Neutron Diffraction Crystallography of *meso*-R(H)Sb−Sb(H)R and Reactions of R(H)Sb−Sb(H)R and $\mathrm{RSbH_2}$ (R = $\mathrm{(Me_3Si)_2CH}$) Leading to Tungsten Carbonyl Complexes, Methylstibanes, and Antimony Homocycles

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The crystal structure of the *meso* form of R(H)Sb−Sb(H)R (**1**; R = $\mathrm{(Me_3Si)_2CH}$) was studied by single-crystal neutron diffraction at 20 K. **1** or $\mathrm{RSbH_2}$ (**2**) reacts with $\mathrm{W(CO)_5THF}$ (THF = tetrahydrofuran) to give *meso*- and *d,l*-$\mathrm{(OC)_5W[R(H)Sb{-}Sb(H)R]W(CO)_5}$ (**3**) or $\mathrm{R(H)_2SbW(CO)_5}$ (**4**). Dehydrogenation of **3** or **4** leads to $\mathrm{[RSb{=}SbR]W(CO)_5}$ (**5**) or $\mathrm{[(OC)_5W]_2SbR}$ (**6**). **1** or **2** reacts with MeI and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give R(Me)Sb−Sb(Me)R (**7**) or R(Me)SbH (**8**). **2** reacts with $\mathrm{SbCl_3}$ and pyridine to form $\mathrm{R_4Sb_8}$ (**9**). Photochemical degradation of **9** gives cyclo-$\mathrm{R_3Sb_3}$ (**10**). Dehydrogenation of **1** in the presence of $\mathrm{LiAlH_4}$ leads to the cis,trans isomer of $\mathrm{R_4Sb_4}$ (**11**), which in the presence of light forms *all-trans*-**11** and **10**. Decomposition of **1** in the presence of $\mathrm{^tBuONa}$ leads to $\mathrm{R_6Sb_8}$ (**12**). The structures of *meso*-**3**, *d,l*-**3**, **4**, **5**, **9**·2THF, and **12** were determined by X-ray diffraction. The deuterium derivatives of **1**, **2**, and **8** were synthesized and characterized spectroscopically.

Introduction

The syntheses of the stable organoantimony hydrides *meso*- and *d,l*-R(H)Sb−Sb(H)R (**1**) and $\mathrm{RSbH_2}$ (**2**) (R = $\mathrm{(Me_3Si)_2CH}$) as well as the results of a single-crystal X-ray structure analysis of *meso*-**1** were described in a previous communication.[1] We report here on a neutron diffraction study of **1** and on reactions of **1** and **2** leading to the tungsten carbonyl complexes *meso*- and *d,l*-$\mathrm{(OC)_5W[R(H)Sb{-}Sb(H)R]W(CO)_5}$ (**3**), $\mathrm{R(H)_2SbW(CO)_5}$ (**4**), $\mathrm{[RSb{=}SbR]W(CO)_5}$ (**5**), and $\mathrm{[(OC)_5W]_2SbR}$ (**6**), to the methylstibanes R(Me)Sb−Sb(Me)R (**7**) and R(Me)SbH (**8**), and to the cyclostibanes $\mathrm{R_4Sb_8}$ (**9**), $\mathrm{R_3Sb_3}$ (**10**), two isomers of $\mathrm{R_4Sb_4}$ (*all-trans*-**11**, *cis,trans*-**11**), and $\mathrm{R_6Sb_8}$ (**12**) (R = $\mathrm{(Me_3Si)_2CH}$). Also, the deuterium derivatives of the stibanes **1**, **2**, and **8** were prepared.

Metal complexes of organoantimony hydride ligands have not been reported before. However, stibane complexes, $\mathrm{H_3SbM(CO)_5}$ (M = Cr, Mo, W), are known.[2] Triorganostibanes, $\mathrm{R_3Sb}$, and tetraorganodistibanes, $\mathrm{R_2Sb{-}SbR_2}$,[3] are well-established ligands, and also complexes with $\mathrm{RPH_2}$,[4,5] R(H)P−P(H)R,[6,7] $\mathrm{RAsH_2}$,[8,9] and R(H)As−As(H)R[9] ligands (R = alkyl, aryl) are known. Closely related to **5** are the distibene complexes $\mathrm{[RSb{=}SbR]Fe(CO)_4}$ (R = $\mathrm{(Me_3Si)_2CH}$)[10] and $\mathrm{[RSb{=}SbR][M(CO)_5]_3}$ (R = $\mathrm{^tBu}$, M = Cr;[11] R = Ph, M = W[12]). The stibinidene complex **6** was prepared before by the reaction of $\mathrm{RSbCl_2}$ (R = $\mathrm{(Me_3Si)_2CH}$) with $\mathrm{Na_2W_2(CO)_{10}}$.[13] The method used for the syntheses of **7** and **8**, i.e., elimination of hydrogen halide from an element hydride and an alkyl halide in the presence of base, was applied to the synthesis of compounds with P═P or As═As bonds.[14,15] Also, very few examples of tetraorganodistibanes of the type RR′Sb−SbR′R (R = Et,[16] $\mathrm{(CH_2)_3}$,[16] $\mathrm{(CH{=}CHCH_2)_2}$,[16] R′ = Ph;[16] R = 2,6-$\mathrm{Trip_2H_3C_6}$ (Trip = $\mathrm{C_6H_2}$-2,4,6-$\mathrm{^iPr_3}$),[17] R′ = Cl[17]) are known. Chiral secondary stibanes have not yet been described. For known primary alkyl or aryl stibanes see ref 18. The polycycle **9**[19] was obtained before as a side product of the deha-

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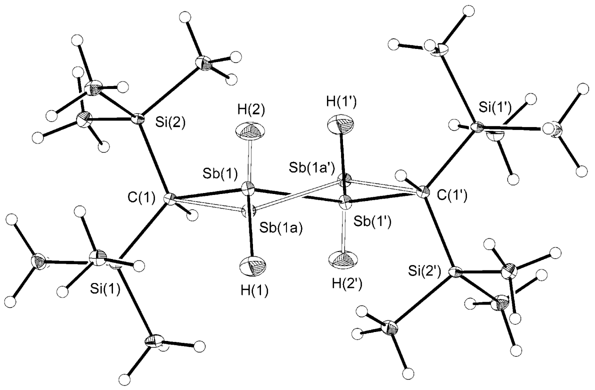

Figure 1. Molecular structure of $(Me_3Si)_2CH(H)Sb-Sb(H)(CH(SiMe_3)_2$ (*meso*-**1**) determined by neutron diffraction. The thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): Sb(1)–Sb(1′) = 2.827(4), Sb(1a)–Sb(1a′) = 2.85(3), Sb(1)–H(1) = 1.705(8), Sb(1a)–H(2) = 1.76(4), Sb(1)–C(1) = 2.1990(19), Sb(1a)–C(1) = 2.209(13); Sb(1′)–Sb(1)–C(1) = 95.36(10), Sb(1a′)–Sb(1a)–C(1) = 94.5(7), C(1)–Sb(1)–H(1) = 95.4(3), C(1)–Sb(1a)–H(2) = 94.5(7).

logenation of $RSbCl_2$ with Mg. P and As analogues of **12** are $^tBu_6P_8$ [20] and $^tBu_6As_8$.[21] Other reported antimony polycycles are the Zintl anions Sb_7^{3-} and Sb_{11}^{3-}.[22] Organoantimony monocycles including **10**[23] and *all-trans*-**11**[24] are well-known. *cis–trans* isomerism was not reported before in cyclostibane or cycloarsane chemistry. A ring closely related to *cis,trans*-**11** is *cis,trans*-$R_4P_4[Cr(CO)_5]_2$ (R = Me_3SiCH_2).[6]

