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Synthesis and Characterization of R_2SbH, R_2BiH, and $R_2Bi{-}BiR_2$ [$R = (Me_3Si)_2CH$]

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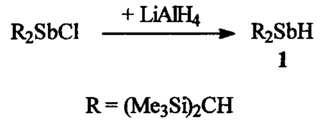
*Summary: R_2SbH (**1**) and R_2BiH (**2**) [$R = (Me_3Si)_2CH$] are formed by reactions of the corresponding chlorides with $LiAlH_4$. **1** is stable up to 100 °C. Decomposition of **2** at room temperature leads to $R_2Bi{-}BiR_2$ (**3**) and H_2. The crystal structure of **3** consists of molecules in a near trans conformation. ^1H NMR studies of **3** in C_6D_6 show that the diastereotopic Me_3Si groups become equivalent with increasing concentration and temperature.*

Stibine, bismuthine, EH_3 (E = Sb, Bi), and many organic derivatives, REH_2 and R_2EH, decompose at or below room temperature with formation of H_2, E, R_3E, or compounds with E−E bonds.[1] Usually hydrides of bismuth are less stable than the corresponding antimony derivatives. Stable organostibines ($RSbH_2$, R = 2,6-(2,4,6-$^iPr_3C_6H_2)_2C_6H_2$,[2] Me_3SiCH_2,[3] Me_3CCH_2,[4] ^{i}Bu,[5] Ph,[6] p-Tol;[7] R_2SbH, R = Mes,[8] Me_3SiCH_2,[3] Me_3CCH_2,[4] ^{i}Bu,[5] Ph,[6] ^{t}Bu[9]) and also a stable bismuthine R_2BiH (R = 2,6-$Mes_2C_6H_3$)[10] were obtained with protection of the Sb−H or Bi−H function by bulky organic groups. In our previous work we studied a sterically protected primary alkylstibine, $RSbH_2$, and the related distibine R(H)Sb−Sb(H)R [$R = (Me_3Si)_2CH$].[11] We report here on the stable secondary stibine R_2SbH (**1**) [$R = (Me_3Si)_2CH$] and on the corresponding bismuthine, R_2BiH (**2**) [$R = (Me_3Si)_2CH$], which decomposes with formation of the novel dibismuthine $R_2Bi{-}BiR_2$ (**3**) [$R = (Me_3Si)_2CH$].

Scheme 1



The history of dibismuthines dates back to 1934, when Paneth reported the formation of $Me_2Bi{-}BiMe_2$.[12] Since then, several other organo derivatives were synthesized and their chemistry was summarized in reviews.[13] Only three dibismuthines, $R_2Bi{-}BiR_2$ (R = Ph,[14] Me_3Si,[15] $R_2 = (CMe{=}CH)_2$[16]), were fully characterized by X-ray diffractommetry. Preliminary structural data were reported for $Me_2Bi{-}BiMe_2$.[17] The phosphorus analogue[18] of **3** is remarkable because of the easy cleavage of the P−P bond with formation of persistent $[(Me_3Si)_2CH]_2P^\bullet$ radicals in solution and in the gas phase. Also the analogous arsenic radical is known.[19] Dissociation of **3** to $[(Me_3Si)_2CH]_2Bi^\bullet$ radicals was not established. Apparently the steric protection by $(Me_3Si)_2CH$ groups is insufficient for the stabilization of this species. The synthesis of $[(Me_3Si)_2CH]_3Bi$ shows that also three of these groups can be introduced at bismuth.[20]

The stibine **1** is obtained in 66% yield by reacting R_2SbCl [$R = (Me_3Si)_2CH$] with $LiAlH_4$ in Et_2O at −50 °C (Scheme 1).[21] It is a colorless, air-sensitive liquid (mp −14 °C) which distills at 105 °C (3 10^{-3} mbar) and is stable at room temperature for a long time. Attempts to synthesize the distibine $R_2Sb{-}SbR_2$ or the radical $R_2Sb^\bullet$ by heating a solution of **1** in C_6D_6 in sealed tubes to 105 °C for several hours or by exposition to UV light were not successful. No signs of decomposition of **1** were observed under these conditions.

