meso*). ^{13}C NMR (200 MHz, C_6D_6, 25 °C, TMS): δ −5.49 (s; CH *meso*), −5.34 (s; CH *d,l*), 2.02 (s; CH_3 *meso*), 2.05 (s; CH_3 *d,l*). IR (Nujol): ν 1849 cm^{-1} (Sb−H). MS (70 eV): *m/z* (%) 564 (23) [M$^+$], 549 (8) [M$^+$ − CH_3], 282 (45) [M$^+$ − RSb], 280 (40) [RSb$^+$]. Anal. Calcd for $C_{14}H_{40}Sb_2Si_4$: C, 29.80; H, 7.14. Found: C, 29.52; H, 6.56.

(11) Crystallographic data for $C_{14}H_{40}Sb_2Si_4$: triclinic, space group $P\bar{1}$ (No. 2), radiation Mo Kα (λ = 0.710 73 Å), a = 6.5360(10) Å, b = 8.2190(10) Å, c = 12.569(2) Å, α = 103.490(10)°, β = 92.330(10)°, γ = 103.070(10)°, V = 0.63644(16) nm^3, Z = 1, absorption coefficient 2.304 mm^{-1}, F(000) = 282, crystal size 0.6 × 0.6 × 0.4 mm^3, T = 173 K, θ range for data collection 2.63−27.50°, index range $-8 \le h \le 1$, $-10 \le k \le 10$, $-16 \le l \le 16$, 3722 reflections collected, 2897 independent reflections (R(int) = 0.0339), completeness to θ = 27.50° 99.2%, absorption correction ψ-scans, refinement method full-matrix least squares on F^2, number of data/restraints/parameters 2897/0/113, goodness of fit on F^2 1.12, final R indices ($I > 2\sigma(I)$) R1 = 0.0272, wR2 = 0.0733, final R indices (all data) R1 = 0.0293, wR2 = 0.0745, largest difference peak and hole 0.654/−0.624 e Å^{-3}.

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(18) Electron densities at ca. 1.6 Å from the antimony atom were found in the Fourier synthesis and refined without any restraints with an isotropic temperature factor U(eq) of 0.33 × 10^{-1} Å^2 as hydrogen atom.

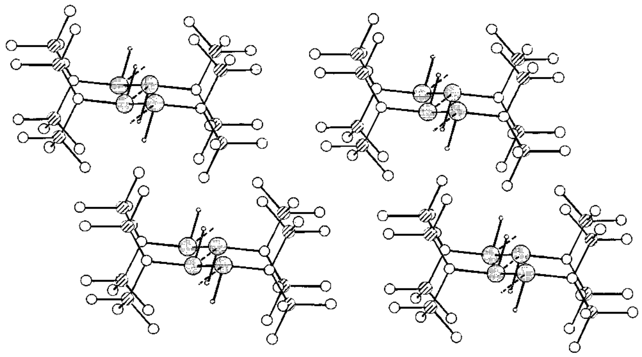

Figure 2. Orientation of the molecules of **2** in the crystal (intermolecular distances Sb···Sb = 4.209(13) Å).

are yellow due to the weak intermolecular Sb···Sb interactions.[19]

It appears that **1** and **2** are also of interest as reagents for the synthesis of organo-antimony compounds. From **1** and $SbCl_3$ in the presence of pyridine the known[15] polycycle R_4Sb_8 (R = $(Me_3Si)_2CH$) is formed. We are currently investigating metalation reactions of **1** and **2**.

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Supporting Information Available: Tables giving experimental details and complete X-ray crystallographic data for $(Me_3Si)_2CH(H)Sb-Sb(H)CH(SiMe_3)_2$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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