Results and Discussion

The single-crystal X-ray analysis of **1** at 173 °C revealed that the structure consists of partially disordered molecules. Ninety percent of the molecules were characterized as the *meso* form in the antiperiplanar conformation (Figure 1 in ref 1). The hydrogen atoms of the remaining molecules were not located. The redetermination of the crystal structure by neutron diffraction was carried out at 20 K on a single-crystal plate of the size 4 × 3.6 × 1 mm^3, which had been grown from a solution in Et_2O at −28 °C. The neutron diffraction study confirmed that the major component is *meso*-**1** in the antiperiplanar conformation and revealed that the disordered molecules (12% at 20 K) can also be described accurately as distibane **1** in the *meso* form. The molecular structure, including disordered molecules, is shown in Figure 1. The Sb–H bonds of the minor component lie opposite to the Sb–H bonds of the major component. The positions of the antimony atoms of the two components differ slightly; all the other atoms have the same positions. The values for the Sb–H bond lengths found by neutron diffraction (1.705(8) Å for the major component and 1.76(4) Å for the minor component) are certainly more reliable than the X-ray data. They compare much better with the sum of the covalent radii of Sb and H (1.730 Å) than the values of the X-ray studies of **1** (Sb–H, 1.58(3) Å) or $ArSbH_2$ (Ar = 2,6-[2,4,6-triisopropylphenyl]$_2C_6H_3$, mean Sb–H, 1.67 Å).[25]

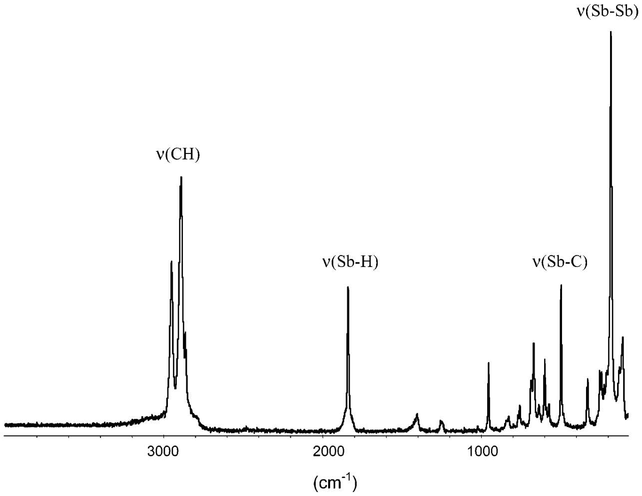

Figure 2. Raman spectrum of *meso*-**1**. Main vibration frequencies (cm^{-1}): 184 (ν(Sb–Sb)), 498 (ν(Sb–C)), 601 ($\nu_{sym}(Si_2C)$), 670, 686 ($\nu_{asym}(SiC_3)$), 955 ($\nu_{sym}(Si_2C)$), 1839 (ν(Sb–H)), 2891, 2951 (ν(C–H)).

The crystals of *meso*-**1** were also characterized by Raman spectroscopy. The strongest signal at 184 cm^{-1} results from the Sb–Sb valence vibration (Figure 2). This value is quite comparable with ν(Sb–Sb) in Me_4Sb_2 (175, 145 cm^{-1}), Et_4Sb_2 (163 cm^{-1}), or Ph_4Sb_2 (141 cm^{-1}).[26] Signals with medium intensity at 498 and 1839 cm^{-1} are assigned to ν(Sb–C) and ν(Sb–H). The other emissions correspond to vibrations of the $(Me_3Si)_2CH$ group. Deuterium derivatives of **1** and **2** are obtained from $RSbCl_2$ and $LiAlD_4$. The infrared spectra of R(D)Sb–Sb(D)R or $RSbD_2$ in Nujol contain signals for the SbD stretching vibrations at 1329 or 1335 cm^{-1} (cf. ν(SbH) 1849 or 1860 cm^{-1} in **1** or **2**).[1] Due to the participation of **1** in the equilibria described in eq 1, there are signals for *meso*- and *d,l*-R(D)Sb–Sb(D)R and $RSbD_2$ as well as $R(D)Sb(SbR)_nSb(D)R$ (n = 1, 2; R = $(Me_3Si)_2CH$) in the ^1H and ^2H NMR spectra of R(D)Sb–Sb(D)R in C_6D_6 or in C_6H_6.

$$2\ \underset{\mathbf{1}}{meso\text{-R(H)Sb}-\text{Sb(H)R}} \rightleftharpoons \underset{\mathbf{2}}{\text{RSbH}_2} + \text{R(H)Sb}-\text{SbR}-\text{Sb(H)R} \rightleftharpoons 2\ \underset{\mathbf{1}}{d,l\text{-R(H)Sb}-\text{Sb(H)R}} \quad (1)$$

Because *meso*-**1** crystallizes exclusively from the equilibrium mixture,[1] there is little chance for a crystallographic characterization of the *d,l* isomer of **1** or of other components. We found that the equilibration between the *meso* and *d,l* forms can be slowed by coordination in metal carbonyl complexes or by substitution of the hydrogen atoms by methyl groups.

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The reaction of the equilibrium mixture containing *meso*- and *d*,*l*-**1** with W(CO)$_5$THF (eq 2) in the absence of light gives complexes of both of the isomers *meso*- and *d*,*l*-(OC)$_5$W[R(H)Sb−Sb(H)R]W(CO)$_5$ (**3**). The separation

$$\underset{\mathbf{1}}{\mathrm{R(H)Sb{-}Sb(H)R}} + 2\ \mathrm{W(CO)_5THF} \xrightarrow{-2\mathrm{THF}} d,l\text{- and } meso\text{-}\underset{\mathbf{3}}{\mathrm{(OC)_5W[(RH)Sb{-}Sb(H)R]W(CO)_5}} \quad (2)$$

is achieved by selective crystallization of a solution in petroleum ether. When the solution is cooled, first the *d*,*l* isomer of **3** (5% yield) and later the *meso* isomer (15%) precipitates. Other products remained in solution and were not identified. Both isomers of **3** are orange-brown solids, unstable at room temperature in the solid state and in solution. *meso*-**3**, in contrast to *d*,*l*-**3**, is very soluble in organic solvents. The ^{1}H NMR spectra of the complexes **3** contain two singlet signals for the diastereotopic Me$_3$Si groups and singlets for the SbH and for the CH groups instead of the signals of an AA′XX′ spin system as observed for *meso*- and *d*,*l*-**1**. The absence (or the small value) of the $^3J_{\mathrm{HH}}$ coupling constant (<0.65 Hz) is possibly a consequence of the orthogonality of the bonds involved.

Both complexes were characterized by a single-crystal structure analysis. *meso*-**3** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with four molecules in the unit cell and *d*,*l*-**3** in the monoclinic space group $C2/c$ with half a molecule in the asymmetric unit as a 1:1 mixture of the *R*,*R* and *S*,*S* enantiomers. The molecular conformation of *meso*-**3** (Figure 3) is between antiperiplanar (trans) and anticlinal and that of *d*,*l*-**3** (Figure 4) between synclinal and synperiplanar. There are almost ecliptic positions of W(1) and C(2) in *meso*-**3** or the hydrogen atoms and the alkyl groups in *d*,*l*-**3**. The coordination spheres of the antimony atoms of both isomers are considerably distorted from the ideal tetrahedral geometry. The bond angles between the heavier atoms are widened by repulsion between the bulky alkyl groups and the W(CO)$_5$ units.

