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Syntheses, Structures, and Dynamic Behavior of Chiral Racemic Organoantimony and -bismuth Compounds RR′SbCl, RR′BiCl, and RR′SbM [R = 2-(Me_2NCH_2)C_6H_4, R′ = CH(Me_3Si)$_2$, M = H, Li, Na]

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RR′SbCl (**1**) and RR′BiCl (**2**) [R = 2-(Me_2NCH_2)C_6H_4, R′ = CH(Me_3Si)$_2$] form by the reaction of R′ECl_2 (E = Sb, Bi) with RLi. The reaction of **1** with $LiAlH_4$ and metalation with *n*-BuLi gives RR′SbH (**3**) and RR′SbLi•2THF (**4**) (THF = tetrahydrofuran). Transmetalation of **4** with sodium *tert*-butoxide in the presence of TMEDA (TMEDA = tetramethylethylenediamine) leads to RR′SbNa•TMEDA (**5**). Structural analyses by ^1H NMR in C_6D_6, $C_6D_5CD_3$, or $(CD_3)_2SO$ with a variation of the temperature (**1**, **2**, **4**, and **5**) and by single-crystal X-ray diffraction (**1**, **2**, **4**, and **5**) revealed the intramolecular coordination of the pendant Me_2N group on the pnicogen centers in **1** and **2** and on Li or Na in **4** or **5**. The variable-temperature ^1H NMR spectra of the hydride **3** in C_6D_6, $C_6D_5CD_3$, or $(CD_3)_2SO$ show that the pyramidal configuration on antimony is stable up to 100 °C, whereas inversion at the nitrogen is not prevented by internal coordination even at –80 °C. The crystals of **1**, **2**, **4**, and **5** consist of discrete molecules with the Sb and Bi atoms in an approximately Ψ-trigonal-bipyramidal environment in the cases of **1** and **2** and in a pyramidal environment in the cases of **4** and **5**. Crystal data for **1**: triclinic, space group $P\bar{1}$, $a = 7.243(4)$ Å, $b = 10.373(3)$ Å, $c = 15.396(5)$ Å, $\alpha = 79.88°$, $\beta = 78.27°$, $\gamma = 71.480(10)°$, $V = 1066.2(7)$ Å^3, $Z = 2$, $R = 0.0614$. **2**: monoclinic, space group $P2_1/n$, $a = 10.665(2)$ Å, $b = 14.241(2)$ Å, $c = 14.058(2)$ Å, $\beta = 90.100(10)°$, $V = 2135.1(6)$ Å^3, $Z = 4$, $R = 0.049$. **4**: monoclinic, space group $P2_1/n$, $a = 11.552(2)$ Å, $b = 16.518(3)$ Å, $c = 15.971(5)$ Å, $\beta = 96.11(2)°$, $V = 3030.2(12)$ Å^3, $Z = 4$, $R = 0.0595$. **5**: monoclinic, space group $P2_1/n$, $a = 9.797(2)$ Å, $b = 24.991(5)$ Å, $c = 14.348(3)$ Å, $\beta = 94.98(3)°$, $V = 3499.66(12)$ Å^3, $Z = 4$, $R = 0.0571$. The dissociation of the intramolecular N–pnicogen bond and inversion at the nitrogen occurs when solutions of **1** or **2** in C_6D_6 or $C_6D_5CD_3$ are heated above 25 or 30° C. **1** and **3**–**5** are stable with respect to inversion of the configuration at the antimony in C_6D_6, $C_6D_5CD_3$, or $(CD_3)_2SO$ up to 160° C. Bismuth inversion, probably via the *edge* mechanism, is observed in solutions of **2** in $(CD_3)_2SO$ at 45 °C but not in $C_6D_5CD_3$ below 125 °C.

Introduction

Antimony(III) and bismuth(III) compounds bearing three different substituents are potential chiral reagents or catalysts for enantioselective syntheses.[1–5] We report here on the efficient syntheses, structural characterization, and dynamic behavior of RR′SbCl (**1**), RR′BiCl (**2**), RR′SbH (**3**), RR′SbLi•2THF (**4**), and RR′SbNa•TMEDA (**5**) [R = 2-(Me_2NCH_2)-C_6H_4, R′ = CH(Me_3Si)$_2$, THF = tetrahydrofuran, and TMEDA = tetramethylethylenediamine]. The antimony and bismuth centers in **1**−**5** are effectively protected by the bis(trimethylsilyl)methyl and the 2-(*N*,*N*-dimethylaminomethyl)phenyl substituents, which combine bulkiness with the potential for supplemental Lewis base interactions. Known examples of unsymmetrical organoantimony(III) halides are [4-(EtO_2C)C_6H_4]ArSbCl (Ar = 4-(Me)C_6H_4, 4-(*cyclo*-C_6H_{11})-C_6H_4, 1-naphthyl),[6] [2-($C_{12}H_9$)][4-(Me)C_6H_4]SbCl,[7] and (C_6H_5-CH_2)MeSbCl.[8] None of them were characterized by X-ray

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diffractometry. Several chiral halobismuthanes stabilized by the intramolecular coordination of sulfonyl,[9] (dimethylamino)methyl,[10] (dimethylamino)ethyl,[11,12] or acyl[13] groups were prepared and characterized by X-ray diffractometry. Chiral triorganostibanes[6,7,14−17] and -bismuthanes[18] have also been described in the literature. Recently, the resolution of an Sb-chiral 1-phenyl-2-trimethylsilylstibindole[19] and of chiral triarylstibanes, (aryl)[2-(*S*)-(1-*N*,*N*-dimethylaminoethyl)phenyl]-(*p*-tolyl)stibane (aryl = phenyl, naphthyl, phenanthryl)[20] were reported. The stereoselective synthesis of an optically pure bismuthane, (4-chlorophenyl){(*S*)-2-[(*R*)-(dimethylamino)ethyl]ferrocenyl}iodobismuthane,[11] was also achieved.