The identity of **1** was proven by elemental analyses, by observation of the molecular ion in the mass spectra, and by analysis of the NMR spectra. The ^1H NMR

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(21) Synthesis of **1**: 1.232 g (2.592 mmol) of $[(Me_3Si)_2CH]_2SbCl$ in 30 mL of Et_2O was added dropwise to a suspension of 0.108 g (2.8481 mmol) of $LiAlH_4$ in 15 mL of Et_2O at −50 °C. The reactions mixture was allowed to warm to room temperature and filtered through a glass frit covered with kiselguhr. Removal of the solvent and distillation at 105 °C (6 × 10^{-3} mbar) gave 0.752 g (65.96%) of **1** as a colorless liquid. ^1H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 0.19 (s, $^2J_{SiH} = 5.6$ Hz, $^1J_{CH} = 118.47$ Hz, 18H; CH_3) 0.21 (s, $^2J_{SiH} = 6.08$ Hz, $^1J_{CH} = 118.44$ Hz, 18H; CH_3) 0.30 (d, $^3J_{HH} = 4.0$ Hz, $^2J_{SiH} = 8.12$ Hz, 1H; CH) 3.11 (t, $^3J_{HH} = 4.0$ Hz, 1H; SbH). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ −1.30 (s; CH) 2.31 (s, $^1J_{SiH} = 50.84$ Hz; CH_3) 2.61 (s, $^1J_{SiH} = 50.38$ Hz; CH_3). IR (Et_2O): ν 1840 cm^{-1} (SbH). MS (70 eV): m/z (%) 440 (30) [M^+], 425 (20) [$M^+ - CH_3$], 280 (50) [$(Me_3Si)_2CHSb^+$], 73 (100) [Me_3Si^+]. Anal. Calcd for $C_{14}H_{39}Sb_1Si_4$: C, 38.08; H, 8.90. Found: C, 38.10; H, 8.80.

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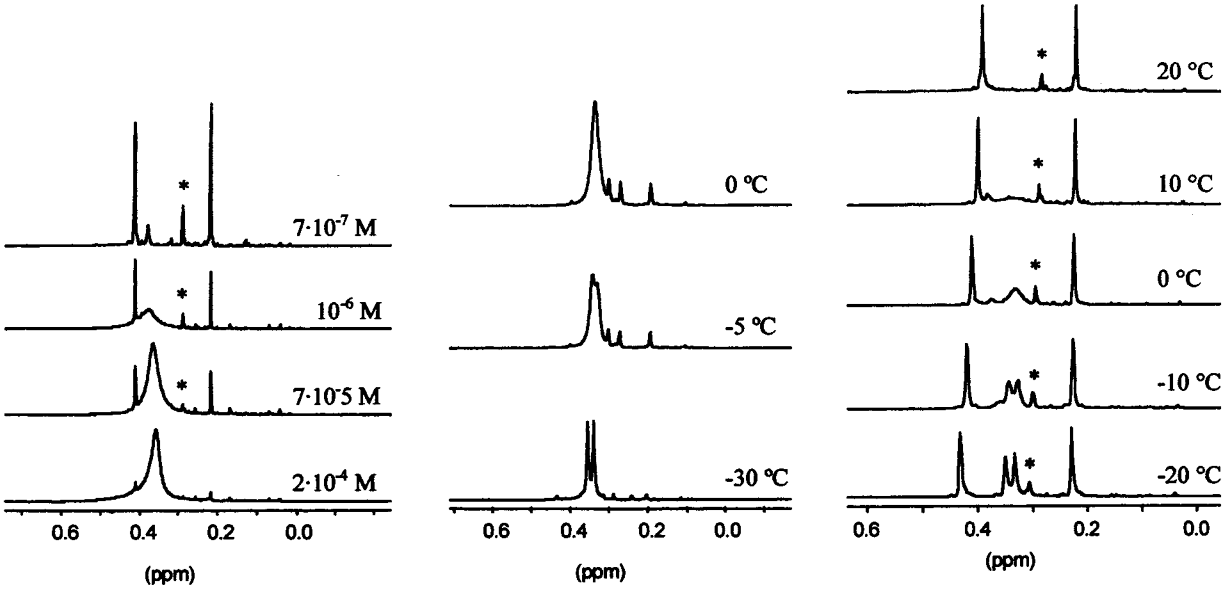
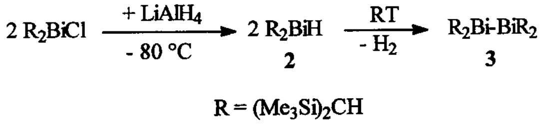


Figure 1. ^1H NMR (200 MHz) spectra of **3**. Left: in C_6D_6 at 25 °C with variation of the concentration. Center: in C_6D_5-CD_3, $c = 3.3 \times 10^{-4}$ mol L^{-1} at different temperatures. Right: in $C_6D_5CD_3$, $c = 8.35 \times 10^{-6}$ mol L^{-1} at different temperatures. The signals marked with * correspond to R_3Bi [R = $(Me_3Si)_2CH$].