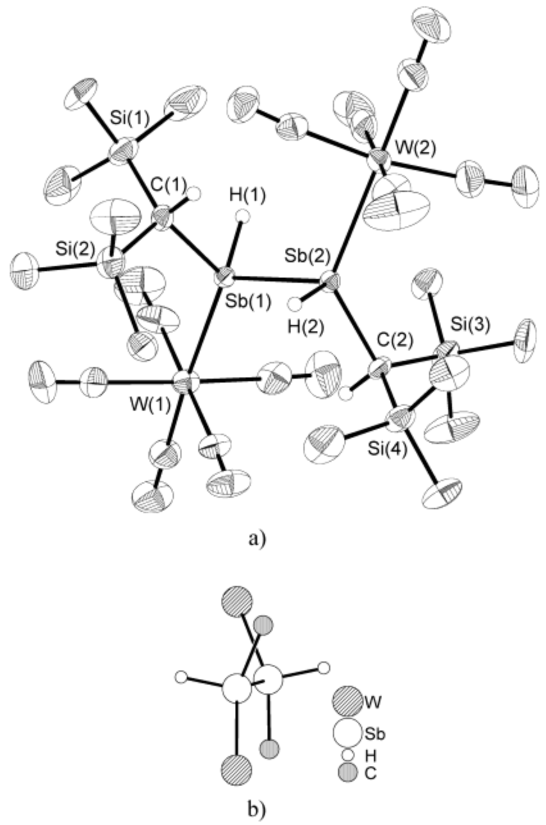
The Sb−Sb (2.833(1) Å in *meso*-**3** and 2.842(1) Å in *d*,*l*-**3**) and Sb−W bond lengths (2.7755(8), 2.792(1) Å in *meso*-**3** and 2.7766(8) Å in *d*,*l*-**3**) lie in the usual range for single bonds between these elements.

The reaction of the primary stibane RSbH$_2$ (**2**) with W(CO)$_5$THF (eq 3) in the dark with cooling gives 87% of R(H)$_2$SbW(CO)$_5$ (**4**; R = (Me$_3$Si)$_2$CH), a colorless crystalline compound which is equally unstable at ambient temperature. A side product of the reaction is

$$\underset{\mathbf{2}}{\mathrm{RSbH_2}} \xrightarrow[-\mathrm{THF}]{+\mathrm{W(CO)_5THF}} \underset{\mathbf{4}}{\mathrm{R(H)_2SbW(CO)_5}} \xrightarrow{-\mathrm{H_2}} \underset{\mathbf{5}}{\mathrm{[RSb{=}SbR]W(CO)_5}} + \underset{\mathbf{6}}{\mathrm{[(CO)_5W]_2SbR}} \quad (3)$$

the blue stibinidene complex [(OC)$_5$W]$_2$SbR (**6**; R = (Me$_3$Si)$_2$CH),[13] which was separated mechanically and identified by ^{1}H NMR, IR, and mass spectrometry.

The stibane complex **4** was identified by the observation of the molecular ions and characteristic fragments in the mass spectrum, by single-crystal X-ray diffraction, and by other methods. The ^{1}H NMR spectrum shows a broad doublet at 2.097 ppm for the SbH$_2$ group with the coupling constant $^3J_{\mathrm{HH}}$ = 3.92 Hz, indicating only weak coupling between the CH and SbH protons. The analogous coupling constant in the free ligand, RSbH$_2$, is 5.86 Hz.[1] Single crystals of R(H)$_2$SbW(CO)$_5$ (**4**; R = (Me$_3$Si)$_2$CH) (monoclinic space group $P2_1/n$ with two independent molecules in the asymmetric unit) are obtained by cooling a solution in petroleum ether. The molecular structure of one of the molecules is shown in Figure 5. It consists of a (Me$_3$Si)$_2$CH−SbH$_2$ unit coordinated to a W(CO)$_5$ fragment. The conformation with respect to the Sb−C bond is synperiplanar. The environment of the antimony atoms is considerably distorted from the ideal tetrahedral geometry. The angles between the bulky alkyl and the W(CO)$_5$ groups (C−Sb−W = 121.0(6), 121.9(5)°) are particularly wide. The Sb−W bond lengths (2.756(2), 2.757(2) Å) and the other geometric parameters are not unusual. The hydrogen atoms directly bonded to antimony could not be located. They were calculated using a riding model.



a)
b)

Figure 3. (a) ORTEP-like drawing of the structure of *meso*-(OC)$_5$W[(Me$_3$Si)$_2$CH(H)Sb−Sb(H)CH(SiMe$_3$)$_2$]W(CO)$_5$ (*meso*-**3**). The thermal ellipsoids are drawn with 30% probability. The hydrogen atoms belonging to the CH$_3$ groups are omitted for clarity. (b) Conformation of *meso*-**3**. Selected bond lengths (Å) and angles (deg): Sb(1)−Sb(2) = 2.8325(14), W(1)−Sb(1) = 2.7918(14), W(2)−Sb(2) = 2.7754(8), Sb(1)−C(1) = 2.155(9), Sb(2)−C(2) = 2.148(9); C(1)−Sb(1)−W(1) = 129.9(3), C(2)−Sb(2)−W(2) = 125.7(3), C(1)−Sb(1)−Sb(2) = 102.1(3), C(2)−Sb(2)−Sb(1) = 97.2(3), W(1)−Sb(1)−Sb(2) = 114.01(4), W(2)−Sb(2)−Sb(1) = 123.33(4), W(1)−Sb(1)−Sb(2)−W(2) = 160.29(4), C(1)−Sb(1)−Sb(2)−C(2) = 157.8(4), H(1)−Sb(1)−Sb(2)−H(2) = 156.29(1), W(2)−Sb(2)−Sb(1)−C(1) = 15.9(3), W(1)−Sb(1)−Sb(2)−C(2) = −57.8(3), W(1)−Sb(1)−Sb(2)−H(2) = 46.50(1), W(2)−Sb(2)−Sb(1)−H(1) = −89.92(1).

Elimination of hydrogen from the distibane or monostibane complexes leads to the corresponding distibene and

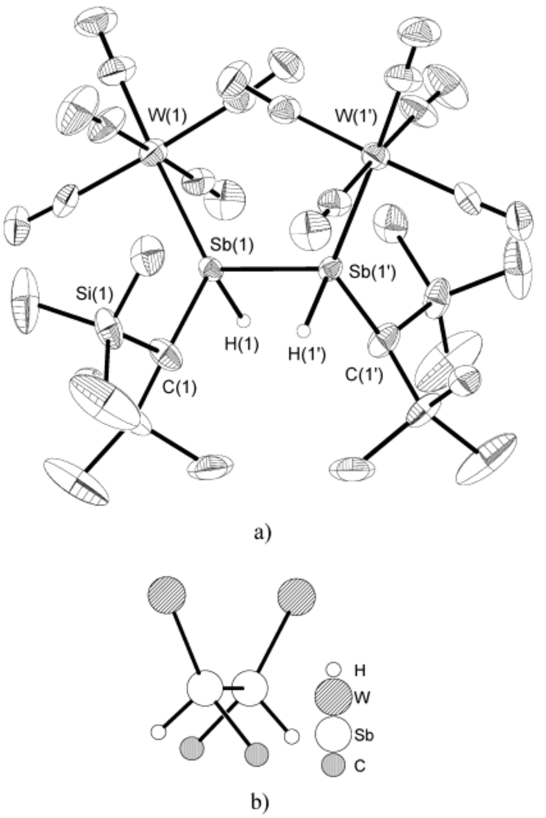


Figure 4. (a) ORTEP-like drawing of the structure of the *S*,*S* enantiomer of d,l-$(OC)_5W[(Me_3Si)_2CH(H)Sb{-}Sb(H)CH(SiMe_3)_2]W(CO)_5$ (d,l-**3**). The hydrogen atoms belonging to the CH_3 and CH groups are omitted for clarity. The thermal ellipsoids are drawn with 30% probability. (b) Conformation of d,l-**3** (*S*,*S* enantiomer). There is a 2-fold rotation axis perpendicular to the Sb−Sb bond. Selected bond lengths (Å) and angles (deg): Sb(1)−Sb(1′) = 2.8417(13), W(1)−Sb(1) = 2.7766(8), Sb(1)−C(1) = 2.158(10); C(1)−Sb(1)−W(1) = 131.6(4), C(1)−Sb(1)−Sb(1′) = 94.1(3), W(1)−Sb(1)−Sb(1′) = 123.724(16), C(1)−Sb(1)−Sb(1′)-C(1′) = 87.69(1), W(1)−Sb(1)−Sb(1′)−W(1′) = 23.74(1), H(1)−Sb(1)−Sb(1′)-C(1′) = −1.03(1), H(1)−Sb(1)−Sb(1′)−H(1′) = 89.74(1), H(1)−Sb(1)−Sb(1′)−W(1′) = 147.0(1).