The only known asymmetrical alkali metal, diorganoantimonide, or PhMeSbNa,[21−23] was reported without structural data as an intermediate in the preparation of asymmetrical tertiary stibanes. Closely related to **4** and **5** are the crystal structures of $[2\text{-}(Me_2NCH_2)C_6H_4][(Me_3Si)_2CH]PLi\cdot 2THF$ and $[2\text{-}(Me_2NCH_2)C_6H_4][(Me_3Si)_2CH]PNa\cdot TMEDA$.[24]

Experimental Section

General Procedures. NMR spectra were run on a Bruker DPX 200 spectrometer. Chemical shifts are reported in δ units (ppm) referenced to C_6D_5H (7.15 ppm, ^1H) and C_6D_6 (128.0 ppm, ^{13}C). Mass spectra were recorded on Finnigan MAT CH7 (A) and Finnigan MAT 8222 spectrometers. The patterns of antimony-containing ions were compared with theoretical values. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller in Göttingen. The reactions and manipulations were performed under an inert atmosphere of dry argon. $2\text{-}(Me_2NCH_2)C_6H_4Li$[25] and $(Me_3Si)_2CHECl_2$ (E = Sb,[26] Bi[27]) were prepared according to reported procedures.

$[2\text{-}(Me_2NCH_2)C_6H_4][(Me_3Si)_2CH]SbCl$ (1). A solution of 2-(*N*,*N*-dimethylaminomethyl)phenyllithium (1.11 g, 7.87 mmol) in toluene (40 mL) was added to a cold (−80 °C) solution of $[(Me_3Si)_2CH]SbCl_2$ (2.77 g, 7.87 mmol) in toluene (30 mL) over 1 h. The reaction was stirred at this temperature for $^1/_2$ h and then allowed to warm to room temperature. The solution was filtered and the solvent removed in vacuo to yield 3.39 g (96%) of **1** as a colorless solid. Mp: 80 °C. Anal. Calcd for $C_{16}H_{31}Si_2SbClN$ (450.81): C, 42.63; H, 6.93. Found: C, 41.96; H, 6.75. ^1H NMR (C_6D_6, 20 °C, 200 MHz): −0.19 (s, 1 H, CH), 0.07 (s, 9 H, SiCH_3, $^2J_{SiH} = 6.3$ Hz), 0.44 (s, 9 H, SiCH_3, $^2J_{SiH} = 6.3$ Hz), 1.59 (s, br, 3 H, NCH_3), 1.75 (s, br, 3 H, NCH_3), AB spin system with A 2.81, B 3.49 (2 H, CH_2, $^2J_{HH} = 14.2$ Hz), 6.8 (d, 1 H, C$_6H_4$, $^3J_{HH} = 7.4$ Hz), 7.01−7.18 (m, 2 H, C$_6H_4$), 8.8 (dd, 1 H, C$_6H_4$, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.2$ Hz). ^1H NMR (C_6D_6, 25 °C, 200 MHz): −0.19 (s, 1 H, CH), 0.07 (s, 9 H, SiCH_3, $^2J_{SiH} = 6.3$ Hz), 0.44 (s, 9 H, SiCH_3, $^2J_{SiH} = 6.3$ Hz), 1.69 [s, br, 6 H, N(CH_3)$_2$], AB spin system with A 2.82, B 3.50 (2 H, CH_2, $^2J_{HH} = 14.3$ Hz), 6.8 (d, 1 H, C$_6H_4$, $^3J_{HH} = 7.4$ Hz), 7.01−7.18 (m, 2 H, C$_6H_4$), 8.8 (dd, 1 H, C$_6H_4$, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.2$ Hz). ^{13}C NMR (C_6D_6, 20 °C, 50 MHz): 3.7 (s, SiCH$_3$), 4.16 (s, SiCH$_3$), 10.07 (s, CH), 44.46 (s, br, NCH$_3$), 45.71 (s, br, NCH$_3$), 65.65 (s, CH$_2$), 126.49 (s, C_6H$_4$), 128.30 (s, C_6H$_4$), 128.94 (s, C_6H$_4$), 137.61 (s, C_6H$_4$), 142.90 (s, C_6H$_4$), 145.42 (s, C_6H$_4$). MS (CI$_{pos}$, NH$_3$): 452 (16) [M$^+$ + H], 416 (100) [M$^+$ − Cl], 292 (28) [RSbCl$^+$], 134 (8) [R$^+$], R = $C_6H_4CH_2NMe_2$. MS (CI$_{neg}$, NH$_3$): 486 (100) [M$^-$ + Cl], 451 (28) [M$^-$].