Scheme 2



$$2\,R_2BiCl \xrightarrow[-80\ °C]{+\,LiAlH_4} \underset{\mathbf{2}}{2\,R_2BiH} \xrightarrow[-\,H_2]{RT} \underset{\mathbf{3}}{R_2Bi\text{-}BiR_2}$$

$$R = (Me_3Si)_2CH$$

spectrum of **1** in C_6D_6 contains two singlet signals for the diastereotopic Me_3Si groups, a doublet for the CH, and a triplet for the SbH protons. The constant for the coupling between the CH and SbH protons ($^3J_{HH} = 4.0$ Hz) is smaller than for $(Me_3Si)_2CHSbH_2$ ($^3J_{HH} = 5.86$ Hz).[11] Also in the ^{13}C NMR spectra in C_6D_6 the expected signals were observed. The IR spectrum of a solution of **1** in diethyl ether shows a strong signal for the SbH stretching vibration at 1840 cm^{-1}. This value compares well with those found for $(Me_3CCH_2)_2SbH$[4] (1840 cm^{-1}) or $(Me_3SiCH_2)_2SbH$[3] (1835 cm^{-1}).

The synthesis of **2** was performed by reaction of R_2-BiCl with $LiAlH_4$ in Et_2O at − 80 °C. **2** is a colorless compound stable in Et_2O or C_6H_6 only below −20 °C. At room temperature after a short time the solution becomes red due to the formation of **3** (Scheme 2). The ^1H NMR spectrum[22] of **2** contains two singlet signals for the diastereotopic Me_3Si groups, one doublet signal for the CH groups, and a signal for the BiH proton, which is broadened due to quadrupolar coupling with the Bi nucleus. The observation of two signals for the Me_3Si groups of **1** and **2** proves that the molecules have stable pyramidal configurations in solution. The Bi−H stretching vibration in **2** is observed in the IR spectrum at 1690 cm^{-1}. For Ar_2BiH (Ar = 2,6-$Mes_2C_6H_3$)[10] the ν-(Bi−H) signal appears at 1759 cm^{-1}.

The synthesis of **3** is achieved in 73% yield when the solution of **2** is warmed to room temperature until the evolution of H_2 is finished.[23] **3** is a dark red crystalline solid, soluble in organic solvents and stable in the solid state for a long time. Solutions of **3** in hydrocarbons decompose however slowly at room temperature with formation of the cyclobismuthines $(RBi)_n$ ($n = 3, 4$)[24] and R_3Bi. ^1H NMR spectra in C_6D_6 at room temperature show the expected signals for intact, inversion stable molecules of **3**, i.e., two singlet signals for the diastereotopic Me_3Si groups and a singlet for the CH protons, only at high dilution ($c = 6.97 \times 10^{-7}$ mol L^{-1}). When the concentration is continually increased the two singlets become less intense and a new broad signal emerges in the region of the methyl protons. Cooling the concentrated solution leads to two separate singlet signals again, however with different chemical shifts compared to the spectra at low concentration (Figure 1). In $C_6D_5CD_3$ with $c = 3.3 \times 10^{-4}$ mol L^{-1} the coalescence temperature for this process is −4 °C. The free activation enthalpy $\Delta G^\ddagger$ is 14.66 kcal mol^{-1}. Much higher energies are required for inversion−rotation processes of tetraorganodiphosphines which occur with $\Delta G^\ddagger$ values between 22.5 and 24 kcal mol^{-1}.[25]

The spectral changes show that at high temperature and high concentration a dynamic process takes place leading to equivalence of the Me_3Si groups. A possible mechanism is proposed in Scheme 3. It implies an exchange of the R_2Bi units between associated molecules resulting in the inversion of the pyramidal configuration

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[22] Spectroscopic data for **2**: ^1H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 0.17 (s, $^2J_{SiH} = 6.32$ Hz, $^1J_{CH} = 118.32$ Hz, 18H; CH_3) 0.26 (s, $^2J_{SiH} = 6.58$ Hz, $^1J_{CH} = 118.3$ Hz, 18H; CH_3) 0.87 (d, $^3J_{HH} = 4.2$ Hz, 2H; CH) 3.24 (s, br, 1H; BiH). IR (petroleum ether): ν 1690 cm^{-1} (Bi−H).