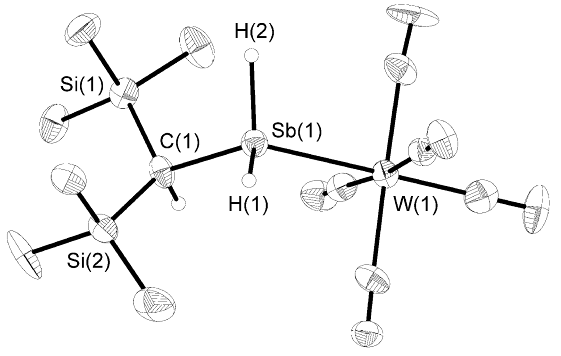


Figure 5. ORTEP-like drawing of the structure of $(Me_3Si)_2CH(H)_2SbW(CO)_5$ (**4**). The thermal ellipsoids are drawn with 30% probability. Selected bond lengths (Å) and angles (deg): Sb(1)−W(1) = 2.7568(17), Sb(2)−W(2) = 2.7564(18), Sb(1)−C(1) = 2.14(2), Sb(2)−C(2) = 2.20(2); C(1)−Sb(1)−W(1) = 121.0(6), C(2)−Sb(2)−W(2) = 121.9(5).

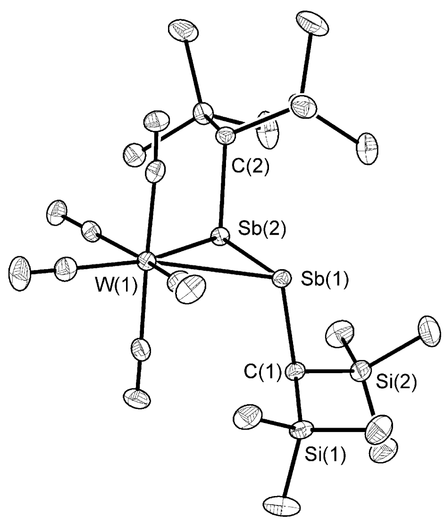
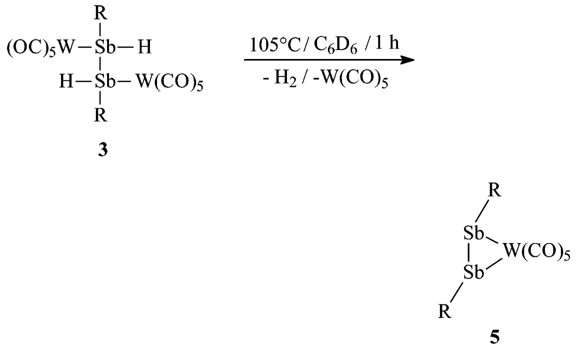


Figure 6. ORTEP-like drawing of the structure of $[(Me_3Si)_2CHSb]_2W(CO)_5$ (**5**). The thermal ellipsoids are drawn with 30% probability. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sb(1)−Sb(2) = 2.7413(9), Sb(1)−W(1) = 2.9912(11), Sb(2)−W(1) = 2.9495(11), Sb(1)−C(1) = 2.226(4), Sb(2)−C(2) = 2.222(3); C(1)−Sb(1)−Sb(2) = 94.41(11), C(2)−Sb(2)−Sb(1) = 109.56(10), C(1)−Sb(1)−W(1) = 106.01(10), C(2)−Sb(2)−W(1) = 103.73(10), C(1)−Sb(1)−Sb(2)−C(2) = −158.25(14).

stibinidene complexes. NMR studies of **3** in C_6D_6 show that at room temperature after several hours isomerization between the *d,l*- and *meso* forms occurs and signals of [*trans*-RSb=SbR]$W(CO)_5$ (**5**; R = $(Me_3Si)_2CH$) emerge. Quantitative transformation of **3** to **5** is achieved at 105 °C in C_6D_6 within 1 h (eq 4).



(4)

For the preparation of **5** on a larger scale it is, however, preferable to react R(H)Sb−Sb(H)R (**1**) directly with $W(CO)_5THF$ in toluene without isolation of the intermediates **3**. The distibene complex **5** is an orange crystalline solid, very soluble in common organic solvents. The ^1H and ^{13}C NMR spectra contain two singlet signals for the diastereotopic Me_3Si groups and a singlet for the methine group. In the ^{13}C NMR spectrum there are only two signals for the different CO groups, possibly due to rotation of the $W(CO)_5$ moiety. In the IR spectra the characteristic signals for a $W(CO)_5$ fragment are observed. Mass spectra of **5** contain the molecular ion at highest mass. Recrystallization from diethyl ether gives single crystals suitable for X-ray structure analyses. **5** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The structure consists of a distibene molecule in the trans configuration, “side on” coordinated to the $W(CO)_5$ fragment (Figure 6). The central part of the distibene ligand is nonplanar (C(1)−Sb(1)−Sb(2)−C(2) = −158.2(2)°) because the alkyl groups are bent away (C(1)−Sb(1)−W(1) = 106.01(10)°, C(2)−Sb(2)−W(1) = 103.73(10)°) from the tungsten atom. The Sb−Sb bond length (2.7413(9) Å) in **5** lies in the normal range for distibene complexes with side-on ($R_2Sb_2Fe(CO)_4$, R = $(Me_3Si)_2CH$, 2.774(1) Å;[10] $R_2Sb_2Pt(PEt_3)_2$, R = ${}^tBuC(O)$, 2.7551(12) Å[27]) or side-on/end-on coordination ($Ph_2Sb_2[W(CO)_5]_3$, 2.706 Å;[12] ${}^tBu_2Sb_2[Cr(CO)_5]_3$, 2.720(3) Å[11]). The Sb−W distances in **5** (Sb(1)−W(1) = 2.991(1) Å; Sb(2)−W(1) = 2.949(1) Å) are longer than the sum of the covalent radii of Sb and W (2.78 Å) or the corresponding values in $Ph_2Sb_2[W(CO)_5]_3$ (Sb−W(side on) = 2.8699 and 2.9050 Å).[12]

Also, the monostibane complex $R(H_2)SbW(CO)_5$ (**4**) reacts with elimination of hydrogen. An NMR tube experiment showed that the stibinidene complex $[(OC)_5W]_2SbR$ (**6**; R = $(Me_3Si)_2CH$) and the distibene complex **5** form. After 14 h at 105 °C in C_6D_6 a mixture of **4**−**6** in a 1:2.4:2.4 molar ratio is obtained.

The substitution of hydrogen by methyl groups in R(H)Sb−Sb(H)R (**1**) is achieved by reaction with MeI (1:2 molar ratio) and DBU in diethyl ether giving R(Me)Sb−Sb(Me)R [R = $(Me_3Si)_2CH$] (**7**) in 68% yield after chromatography as a 1:1.4 mixture of the *meso*- and *d,l*-isomers (eq 5). **7** is a yellow, air-sensitive liquid,

$$\underset{\mathbf{1}}{\mathrm{R(H)Sb\text{-}Sb(H)R}} + 2\mathrm{MeI} + 2\mathrm{DBU} \rightarrow \underset{\mathbf{7}}{\mathrm{R(Me)Sb{-}Sb(Me)R}} + 2\mathrm{DBU{\cdot}HI} \quad (5)$$

thermally stable up to 110 °C and very well soluble in organic solvents. The ^1H NMR spectrum in C_6D_6 contains two singlet signals for the diastereotopic Me_3Si groups: one singlet signal for the MeSb groups and one singlet signal for the CH protons of each isomer. Equilibria analogous to eq 1 are not observed. The identity of **7** was also proven by elemental analyses and by the observation of the molecular ion and characteristic fragments in the mass spectrum. A probable mechanism for the formation of **7** involves addition of MeI to **1** with formation of distibonium iodides and deprotonation of $[R(H)Sb-Sb(H)(R)Me]^+$ or $[Me(R)(H)Sb-Sb(R)Me]^+$ by DBU.