$[2\text{-}(Me_2NCH_2)C_6H_4][(Me_3Si)_2CH]BiCl$ (2). The reaction of 2.17 g (4.94 mmol) of $[(Me_3Si)_2CH]BiCl_2$ with 0.69 g (4.89 mmol) of 2-(*N*,*N*-dimethylaminomethyl)phenyllithium in 75 mL of toluene and the workup procedures were performed in an analogous way to that in the synthesis of **1**. After filtration of the reaction mixture and removal of the solvent, 2.42 g (91%) of **2** were obtained as a colorless solid. Mp: 141−143 °C dec. Anal. Calcd for $C_{16}H_{31}Si_2BiClN$ (538.04): C, 35.72; H, 5.81. Found: C, 36.05; H, 5.69. ^1H NMR (C_6D_6, 20 °C, 200 MHz): −0.17 (s, 1 H, CH), 0.14 (s, 9 H, SiCH_3), 0.39 (s, 9 H, SiCH_3), 1.55 (s, 3 H, NCH_3), 1.74 (s, 3 H, NCH_3), AB spin system with A 3.02, B 3.44 (2 H, CH_2, $^2J_{HH} = 14.4$ Hz), 7.07−7.34 (m, 3 H, C$_6H_4$), 9.32 (d, 1 H, C$_6H_4$, $^3J_{HH} = 7.6$ Hz). ^1H NMR (C_6D_6, 30 °C, 200 MHz): −0.17 (s, 1 H, CH), 0.13 (s, 9 H, SiCH_3), 0.39 (s, 9 H, SiCH_3), 1.67 [s, br, 6 H, N(CH_3)$_2$], AB spin system with A 3.04, B 3.46 (2 H, CH_2, $^2J_{HH} = 14.2$ Hz), 7.07−7.34 (m, 3 H, C$_6H_4$), 9.30 (d, 1 H, C$_6H_4$, $^3J_{HH} = 7.4$ Hz). ^1H NMR [$(CD_3)_2SO$, 20 °C, 200 MHz]: −0.21 (s, br, 9 H, SiCH_3), 0.07 (s, 1 H, CH), 0.23 (s, br, 9 H, SiCH_3), 2.49 [s, br, 6 H, N(CH_3)$_2$], 4.02 (s, br, 2 H, CH_2), 7.33−7.58 (m, 3 H, C$_6H_4$), 8.64 (d, 1 H, C$_6H_4$, $^3J_{HH} = 7.1$ Hz). ^1H NMR [$(CD_3)_2SO$, 45 °C, 200 MHz]: 0.07 (s, br, 19 H, SiCH_3 + CH), 2.50 [s, 6 H, N(CH_3)$_2$], 4.02 (s, 2 H, CH_2), 7.33−7.58 (m, 3 H, C$_6H_4$), 8.66 (dd, 1 H, C$_6H_4$, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.5$ Hz). ^{13}C NMR (C_6D_6, 20 °C, 50 MHz): 4.26 (s, SiCH$_3$), 5.54 (s, SiCH$_3$), 31.58 (s, CH), 44.53 (s, NCH$_3$), 46.6 (s, NCH$_3$), 68.99 (s, CH$_2$), 128.13 (s, C_6H$_4$), 128.29 (s, C_6H$_4$), 128.94 (s, C_6H$_4$), 130.79 (s, C_6H$_4$), 140.55 (s, C_6H$_4$), 147.48 (s, C_6H$_4$). MS (CI$_{pos}$, NH$_3$): 538 (14) [M$^+$ + H], 502 (100) [M$^+$ − Cl], 136 (70) [R$^+$ + H], R = $C_6H_5CH_2NMe_2$. MS (CI$_{neg}$, NH$_3$): 572 (92) [M$^-$ + Cl], 537 (100) [M$^-$], 403 (10) [$(Me_3Si)_2CHBiCl^-$].

$[2\text{-}(Me_2NCH_2)C_6H_4][(Me_3Si)_2CH]SbH$ (3). A solution of 2.6 g (5.77 mmol) of **1** in Et_2O (50 mL) was added dropwise to a cold (−80 °C) suspension of $LiAlH_4$ (0.23 g, 6.05 mmol) in Et_2O (30 mL). The mixture was warmed to 0 °C and filtered through a D4 frit covered with kieselguhr. Removal of the solvent under a reduced pressure gave 2.08 g (87%) of **3** as a colorless, viscous oil, unstable

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Table 1. Crystal Data, Data Collection, and Structure-Refinement Parameters for **1**, **2**, **4**, and **5**·Et_2O

	1	**2**	**4**	**5**·Et_2O
empirical formula	$C_{16}H_{31}ClNSbSi_2$	$C_{16}H_{31}BiClNSi_2$	$C_{24}H_{47}LiNO_2SbSi_2$	$C_{26}H_{57}N_3NaOSbSi_2$
fw	450.8	538.03	566.50	628.67
color	colorless	colorless	red	orange
temp, K	173(2)	173(2)	173(2)	173(2)
cryst size, mm	0.3 × 0.2 × 0.2	0.6 × 0.4 × 0.1	0.6 × 0.5 × 0.1	0.5 × 0.4 × 0.3
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	7.243(4)	10.665(2)	11.552(2)	9.797(2)
b, Å	10.373(3)	14.241(2)	16.518(3)	24.991(5)
c, Å	15.396(5)	14.058(2)	15.971(5)	14.348(3)
α, deg	79.88	90	90	90
β, deg	78.27	90.1(1)	96.11(2)	94.98(3)
γ, deg	71.48(1)	90	90	90
V, Å^3	1066.2(7)	2135.1(6)	3030.2(12)	3499.7(12)
Z	2	4	4	4
d_{calcd}, g·cm^{-3}	1.404	1.674	1.242	1.193
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73
μ, mm^{-1}	1.527	8.491	1.007	0.889
F(000)	460	1048	1184	1328
scan range (deg)	$2.62 \le \theta \le 25$	$2.79 \le \theta \le 27.55$	$2.57 \le \theta \le 27.51$	$2.56 \le \theta \le 26.18$
no. of measd data	4779	11 998	8538	35 477
no. of unique data	3744 [R(int) = 0.0519]	4886 [R(int) = 0.1185]	6872 [R(int) = 0.0304]	6428 [R(int) = 0.0852]
no. of params	202	203	292	326
wR2^a (all data)	0.1275	0.123	0.1787	0.1606
R1^a (all data)	0.1197	0.075	0.0749	0.0918
wR2^a [$I > 2\sigma(I)$]	0.1076	0.1113	0.1672	0.1411
R1^a [$I > 2\sigma(I)$]	0.0614	0.049	0.0595	0.0571
GOF on F^2	0.985	1.014	1.065	1.031
residual density, e·Å^{-3}	+0.820; −0.932	+1.967; −2.389	+1.066; −1.648	+0.701; −0.44