[23] Synthesis of **3**: 2.198 g (3.908 mmol) of $[(Me_3Si)_2CH]_2BiCl$ in 80 mL of Et_2O was added dropwise to a suspension of 0.163 g (4.289 mmol) of $LiAlH_4$ in 20 mL of Et_2O at −80 °C. The reactions mixture was allowed to warm to room temperature and filtered through a glass frit covered with kiselguhr when the solution became red. The resulting solution was reduced to ca. 10 mL. After several days at −28 °C 1.508 g (73.24%) of red crystals of **3** (mp 104 °C) was formed. ^1H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 0.22 (s, $^2J_{SiH} = 6.14$ Hz, $^1J_{CH} = 118.32$ Hz, 18H; CH_3) 0.42 (s, $^2J_{SiH} = 6.48$ Hz, $^1J_{CH} = 118.28$ Hz, 18H; CH_3) 1.18 (s, $^2J_{SiH} = 7.74$ Hz, 1H; CH). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ 3.18 (s; CH_3) 3.55 (s; CH_3). MS (70 eV): *m/z* (%) 527 (30) $[\{(Me_3Si)_2CH\}_2Bi^+]$, 368 (15) $[(Me_3Si)_2CHBi^+]$, 353 (15) $[(Me_3Si)(Me_2Si)CHBi^+]$, 73 (100) $[Me_3Si^+]$. Anal. Calcd for $C_{28}H_{76}Bi_2Si_4$: C, 31.86; H, 7.26. Found: C, 31.30; H, 6.96.

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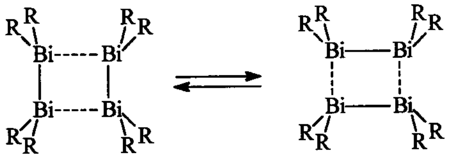
Scheme 3



at bismuth comparable to the Walden inversion in the S_N2 mechanism.[26] The diastereotopic species observed at low temperature is possibly a loosely associated dimer of molecules with frozen inversion. Intermolecular association giving dimers or trimers was also observed in solutions of Me_4P_2 and $Me_2Ph_2P_2$.[27] Association in solution[28] and the formation of chains[29,30] are also not unusual for distibines or dibismuthines. The reversible dissociation of **3** with formation of $R_2Bi^•$ radicals would also lead to equivalent Me_3Si groups. This process should however prevail at low concentration, which is in contrast to our observations. Dissociation is possible in the gas phase. EI-mass spectra of **3** contain signals for R_2Bi^+ ions at highest mass.

Single crystals of **3** suitable for X-ray structure analysis are obtained from a solution in petroleum ether at −28 °C. The crystals belong to the monoclinic space group $P\bar{1}$ (No. 2) with one molecule in the asymmetric unit.[31] The structure of **3** is depicted in Figure 2. It consists of $R_2Bi-BiR_2$ molecules with a near *trans* (antiperiplanaric) conformation (lp−Bi−Bi−lp 164.23(3)°, lp = assumed direction of the lone pairs at Bi). The bis(trimethylsilyl)methyl ligands in the R_2Bi fragments are orientated almost perpendicular to each other. They adopt a near *syn*−*anti* conformation with two pairs of H−C−Bi−C dihedral angles of 0.1°, 5° and 130°, 134°. Bending of the ligands away from the central part of the molecule leads to dissimilar Bi−C−Si angles (106−111°, 120−123°) at each ligand. Also the wide range of the bond angles around bismuth (87−111°) reflects the steric strain in this molecule.