Also $RSbH_2$ (**2**) reacts with MeI/DBU with substitution of hydrogen by methyl groups. When the reagents are used in a 1:1:1 molar ratio, the remarkable secondary stibane R(Me)SbH (**8**) is formed in 82% yield as a racemic mixture (eq 6). **8** is a colorless air-sensitive

$$\underset{\mathbf{2}}{\mathrm{RSbH_2}} + \mathrm{MeI} + \mathrm{DBU} \rightarrow \underset{\mathbf{8}}{\mathrm{R(Me)SbH}} + \mathrm{DBU{\cdot}HI} \quad (6)$$

liquid, which is stable upon exposition to UV light or to temperatures up to 100 °C under an inert atmosphere. The ^1H NMR spectrum in C_6D_6 (Figure 7) at room temperature shows two singlet signals for the diastereotopic Me_3Si groups, doublets for the CH and MeSb groups, and a quartet of doublets for the SbH groups. This pattern of signals proves the stability of **8** toward the inversion of configuration. The inspection of the coupling constants reveals that coupling between the SbH and the $SbCH_3$ group ($^3J_{HH}$ = 5.98 Hz) is stronger than between the SbH and the CH group of the $(Me_3Si)_2CH(R)$ substituent ($^3J_{HH}$ = 2.22 Hz). Preferences for a conformer with the dihedral angle $H-CR_2-Sb-H$ and/or H−Sb−C bond angles close to 90° are possibly responsible for the weaker coupling. The ν(SbH) vibration appears in the IR spectrum as a strong absorption at 1846 cm^{-1}.

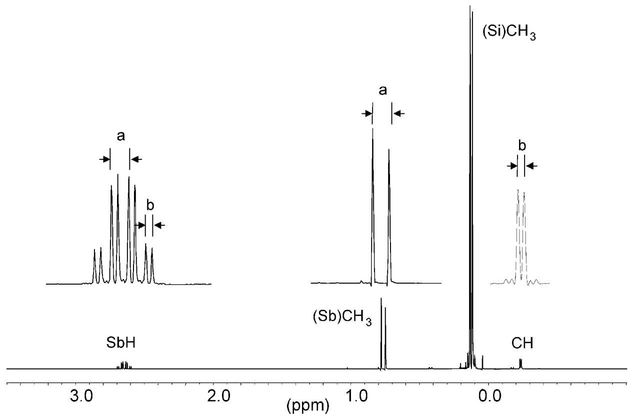


Figure 7. ^1H NMR (200 MHz) spectra of $(Me_3Si)_2CH(Me)SbH$ (**8**) in C_6D_6 at room temperature: (a) coupling between the CH_3 and SbH protons (5.98 Hz); (b) coupling between the CH and SbH protons (2.22 Hz).

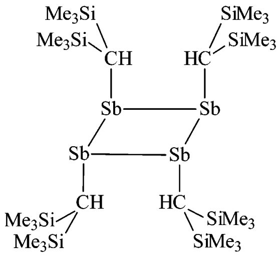


Figure 8. Structure of *cis,trans*-$[(Me_3Si)_2CH]_4Sb_4$ (*cis,trans*-**11**).

The analogous deuterium compound R(Me)SbD (*deuterio*-**8**) was obtained in 82% yield by reaction of $RSbD_2$ and MeI/DBU. The characterization was achieved spectroscopically (^1H, ^2H, ^{13}C NMR; IR, MS). The value for the ν(SbD) vibration (1326 cm^{-1}) compares well with ν(SbD) in $RSbD_2$ (1335 cm^{-1}) and R(D)Sb−Sb(D)R (1329 cm^{-1}) (R = $(Me_3Si)_2CH$).

The distibane **1** is also useful for the synthesis of antimony homocycles. Controlled removal of hydrogen is achieved when $LiAlH_4$ is added to a solution of **1** in diethyl ether at room temperature. After separation of the products by chromatography and crystallization, the known tristibirane R_3Sb_3 (**10**; 72%) and a novel ring, the *cis,trans* isomer of cyclo-R_4Sb_4 (**11**; 8.3%), are obtained. *cis,trans*-**11**, like the known *all-trans* isomer, is an air-sensitive orange solid, soluble in organic solvents. Dissolution is remarkably slower for the *cis,trans* form than for the *all-trans* isomer, and the melting points are different (130−133 °C[24] for *all-trans*-**11** and 143 °C for *cis,trans*-**11**). The identity of *cis,trans*-**11** was proven by the mass spectrum, where the molecular ions are observed as base peaks, and by the ^1H NMR spectrum, showing two singlet signals for the diastereotopic Me_3Si groups and one singlet signal for the CH protons (Figure 8). Solutions of *cis,trans*-**11** are photosensitive. In a first step ($\tau_{1/2} \approx 2$ h in sunlight in C_6D_6) the irreversible isomerization to *all-trans*-**11**[24] takes

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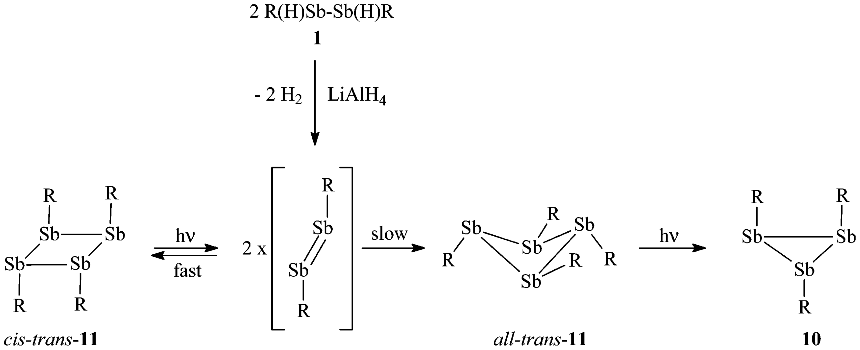
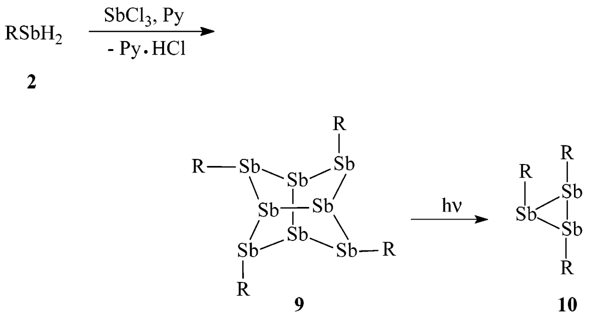
(27) Black, S. J.; Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Steed, J. W. *Chem. Commun.* **1998**, 219.