[a] Definition of the R values: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{[w\Sigma(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (\alpha P)^2 + bP$.

at room temperature. ^{1}H NMR (C_6D_6, 20 °C, 200 MHz): 0.1 (d, 1 H, C*H*, $^3J_{HH}$ = 3.3 Hz), 0.17 (s, 9 H, SiC*H*$_3$), 0.24 (s, 9 H, SiC*H*$_3$), 1.92 (s, 6 H, NC*H*$_3$), AB spin system with A 3.38, B 3.54 (2 H, C*H*$_2$, $^2J_{HH}$ = 13.1 Hz), 4.34 (d, 1 H, Sb*H*, $^3J_{HH}$ = 3.3 Hz), 6.86−7.11 (m, 3 H, C_6H_4), 7.69−7.74 (m, 1 H, C_6H_4). IR (toluene-d_6): 1791 cm^{-1} (ν Sb−H). HRMS (EI, 70 eV): 415.110 19 (calcd 415.111 16 amu, $C_{16}H_{32}NSi_2Sb^{121}$, M$^+$). MS (EI, 70 eV): 415 (5) [M$^+$], 400 (5) [M$^+$ − Me], 256 (100) [RSbH$^+$], 134 (28) [R$^+$]. MS (CI$_{pos}$, NH_3): 416 (100) [M$^+$ + H], 256 (26) [RSbH$^+$], 136 (40) [R$^+$ + 2H], R = $C_6H_4CH_2NMe_2$. MS (CI$_{neg}$, NH_3): 414 (100) [M$^-$], 159 (25) [$(Me_3Si)_2CH^-$].

[2-(Me_2NCH_2)C_6H_4][(Me_3Si)$_2$CH]SbLi·2THF (4). A solution of **3** (1.8 g, 4.42 mmol) in THF (40 mL) was treated dropwise with 2.7 mL of *n*-BuLi (15% in hexane) at −80 °C. The reaction mixture was warmed to −30 °C with stirring, and the color became red. Filtration through a cooled (−30 °C) frit covered with kieselguhr, reducing the volume in vacuo for 50%, and cooling for 12 h at −28 °C gave 1.5 g (62%) of **4** as red crystals (48−52 °C dec). ^{1}H NMR (C_6D_6, 20 °C, 200 MHz): −0.38 (s, 1 H, C*H*), 0.04 (s, 18 H, SiC*H*$_3$), 1.19 (m, 8 H, THF), 2.07 (s, 6 H, NC*H*$_3$), AB spin system with A 3.22, B 3.35 (2 H, C*H*$_2$, $^2J_{HH}$ = 11.6 Hz), 3.56 (m, 8 H, THF), 7.03 (m, 3 H, C_6H_4), 7.74 (m, 1 H, C_6H_4).

[2-(Me_2NCH_2)C_6H_4][(Me_3Si)$_2$CH]SbNa·TMEDA (5). A solution of 1.0 g (1.76 mmol) of **4** in 30 mL of diethyl ether was added at −50 °C to a slurry of 0.18 g (1.87 mmol) of NaOBu^t in 10 mL of diethyl ether. The reaction mixture was warmed with stirring to 10 °C and then filtered at −30 °C through a frit covered with kieselguhr. Addition of 0.25 mL (1.72 mmol) of TMEDA and stirring at −30 °C for 1 h, followed by reduction of the volume to 10 mL, gave 0.43 g (44%) of **5** as orange crystals (65−70 °C dec). ^{1}H NMR (C_6D_6, 20 °C, 200 MHz): 0.08 (s, 1 H, C*H*), 0.60 (s, 18 H, SiC*H*$_3$, $^2J_{SiH}$ = 6.2 Hz), 1.76 (s, 12 H, TMEDA), 1.80 (s, 4 H, TMEDA), 1.93 (s, 6 H, NC*H*$_3$), 3.42 (s, br, 2 H, C*H*$_2$), 6.67−6.97 (m, 3 H, C_6H_4), 8.00 (dd, 1 H, C_6H_4, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz). ^{1}H NMR ($C_6D_5CD_3$, 20 °C, 200 MHz): 0.21 (s, 1 H, C*H*), 0.52 (s, 18 H, SiC*H*$_3$, $^2J_{SiH}$ = 6.2 Hz), 1.77 (s, 12 H, TMEDA), 1.82 (s, 4 H, TMEDA), 1.99 (s, 6 H, NC*H*$_3$), 3.37 (s, br, 2 H, C*H*$_2$), 6.63−7.16 (m, 3 H, C_6H_4), 7.91 (d, 1 H, C_6H_4, $^3J_{HH}$ = 7.4 Hz). ^{1}H NMR ($C_6D_5CD_3$, −85 °C, 200 MHz): 0.38 (s, 1 H, C*H*), 0.70 (s, br, 9 H, SiC*H*$_3$), 0.77 (s, br, 9 H, SiC*H*$_3$), 1.69−1.93 (m, 22 H, TMEDA + NC*H*$_3$), 3.52 (s, br, 2 H, C*H*$_2$), 6.75−8.02 (m, 4 H, C_6H_4).