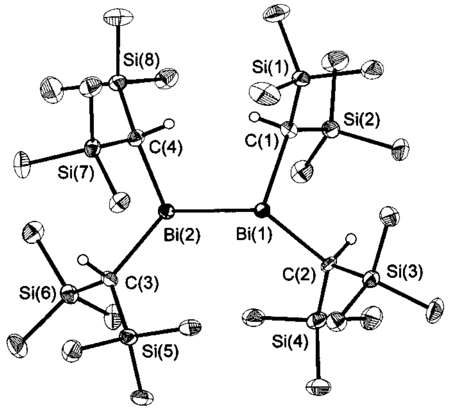


Figure 2. ORTEP-like representation of the crystal structure of **3**. The ellipsoids represent 30% probability. The hydrogen atoms belonging to the CH_3 groups are omitted for clarity. Selected distances (Å) and angles (deg): Bi(1)−Bi(2) = 3.0534(13), Bi(1)−C(1) = 2.347(10), Bi(1)−C(2) = 2.319(10), Bi(2)−C(3) = 2.336(10), Bi(2)−C(4) = 2.344(11), Si(1)−C(1) = 1.880(11), Si(2)−C(1) = 1.865(11), Si(3)−C(2) = 1.872(12), Si(4)−C(2) = 1.894(11), Si(5)−C(3) = 1.873(11), Si(6)−C(3) = 1.894(12), Si(7)−C(4) = 1.880(13), Si(8)−C(4) = 1.896(11); Bi(2)−Bi(1)−C(1) = 89.3(3), Bi(2)−Bi(1)−C(2) = 111.4(3), Bi(1)−Bi(2)−C(3) = 108.6(3), Bi(1)−Bi(2)−C(4) = 86.6(3), C(1)−Bi(1)−C(2) = 99.7(4), C(3)−Bi(2)−C(4) = 103.7(4), Bi(1)−C(1)−Si(1) = 110.9(4), Bi(1)−C(1)−Si(2) = 120.2(5), Bi(1)−C(2)−Si(3) = 105.9(5), Bi(1)−C(2)−Si(4) = 123.4(6), Bi(2)−C(3)−Si(5) = 125.3(6), Bi(2)−C(3)−Si(6) = 104.2(5), Bi(2)−C(4)−Si(7) = 119.5(5), Bi(2)−C(4)−Si(8) = 110.0(5), = C(1)−Bi(1)−Bi(2)−C(3) = −170.7(4), C(1)−Bi(1)−Bi(2)−C(4) = −67.4(4), C(2)−Bi(1)−Bi(2)−C(3) = 89.2(4), C(2)−Bi(1)−Bi(2)−C(4) = −167.5(4), H(1)−C(1)−Bi(1)−Bi(2) = 22.12(4), H(2)−C(2)−Bi(1)−Bi(2) = 93.15(4), H(3)−C(3)−Bi(2)−Bi(1) = 95.87(4), H(4)−C(4)−Bi(2)−Bi(1) = 21.50(4), H(1)−C(1)−Bi(1)−C(2) = 133.73(4), H(2)−C(2)−Bi(1)−C(1) = 0.11(4), H(3)−C(3)−Bi(2)−C(4) = 4.87(4), H(4)−C(4)−Bi(2)−C(3) = 129.82(4).

Nevertheless the Bi−Bi bond length (3.0534(13) Å) corresponds to a normal bismuth−bismuth single bond as found in Ph_4Bi_2 (2.990(2) Å;[14a] 2.988(1) Å[14b]), $(Me_3Si)_4Bi_2$ (3.035(3) Å),[15] or R_4Bi_4 (R = $(Me_3Si)_2CH$; mean 3.005 Å).[24]

The comparison of **3** with the corresponding diphosphine reveals similarities with respect to the conformational preferences. Due to the larger size of the bismuth atoms compared with phosphorus, there is however less steric repulsion between the bulky alkyl groups and, consequently, despite a weaker E−E bond the dissociation with formation of $R_2E^•$ radicals is less favored for E = Bi than for E = P.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for the financial support.

Supporting Information Available: Experimental details, spectra, and complete X-ray crystallographic data for $[(Me_3Si)_2CH]_2Bi-Bi[CH(SiMe_3)_2]_2$ (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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[31] Crystallographic data for $C_{28}H_{76}Bi_2Si_8$: triclinic, space group $P\bar{1}$ (No. 2), radiation Mo Kα ($\lambda = 0.71073$ Å), $a = 9.461(5)$ Å, $b = 11.585(4)$ Å, $c = 23.285(6)$ Å, $\alpha = 100.85(2)°$, $\beta = 96.73(3)°$, $\gamma = 108.16(3)°$, $V = 2339.0(16)$ Å^3, $Z = 2$, absorption coefficient 7.734 mm^{-1}, $F(000)$ 1044, crystal size 0.2 × 0.3 × 0.5 mm^3, $T = 173$ K, θ range for data collection 2.59−27.50°, index range $-12 \leq h \leq 1$, $-14 \leq k \leq 14$, $-30 \leq l \leq 30$, 12 612 reflection collected, 10 514 independent reflections (R(int) = 0.0340), completeness to $\theta = 27.50°$ 97.8%, absorption correction empirical (Difabs), refinement method full-matrix least-squares on F^2, data/restraints/parameters 10514/0/369, goodness-of-fit an F^2 1.049, final R indices ($I > 2\sigma(I)$) R1 = 0.0584, wR2 = 0.1399, final R indices (all data) R1 = 0.0932, wR2 = 0.1599, largest difference peak and hole 2.882/−2.448 e Å^{-3}.