Scheme 1



place. A subsequent slow photochemical reaction gives the tristibirane **10**.[23] These transformations can easily be monitored by ^{1}H NMR spectroscopy. The mechanisms for the formation and the photochemical isomerization of *cis,trans*-**11** are not known. In Scheme 1 we propose *trans*-RSb═SbR as an intermediate, because this distibene was trapped in the complex **5** and by analogy with the formation of *cis,trans*-[$Me_3SiCH_2P]_4[Cr(CO)_5]_2$[6] from a diphosphene complex precursor. Alternative mechanisms considering *cis*-distibene, stibinidene, or radical intermediates or atomic inversion at antimony should require higher activation energies. Crystals of *cis,trans*-**11** were obtained from tetrahydrofuran. They were analyzed by X-ray diffraction, but a strong disorder hindered a satisfying refinement of the data. Only the essential features of the molecular structure, a Sb_4 square and two pairs of organic groups in cis positions above and below the plane of the antimony atoms, were determined. These data confirm the results of the structure analysis by NMR and MS. The planarity of the cyclo-Sb_4 unit is not unexpected, because *cis,trans*-$(Me_3SiCH_2P)_4[Cr(CO)_5]_2$ also contains a planar pnicogen ring.[6]

Searching for a viable access to polycyclic stibanes, we investigated the reaction of **2** with $SbCl_3$ in the presence of pyridine and found that the known polycycle R_4Sb_8 (**9**)[19] is formed in 32% yield together with unidentified black products (eq 7). Crystallization of **9** from THF leads to deep orange crystal cubes of the solvate **9**·*n*THF ($n \leq 2$). The solvent molecules can easily diffuse from the crystal, leaving variable THF concentrations. Determinations by NMR, elemental analyses, or X-ray diffraction gave $n = 0.7$, 1.3, 2. Unsolvated **9** crystallizes in the triclinic crystal system with one R_4Sb_8 molecule in the asymmetric unit.[19] Crystals of **9**·2THF belong to the tetragonal system in the *P*4/*nnc* space group, where due to the high symmetry only a RSb−Sb fragment is in the asymmetric unit. The structures of the R_4Sb_8 molecules in **9**[19] and in the solvate are nevertheless similar (Sb−Sb = 2.7980(4)-2.8592(5) Å in **9**·2THF and 2.784(4)−2.852(4) Å in unsolvated **9**[19]), but the arrangements in the crystal differ considerably. In **9**·2THF there are stacks with alternating positions of the R_4Sb_8 units in an ABAB type arrangement. Disordered solvent molecules fill holes between the stacks. A view of the crystal structure of **9**·2THF is shown in Figure 9. The molecular structure of unsolvated **9** is depicted in Figure 1 in ref 19.



(7)

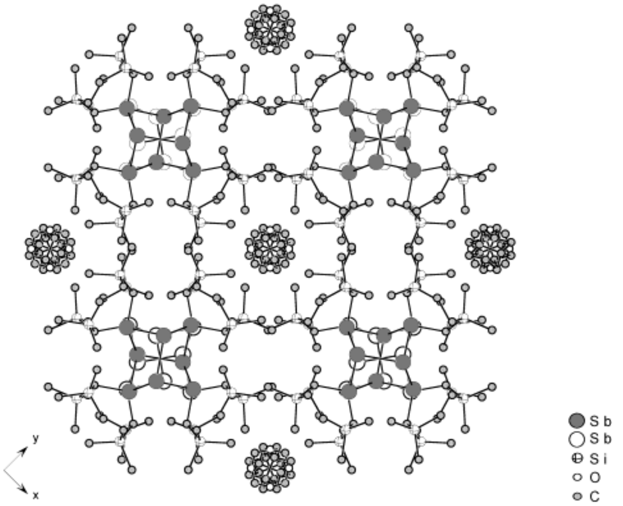


Figure 9. Arrangement of $[(Me_3Si)_2CH]_4Sb_8{\cdot}2THF$ (**9**·2THF) in the crystal. The view along the *z* axis. The hydrogen atoms are omitted.

The properties of **9** in solution were not studied before. The polycycle is an air- and light-sensitive compound, soluble in benzene, petroleum ether, and other organic solvents. The color of the solutions is orange. The ^{1}H NMR spectra contain two singlet signals for the diastereotopic Me_3Si groups and one singlet signal for the CH groups. The same pattern was observed in the ^{13}C NMR spectra. Exposure to light leads to photochemical ring contraction with formation of the tristibirane **10** (eq 7). The solution becomes dark brown, but no precipitation of elemental antimony or of polymeric organoantimony species is visible. The kinetics of the photochemical reaction were studied in solution in C_6D_6 in a NMR tube in the light of a halogen lamp with an intensity of 16 mW/cm^{-2}. The degradation of **9** follows first-order kinetics ($\tau_{1/2} = 2$ h), as expected for the photochemical reaction being the slowest step.

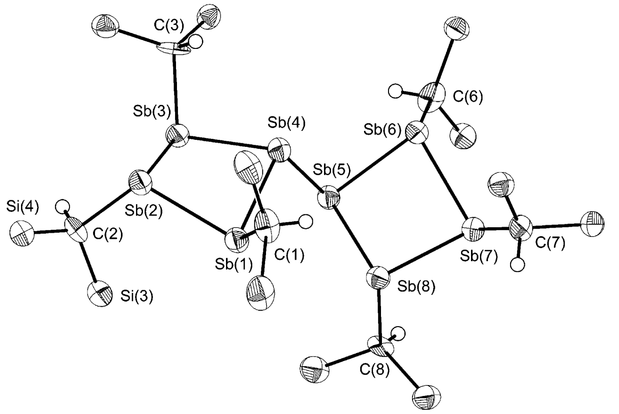
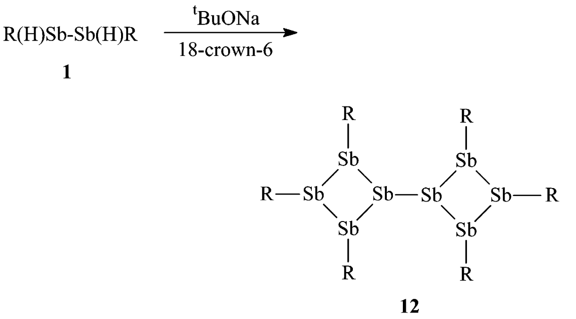


Figure 10. ORTEP-like drawing of the structure of $[(Me_3Si)_2CH]_6Sb_8$ (**12**). The thermal ellipsoids are drawn with 30% probability. The CH_3 groups are omitted. Selected bond lengths (Å) and angles (deg): Sb(1)−Sb(2) = 2.855(3), Sb(1)−Sb(4) = 2.823(3), Sb(2)−Sb(3) = 2.851(3), Sb(3)−Sb(4) = 2.844(3), Sb(4)−Sb(5) = 2.837(3), Sb(5)−Sb(6) = 2.845(3), Sb(5)−Sb(8) = 2.873(3), Sb(6)−Sb(7) = 2.861(3), Sb(7)−Sb(8) = 2.862(3), Sb−C = 2.21(3)−2.28(3); Sb(4)−Sb(1)−Sb(2) = 85.15(8), Sb(3)−Sb(2)−Sb(1) = 85.48(8), Sb(4)−Sb(3)−Sb(2) = 84.84(8), Sb(1)−Sb(4)−Sb(5) = 99.81(9), Sb(1)−Sb(4)−Sb(3) = 86.21(8), Sb(5)−Sb(4)−Sb(3) = 98.49(9), Sb(4)−Sb(5)−Sb(6) = 86.88(8), Sb(4)−Sb(5)−Sb(8) = 94.01(8), Sb(6)−Sb(5)−Sb(8) = 87.76(8), Sb(5)−Sb(6)−Sb(7) = 83.98(8), Sb(6)−Sb(7)−Sb(8) = 87.65(7), Sb(7)−Sb(8)−Sb(5) = 83.45(8), Sb−Sb−C = 95.8(11)−109.7(9).