X-ray Crystallography. The details of the crystal structure determination and refinement are given in Table 1. Data were collected on a Siemens P4 four-circle diffractometer (**1**, **2**, and **4**) and on a Stoe-IPDS diffractometer (**5**) using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). For this purpose, the crystals were attached with Kel-F-oil to a glass fiber and cooled under a nitrogen stream to 173 K. The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement, the software package SHELX-97 was used.[28] The drawings were created with the DIAMOND program.[29]

Results and Discussion

The chiral alkylarylantimony and -bismuth chlorides **1** and **2** form in high yields (96% **1** and 91% **2**) by reactions of 2-(Me_2NCH_2)C_6H_4Li[25] with (Me_3Si)$_2$CHECl$_2$ (E = Sb,[26] Bi[27]) in toluene at −80 °C.

$$2\text{-}(Me_2NCH_2)C_6H_4Li + (Me_3Si)_2CHECl_2 \xrightarrow[-80\ ^\circ C]{toluene} [2\text{-}(Me_2NCH_2)C_6H_4][(Me_3Si)_2CH]ECl + LiCl$$

E = Sb (**1**), Bi (**2**)

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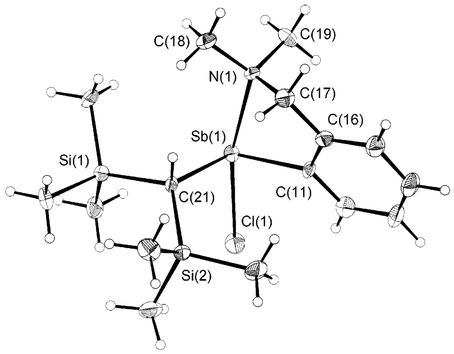

Figure 1. ORTEP-like representation at 50% probability and atom numbering scheme for (*R*)-**1**.

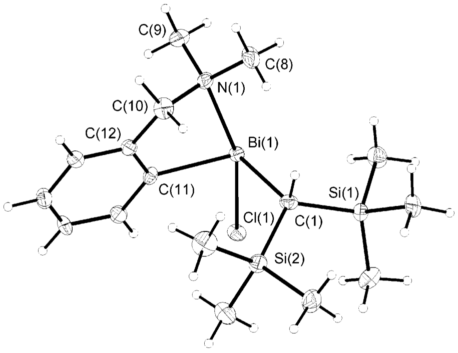

Figure 2. ORTEP-like representation at 50% probability and atom numbering scheme for (*S*)-**2**.

The reaction of **1** with $LiAlH_4$ in Et_2O gives the antimony hydride **3** (87%).

$$\mathbf{1} + \mathrm{LiAlH_4} \xrightarrow[-80\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} \mathbf{3} + \mathrm{LiCl} + \mathrm{AlH_3}$$

The chlorides **1** and **2** are colorless, air-sensitive crystalline compounds slightly soluble in petroleum ether but readily soluble in THF, diethyl ether, aromatic hydrocarbons, and other organic solvents. The hydride **3** is an air-sensitive colorless oil that is soluble in common organic solvents including petroleum ether. **1** and **2** are stable in an inert atmosphere at room temperature for several days. **3** is stable at −28 °C. It decomposes at 20 °C in the course of 2 days but can be warmed in solution up to 100 °C for 0.5 h. Characteristic mass spectra have been obtained by chemical ionization and electron impact techniques, and the composition was proved by elemental analyses (**1** and **2**) and high-resolution mass spectrometry (**3**).

Single crystals of **1** and **2** were obtained by cooling solutions in toluene. X-ray diffraction studies revealed that **1** and **2** crystallize as racemates. The molecular structures of the *R* isomer of **1** and of the *S* isomer of **2** are shown in Figures 1 and 2. Selected bond distances and angles are given in Table 2.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**, **2**, **4**, and **5**

Compound **1**			
Sb(1)−C(11)	2.145(8)	Sb(1)−Cl(1)	2.50(3)
Sb(1)−C(21)	2.181(8)	Sb(1)−N(1)	2.533(7)
C(11)−Sb(1)−C(21)	104.3(3)	Cl(1)−Sb(1)−N(1)	163.60(16)
C(11)−Sb(1)−Cl(1)	90.7(2)	C(17)−N(1)−Sb(1)	103.2(5)
C(21)−Sb(1)−Cl(1)	91.5(2)	N(1)−C(17)−C(16)	110.9(7)
C(11)−Sb(1)−N(1)	73.1(3)	C(16)−C(11)−Sb(1)	119.1(6)
C(21)−Sb(1)−N(1)	90.5(3)	C(11)−C(16)−C(17)	118.4(8)
Compound **2**			
Bi(1)−C(11)	2.259(8)	Bi(1)−Cl(1)	2.6816(18)
Bi(1)−C(1)	2.295(8)	Bi(1)−N(1)	2.579(6)
C(11)−Bi(1)−C(1)	101.0(3)	Cl(1)−Bi(1)−N(1)	162.85(16)
C(11)−Bi(1)−Cl(1)	92.4(2)	C(10)−N(1)−Bi(1)	105.9(5)
C(1)−Bi(1)−Cl(1)	95.5(2)	N(1)−C(10)−C(12)	111.6(7)
C(11)−Bi(1)−N(1)	72.1(3)	C(12)−C(11)−Bi(1)	117.9(6)
C(1)−Bi(1)−N(1)	94.6(3)	C(11)−C(12)−C(10)	120.7(7)
Compound **4**			
Sb(1)−C(1)	2.239(4)	Li−N(1)	2.123(9)
Sb(1)−C(8)	2.180(4)	Li−O(1)	1.933(9)
Sb(1)−Li	2.856(8)	Li−O(2)	1.958(8)
C(1)−Sb(1)−C(8)	98.69(16)	C(13)−C(8)−Sb(1)	119.0(3)
C(1)−Sb(1)−Li	123.43(19)	N(1)−C(14)−C(13)	112.5(4)
C(8)−Sb(1)−Li	71.84(19)	Li−N(1)−C(14)	111.6(4)
N(1)−Li−Sb(1)	91.0(3)		
Compound **5**			
Sb(1)−C(1)	2.255(5)	N(2)−Na(1)	2.454(6)
Sb(1)−C(8)	2.186(6)	N(3)−Na(1)	2.472(8)
Sb(1)−Na(1)	3.101(3)	C(8)···Na(1)	3.041(7)
N(1)−Na(1)	2.502(6)		
C(1)−Sb(1)−C(8)	97.7(2)	C(13)−C(14)−N(1)	112.7(6)
C(8)−Sb(1)−Na(1)	67.69(17)	C(14)−N(1)−Na(1)	108.7(4)
Sb(1)−C(8)−C(13)	120.0(5)	N(1)−Na(1)−Sb(1)	83.18(15)
C(8)−C(13)−C(14)	120.5(6)	N(2)−Na(1)−N(3)	74.8(2)