The novel bicycle R_6Sb_8 (**12**; R = $(Me_3Si)_2CH$) and R_3Sb_3 (**10**) were formed in low yield in an attempt to metalate **1** with ^tBuONa in the presence of 18-crown-6 (eq 8). **12** is an orange solid that is very soluble in organic solvents. Solutions of **12** are photosensitive as well. Decomposition in sunlight gives R_3Sb_3 (**10**) and brown soluble species. The ^1H NMR spectra of **12** in C_6D_6 at room temperature show two singlet signals in 1:2 intensity ratio for both the methyl and methine groups because the Me_3Si groups of the substituents on the four chiral Sb centers adjacent to the central Sb_2 unit are accidentally isochronic. In the ^{13}C NMR spectra, however, the expected three singlet signals for the Me_3Si groups and two singlet signals for the CH groups are observed. Mass spectra obtained with the chemical ionization technique (CI negative) at highest mass contain the fragment $M^-/2$. Single crystals were grown from toluene at −28 °C. **12** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. In the structure of **12** there are two folded Sb_4 rings, in the *all-trans* configuration, connected through an Sb−Sb bond to give 2,2′,3,3′,4,4′-hexakis[bis(trimethylsilyl)methyl]-1,1′-bicyclotetrastibane (Figure 10). Similar arrangements were observed in the structures of $^tBu_6P_8$[20] and $^tBu_6As_8$.[21]



(8)

In contrast to the phosphorus or arsenic analogues in **12** the R_3Sb_4 units are asymmetric with respect to each other. The conformation along the Sb(4)−Sb(5) bond is between anticlinal and antiperiplanar (trans) with dihedral angles lp−Sb(4)−Sb(5)−lp = 135.19(1)° (lp = assumed direction of the lone pairs of electrons at the Sb atoms). The deviation from the ideal trans conformation results probably from effects related to the packing of the bis(trimethylsilyl)methyl substituents. The Sb_4 cycles in **12** are less folded (fold angles 134.5−136.9°) than in *all-trans*-**11** (fold angles 115.27 and 115.48°).[24] The transannular Sb−Sb distances lie between 3.82 and 3.96 Å. The bond lengths (Sb−Sb = 2.823(3)−2.873(3) Å, Sb−C = 2.21(3)−2.28(3) Å) and angles (Sb−Sb−Sb = 83.45(8)−99.81(9)°; Sb−Sb−C = 95.8(11)−109.7(9)°) compare well with those found in *all-trans*-**11** (Sb−Sb = 2.822(1)-2.878(1) Å, Sb−C = 2.226(4)−2.232(4) Å, Sb−Sb−Sb = 80.14(2)−80.75(1)°, Sb−Sb−C = 96.7(1)−110.6(1)°).[24]

Experimental Section

General Comments. The reactions and manipulations of the compounds were performed under an atmosphere of dry argon. All solvents were dried and freshly distilled prior to use. **1** and **2** were prepared as described.[1] The following spectrometers were used: MS, Finnigan MAT 8200, Finnigan MAT-8222; NMR, Bruker DPX 200; IR, Perkin-Elmer, FT-IR SPEKTRUM 1000. For the synthesis of $W(CO)_5THF$ a TQ 150 mercury lamp from the company Hanau was used. The intensity of the light in the photochemical reaction of **9** was measured with a bolometer from Kipp & Son. Elemental analyses were performed at Mikroanalytisches Labor Beller, Göttingen, Germany.

Neutron Diffraction Study of *meso*-1. For the neutron experiment at ILL (Institut Laue-Lagevin) a single crystal of small mosaic spread, a plate of 5 × 3.4 × 1 mm^3 and volume 17 mm^3 was selected and wedged between quartz wool wads in a special quartz capillary. This tube was fixed with an O-ring seal to an Al base, the ensemble being especially designed for direct mounting on the Displex cryorefrigerator[28] on the thermal-beam instrument D19 at ILL equipped with a 4° × 64° position-sensitive detector[29] and also with a new square 2-D detector[30] based on the microstrip principle.[31] During the experiment both detectors were used when possible geometrically, and overlapping reflections were measured to provide empirical scaling between the two detectors. Agreement was good. The wavelength was 1.3213(1) Å from a Ge (115) monochromator. The crystal was cooled at 3 K/min to 20 K while monitoring a strong reflection. Reflections were measured to preset monitor counts in equatorial or normal-beam geometry,[32] the time per step in ω being between 5 and 8 s. Most of the unique reflections up to 2θ of approximately 90° were recorded, and some further reflections were measured to 118°. Two standard reflections were measured regularly on the low-angle detector and one on the square high-angle detector when normal-beam geometry was used. The unit cell dimensions were calculated as 6.4844(4), 8.1082(5), and 12.457-

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(32) ILL programs: Hklgen and Mad.

Table 1. Crystallographic Data for *meso*-1, 3, 4, 5, 9·2THF, 12 and Structure Determination Details

	meso-**1**	*meso*-**3**	*d,l*-**3**	**4**	**5**	**9**·2THF	**12**
formula	$C_{14}H_{40}Sb_2Si_4$	$C_{24}H_{40}O_{10}Sb_2Si_4W_2$	$C_{24}H_{40}O_{10}Sb_2Si_4W_2$	$C_{12}H_{21}O_5SbSi_2W$	$C_{19}H_{38}O_5Sb_2Si_4W$	$C_{28}H_{76}O_2Sb_8Si_8$	$C_{42}H_{114}Sb_8Si_{12}$
fw	563.50	1212.12	1212.12	607.05	886.20	1682.0	1930.45
color	yellow	deep red	brown	colorless	orange	orange	orange
temp (K)	20	173	173	173	173	173	173
cryst size (mm)	5.0 × 3.4 × 1.0	0.5 × 0.2 × 0.1	0.6 × 0.4 × 0.3	0.4 × 0.15 × 0.1	0.4 × 0.3 × 0.2	0.5 × 0.4 × 0.3	0.4 × 0.3 × 0.1
wavelength (Å)	1.321 30 (Ge(115))	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
cryst syst	triclinic	triclinic	monoclinic	monoclinic	triclinic	tetragonal	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$	$P2_1/n$	$P\bar{1}$ (No. 2)	$P4/nnc$	$P2_1/c$
a (Å)	6.4844(10)	9.0740(10)	23.062(3)	6.4770(10)	9.220(2)	18.894(3)	14.666(3)
b (Å)	8.1082(10)	13.8670(10)	10.8560(10)	34.913(7)	11.608(2)	18.894(3)	38.741(8)
c (Å)	12.457(2)	16.301(2)	16.787(2)	18.514(4)	16.215(3)	17.399(4)	13.993(3)
α (deg)	103.315(10)	85.970(10)	90	90	78.92(3)	90.0	90.0
β (deg)	92.221(10)	86.240(10)	107.040(10)	98.97(3)	73.93(3)	90.0	90.37(3)
γ (deg)	102.808(10)	81.510(10)	90	90	83.37(3)	90.0	90.0
Z	1	4	4	8	2	4	4
V (Å^3)	618.71(16)	2020.5(4)	4018.3(8)	4135.4(14)	1633.0(5)	6211(2)	7950(3)
d_{calcd} (g cm^{-3})	1.315	1.992	2.004	1.950	1.802	1.758	1.613
μ (mm^{-1})	2.95	7.157	7.198	6.994	5.326	3.598	2.88
F(000)	−29	1140	2280	2288	848	3120	3768
θ range (deg)	3.14−65.75	2.51−27.51	2.54−27.50	2.30−25.00	2.82−25.87	2.68−25.89	2.52−22.5
index ranges	$-4 \leq h \leq +8$, $-10 \leq k \leq +9$, $-16 \leq l \leq +16$	$-1 \leq h \leq +11$, $-17 \leq k \leq +17$, $-21 \leq l \leq +21$	$-1 \leq h \leq +29$, $-14 \leq k \leq +4$, $-21 \leq l \leq +20$	$-7 \leq h \leq +7$, $-41 \leq k \leq +41$, $-22 \leq l \leq +22$	$-11 \leq h \leq +11$, $-14 \leq k \leq +14$, $-19 \leq l \leq +19$	$-23 \leq h \leq +23$, $-23 \leq k \leq +23$, $-21 \leq l \leq +21$	$-15 \leq h \leq +15$, $-41 \leq k \leq +41$, $-14 \leq l \leq +14$
no. of measd data	6214	11 087	5506	33 309	22 844	81 886	21 256
no. of unique data (R(int))	4802 (0.0404)	9195 (0.0379)	4564 (0.0264)	6541 (0.1919)	5829 (0.0413)	3015 (0.0714)	8265 (0.1880)
no. of data/ restraints/ params	4802/0/842	9195/0/415	4564/0/207	6541/0/393	5828/0/294	3015/0/127	8265/0/596
abs cor	empirical	empirical	empirical	empirical	empirical	empirical	empirical
R1 ($I > 2\sigma(I)$)	0.0354	0.0558	0.0509	0.0847	0.0211	0.0198	0.0907
wR2 ($I > 2\sigma(I)$)	0.064	0.1185	0.1117	0.2001	0.0480	0.0514	0.1858
R1 (all data)	0.0393	0.0942	0.0739	0.1284	0.0278	0.0303	0.1686
wR2 (all data)	0.0735	0.1354	0.1232	0.2310	0.0492	0.0541	0.2223
goodness of fit on F^2	1.139	1.021	1.043	0.990	0.981	0.904	0.925
resid density (e Å^{-3})	+0.444; −0.422	+1.963; −2.586	+1.665; −2.794	+1.254; −1.295	+0.938; −1.044	+0.399; −0.241	+1.003; −0.793