The antimony and bismuth atoms in **1** and **2** are in the trigonal-pyramidal environments of C(11), C(21), Cl(1) and C(11), C(1), Cl(1), respectively. Internal coordination of the Me_2N group trans to the Sb−Cl or Bi−Cl bond leads to approximately Ψ-trigonal-bipyramidal geometries with the C atoms in equatorial positions and the Cl and N atoms in axial positions [**1**, N(1)−Sb(1)−Cl(1) 163.60(16)°; **2**, N(1)−Bi(1)−Cl(1) 162.85(16)°]. The N−Sb [**1**, 2.533(7) Å] and the N−Bi [**2**, 2.579(6) Å] distances lie between the sums of the respective covalent (N and Sb, 2.2 Å; N and Bi, 2.14 Å) and van der Waals radii (N and Sb, 3.8 Å; N and Bi, 4.0 Å). Similar values were also found for the N−Sb distances in $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbCl$ [2.463(2) Å][30] and $[8\text{-}(Me_2NCH_2)\text{-}C_{10}H_6]_2SbCl$ [2.519(4) Å][30] and for the N−Bi distances in $[C_6H_4C(CF_3)_2O]Bi[2\text{-}(Me_2NCH_2)C_6H_4]$ [2.62(1) Å][31,32] and $[2\text{-}(Me_2NCH_2)C_6H_4][4\text{-}(CH_3)C_6H_4]BiCl$ [2.525(6) Å].[10] The geometric parameters, including the elongation of the Sb−Cl and Bi−Cl bond distances in **1** [2.500(3) Å] and **2** [2.6816(18) Å] compared to $[(Me_3Si)_2CH]_2SbCl$ [2.398(12) Å][33] and $[(Me_3Si)_2CH]_2BiCl$ [2.530(2) Å],[27] are consistent with the view that the Lewis acidity of organopnicogen(III) halides is related to the E−X σ^* orbitals (X = halogen).[30,34,35] The five-membered chelate ring generated by the intramolecular coordination of the amine arm is folded along the Sb(1)−C(17) and the Bi(1)−C(10) vectors, respectively; N(1) lies above the Sb(1)−C(11)−C(16)−C(17) plane in **1** and

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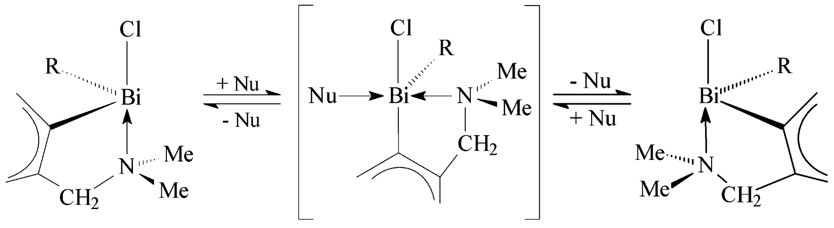
Scheme 1 *Edge*-Inversion Process for **2** with a T-Shaped Transition State



R = $CH(SiMe_3)_2$
Nu = $(CD_3)_2SO$

above the Bi(1)−C(10)−C(12)−C(11) plane in **2**, generating an angle of 38.9° between the Sb(1)−C(17)−C(16)−C(17) and Sb(1)−C(17)−N(1) planes in **1** and of 34.1° between the Bi(1)−C(10)−C(12)−C(11) and Bi(1)−C(10)−N(1) planes in **2**. An interesting aspect of the structures of **1** and **2** is the presence of a weak interaction between the proton ortho to antimony or bismuth and the chlorine atom (2.643 Å in **1** and 2.746 Å in **2**), which is shorter than the sum of the van der Waals radii of Cl and H (2.81 Å). A similar weak H···Cl interaction caused a large downfield shift in the aromatic region of the ^{1}H NMR spectra of $[2\text{-}(Me_2NCH_2)C_6H_4][4\text{-}MeC_6H_4]BiCl$[10] and $[2\text{-}(t\text{-}BuSO_2)C_6H_4][4\text{-}MeC_6H_4]BiCl$,[9] which are structurally related to **1** and **2**.

The ^{1}H NMR spectra of **1** and **2** at 20 °C in C_6D_6 or in $C_6D_5CD_3$ contain two singlet signals for Me_3Si and NMe_2 and two doublets for the CH_2 protons, showing that these groups are diastereotopic. The spectral findings suggest that the chiral configuration found in solid **1** and **2** is preserved at 20 °C and also in solutions of **1** and **2** in C_6D_6 or $C_6D_5CD_3$. There is a large downfield shift of the signal of the hydrogen ortho to the antimony or bismuth atoms.

To study the configurational stability of **1** and **2**, ^{1}H NMR spectra were recorded with a variation of the temperature between 20 and 160 °C. The signals of the NMe_2 groups show coalescence at 25 °C [**1** in C_6D_6, $C_6D_5CD_3$, or $(CD_3)_2SO$], 30 °C (**2** in C_6D_6 or $C_6D_5CD_3$), or 20 °C [**2** in $(CD_3)_2SO$] because of the dissociation of the intramolecular E−N (E = Sb, Bi) coordination bond and inversion at the nitrogen atom.[36,37]

Heating solutions of **1** or **2** in C_6D_6 up to 80 °C, of **1** or **2** in $C_6D_5CD_3$ up to 125 °C, or of **1** in $(CD_3)_2SO$ up to 160 °C or varying the concentration does not lead to coalescence of the Me_3Si peaks. Apparently, inversion at the antimony and bismuth atoms does not occur under these conditions. Coalescence of the Me_3Si signals was, however, observed at 45 °C in solutions of **2** in $(CD_3)_2SO$ (Figure 3). The inversion energy $\Delta G^\ddagger$ was determined to be 15.5 kcal mol^{-1} at 45 °C.

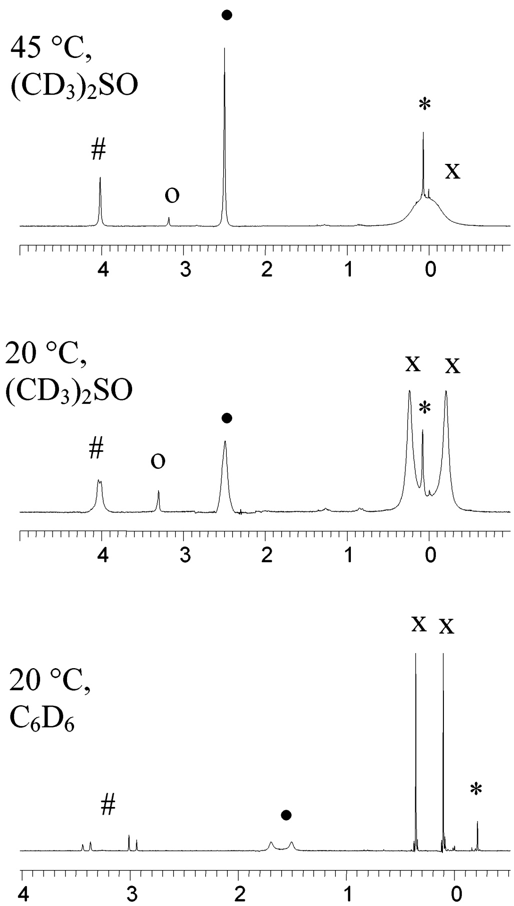


Figure 3. Variable-temperature ^{1}H NMR spectra of racemic **2**. Only the high-field part of the spectra is shown: #, CH_2; ●, NMe_2; ×, Me_3Si; *, CH; ○, H_2O (impurity).

The relatively low barrier for the bismuth inversion and the pronounced effect of the stronger donor solvent dimethyl sulfoxide (DMSO) are consistent with the predictions for *edge* inversion,[38] where the T-shaped transition state is stabilized both by the internal coordination of the pendant dimethylamino group and by the coordination of DMSO with electron donation into an empty 6p orbital at the bismuth (Scheme 1). A similar mechanism was also reported for $[2\text{-}\{OC(CF_3)_2\}C_6H_4]Bi[2\text{-}(R)C_6H_4]$ in $(CD_3)_2SO$ [R, $\Delta G^\ddagger$ (kcal mol^{-1}) = Me_2NCH_2, 15.5; $Me(H)NCH_2$, 15.4; $MeOCMe_2$, 18.6; $MeOC(CF_3)_2$, 19.7].[31]

The ^{1}H NMR spectra of the hydride **3** at 20 °C in C_6D_6, $C_6D_5CD_3$ (−80 up to +20 °C), or $(CD_3)_2SO$ (−100 up to +20 °C) contain two singlet and two doublet signals

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respectively for the diastereotopic Me_3Si and CH_2 groups and one singlet for the NMe_2 group. The spectral data show that the pyramidal configuration on antimony is stable up to 100 °C (dec), whereas inversion at the nitrogen is not prevented by internal coordination even at −80 °C. $^3J_{HH}$ coupling leads to doublet signals for the Sb−H (4.34 ppm) and methine (0.1 ppm) protons. In the IR spectrum, there is a strong absorption for ν Sb−H at 1791 cm^{-1}. This value compares with those found for $[(Me_3Si)_2CH]_2SbH$[39] (1840 cm^{-1}) and $(Me_3SiCH_2)_2SbH$[40] (1835 cm^{-1}).

The treatment of **3** with *n*-BuLi in THF and crystallization give **4** (62%).

$$[2\text{-}(Me_2NCH_2)C_6H_4][(Me_3Si)_2CH]SbH + n\text{-BuLi} + 2THF \xrightarrow[-80\ °C]{THF} \mathbf{4} + n\text{-BuH}$$

The transmetalation of **4** with sodium *tert*-butoxide in the presence of TMEDA at −50 °C and crystallization give **5** (44%).

$$\mathbf{4} + NaOBu^t \xrightarrow[-50\ °C]{Et_2O/TMEDA} \mathbf{5} + LiOBu^t + 2THF$$

Both **4** and **5** are air- and moisture-sensitive solids that decompose at room temperature but can be stored for a long time in an inert atmosphere at −30 °C. They are slightly soluble in petroleum ether or hexane and readily soluble in THF and aromatic hydrocarbons. The hydrolysis of **4** and **5** gives the hydride **3**. The ^1H NMR spectra of **4** and **5** at 20 °C contain singlet signals for the Me_3Si and NMe_2 groups and two doublets (**4**) or a broad signal (**5**) for the CH_2 protons. These data suggest that M−Sb (M = Li, Na) bond scission, inversion at the nitrogen, and rotation around the Sb−C bond of the alkyl substituent take place in solutions of **4** and **5**. These processes probably do not involve a loss of chirality at the antimony centers because the nonequivalence of the CH_2 protons is preserved. A similar spectral pattern was also observed in the case of the analogous phosphorus compounds.[24] In the case of **5**, ^1H NMR spectra at low temperatures were also recorded. Cooling a solution of **5** in CD_5CD_3 to temperatures below −85 °C leads to a freezing of the dynamic process. At this temperature, the spectra contain two signals that indicate the nonequivalence of the Me_3Si groups, as is expected from the X-ray data.

X-ray diffraction studies revealed that **4** and **5** crystallize as racemates. The antimony centers in **4** and **5** are in trigonal-pyramidal environments. The molecular structures of the *S* isomer of **4** and of the *S* isomer of **5** are shown in Figures 4 and 5. Selected bond distances and angles are given in Table 2. The bidentate Sb−N coordination of the amino antimonide ligand to the alkali metal forms six-membered chelate rings with a ligand bite angle of 91.0(3)° in the case of **4** and 83.18(15)° in the case of **5**. The six-membered chelate rings are puckered along the Sb−C(14) vectors, generating a fold angle between the Sb(1)−C(8)−C(13)−C(14) and C(14)−N(1)−M−Sb(1) (M = Li, Na) planes of 94.9° in the case of **4** and 93.5° in the case of **5**. The lithium atom in **4** lies in a tetrahedral environment coordinated by the antimony and nitrogen atoms of the amino antimonide ligand and the oxygen atoms of two THF molecules. The Sb(1)−Li distance of 2.856(8) Å is comparable to that found in $Ph_2SbLi\cdot 3THF$ [2.881(4) Å].[41] The sodium atom in **5** is essentially four-coordinated with bonds to the Sb and N atoms of the antimonide ligand and to the nitrogen atoms of the TMEDA ligand. The coordination geometry is distorted tetrahedral. The Na(1)−C(8) distance of 3.041(7) Å indicates a weak transannular interaction. A similar interaction was also found in the structure of $[2\text{-}(Me_2NCH_2)C_6H_4][(Me_3Si)_2CH]PNa\cdot TMEDA$ [$Na\cdots C_{ipso}$, 3.0040(18) Å].[24] The Sb(1)−Na(1) bond [3.101(3) Å] in **5** is shorter than the bonds in the triantimonide $Na(L)Bu^t{}_4Sb_3$ [L = $(Me_2NCH_2CH_2)_2NMe$; Sb−Na, 3.303(2) and 3.225(1) Å].[42] These differences reflect the lower coordination number of the sodium atom in **5**. The Na(1)−N(1) distance [2.502(6) Å] is only a little longer than the two Na(1)−N(TMEDA) distances [2.454(6) and 2.472(8) Å] in **5**, and all three distances compare well with the Na−N distances in the triantimonide $Na(L)^tBu_4Sb_3$ [L = $(Me_2NCH_2CH_2)_2NMe$; 245.0(5)−249.5(5) Å].[42]

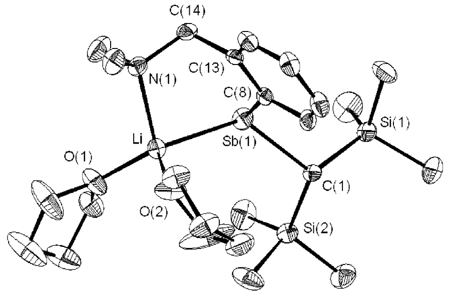

Figure 4. ORTEP-like representation at 50% probability and atom numbering scheme for (*S*)-**4**.

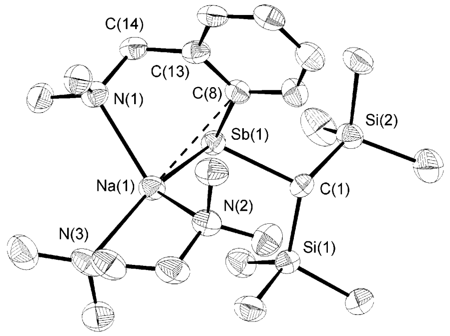

Figure 5. ORTEP-like representation at 50% probability and atom numbering scheme for (*S*)-**5**.

The present results show that the combination of a bulky alkyl group and an aryl group capable of internal coordination of a pendant methylamino group is suitable for the effective synthesis and protection of the primary chlorides, hydrides, and alkali-metal derivatives of antimony and bismuth with Sb- or Bi-centered chirality.

The configurations at the antimony or bismuth were found to be stable in benzene or toluene solutions up to 160 °C in

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the cases of the chlorides and the antimony hydride. Attempts to resolve the isomers have, however, not yet been made. Inversion of configuration was only observed when the alkylarylbismuth chloride was solved in the strong donor solvent DMSO. The chiral configurations of the antimonides are stable in the crystal form and in solution only at low temperature. The use of **1**−**5** as chiral reagents or catalysts, taking advantage of specific properties of organoantimony or -bismuth reagents,[1−5] should be possible. However, low-temperature reactions and noncoordinating solvents should be preferred.

Acknowledgment. The support of this work by Deutsche Forschungsgemeinschaft and by Universität Bremen is gratefully acknowledged.

Supporting Information Available: Listings of crystallographic files in CIF and pdf format for the four reported structures. Variable-temperature ^{1}H NMR spectra of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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