(1) Å and 103.315(3), 92.221(4), and 102.808(4)° from the centroids in 3 dimensions of 804 strong reflections,[33] the minimum and maximum 2θ used being 6.2 and 74.1°. Bragg intensities were integrated in 3-D using the ILL program Retreat.[34] The intensities were corrected for attenuation by the crystal (calculated 2.95 cm^{-1}, e.g. minimum and maximum transmission coefficients 0.38 and 0.76 for data recorded on the curved detector) with the program D19abs, based on the ILL version of the CCSL system;[35] the crystal was described by 6 faces. 6214 reflections were recorded, yielding 4802 unique reflections: R(int)= 0.0399, and $R(\sigma) = 0.0279$. Preliminary refinement with SHELXL from SHELX-97[36] gave R1 = 0.0355 (wR2 = 0.064) with about 800 parameters. The coherent scattering amplitudes were those tabulated by Sears.[37]

X-ray Crystallography. The positions of the hydrogen atoms directly bound to the antimony atoms in **3** and **4** were calculated with a riding model, assuming a tetrahedral environment of the antimony atoms. The Sb−H bond lengths were fixed at 1.7 Å. The thermal vibration of the hydrogen atoms on Sb was fixed as 1.2 times the thermal motion of the antimony atom.

In *meso*-**3** the antimony atoms and one tungsten atom were located in two different positions with 90% and 10% occupancy. In *d,l*-**3** an electron density at 0.965 Å from antimony was interpreted as 5% disorder of antimony. For other atoms no disorder was observed. In **12** the 118 most disagreeable reflections were extracted from the refinement.

Table 1 contains a summary of the structural analyses reported in this paper. Data for **3** were collected on a Siemens P4 four-circle diffractometer. For **4**, **5**, **9**·2THF, **11**, and **12** the data were collected using a STOE IPDS diffractometer. In both cases a graphite monochromator with the wavelength (Mo Kα) 0.710 73 Å was used. The crystals were attached with Kel-F oil to a glass fiber and cooled under a nitrogen stream at 173 K. The structures were solved by direct methods (full-matrix least squares on F^2). All non-hydrogen atoms were refined with anisotropic thermal parameters. For structure solving and refinement the software package SHELX-97 was used.[36] The drawings were created by the Diamond program by Crystal Impact GbR.[38]

Synthesis of *meso*- and *d,l*-(OC)$_5$W[R(H)Sb−Sb(H)R]W(CO)$_5$ (3; R = (Me$_3$Si)$_2$CH). A 0.34 g (0.97 mmol) portion of W(CO)$_6$ was dissolved in 120 mL of THF and irradiated for 2 h with UV light. The resulting yellow solution of W(CO)$_5$THF was added to 0.52 g (0.92 mmol) of **1** in 30 mL of THF and the mixture stirred for 12 h at room temperature. The solvent was removed, and the resulting residue was extracted with petro-

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(33) ILL program: Rafd19.

(34) Wilkinson, C.; Khamis, H. W.; Stansfield, R. F. D.; McIntyre, G. J. *J. Appl. Crystallogr.* **1988**, *21*, 471.

(35) Matthewman, J. C.; Thompson, P.; Brown, P. J. *J. Appl. Crystallogr.* **1982**, *15*, 167.

(36) Sheldrik, G. M. SHELX-97; Universität Göttingen, Göttingen, Germany, 1997.

(37) Sears, V. F. *Neutron News* **1992**, *3*, 26.

(38) Brandenburg, K. DIAMOND, Version 2.1c; Crystal Impact GbR, 1999.

leum ether. Subsequent crystallization after the solution was concentrated at −28 °C gave 0.03 g (4.8%) of *d,l*-**3** (brown-orange crystals, mp 126−128 °C) and 0.09 g (14.9%) of *meso*-**3** (brown-orange needles, mp 122−123 °C dec). The amount of *d,l*-**3** was not sufficient for elemental analyses. *meso*-**3** decomposed by the time it was received by the analytical laboratory. *d,l*-**3**: ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS) δ 0.095 (s, $^2J_{SiH}$ = 6.40 Hz, $^1J_{CH}$ = 120.0 Hz, 9H; CH_3), 0.186 (s, $^2J_{SiH}$ = 6.38 Hz, $^1J_{CH}$ = 120.0 Hz, 9H; CH_3), 1.423 (s, $^2J_{SiH}$ = 7.32 Hz, 1H; CH), 3.935 (s, 1H; SbH); ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS) δ 1.59 (s; CH_3), 2.39 (s; CH_3), 196.95 (s; CO); IR (petroleum ether) ν 1943, 2078 cm^{-1} (CO). *meso*-**3**: ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS) δ 0.137 (s, $^2J_{SiH}$ = 6.56 Hz, $^1J_{CH}$ = 120.2 Hz, 9H; CH_3), 0.210 (s, $^2J_{SiH}$ = 6.08 Hz, $^1J_{CH}$ = 119.38 Hz, 9H; CH_3), 1.502 (s, $^2J_{SiH}$ = 7.72 Hz, 1H; CH), 3.576 (s, 1H; SbH); ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS) δ 1.39 (s; CH_3), 2.57 (s; CH_3), 197.17 (s; CO); IR (petroleum ether) ν 1952, 1983, 2068 cm^{-1} (CO).

Synthesis of $R(H)_2SbW(CO)_5$ (4) and $[(OC)_5W]_2SbR$ (6) (R = $(Me_3Si)_2CH$). A solution of $W(CO)_5THF$ prepared by irradiation of 1.30 g (3.71 mmol) of $W(CO)_6$ in 120 mL of THF was added to 0.95 g (3.37 mmol) of $(Me_3Si)_2CHSbH_2$ (**2**) in 30 mL of THF and stirred for 12 h at room temperature. The solvent was removed, and the resulting blue residue was extracted with 50 mL of petroleum ether and concentrated to ca. 10 mL. After 2 weeks at −28 °C, 1.86 g (91%) of small colorless crystals of **4** (mp 40−42 °C) and a blue precipitate of **6** are formed. **4** decomposed by the time it was received by the analytical laboratory. **4**: ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS) δ −0.05 (s, $^2J_{SiH}$ = 6.46 Hz, $^1J_{CH}$ = 119.24 Hz, 18H; CH_3), 0.23 (t, $^3J_{HH}$ = 3.92 Hz, 1H; CH), 2.09 (d, $^3J_{HH}$ = 3.92 Hz, 2H; SbH_2); ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS) δ 0.86 (s, $^1J_{SiC}$ = 52.67 Hz; CH_3), 0.45 (s; CH), 196.61 (s; *cis*-CO), 198.37 (s; *trans*-CO); IR (petroleum ether) ν 1950, 2074 cm^{-1} (CO); MS (EI, 70 eV) *m*/*z* (relative intensity, %) 608 (20) [M$^+$], 578 (22) [M$^+$ − CO − 2H], 563 (5) [M$^+$ − CO − 2H − Me], 550 (10) [M$^+$ − 2CO − 2H], 535 (4) [M$^+$ − 2CO − 2H − Me], 522 (18) [M$^+$ − 3CO − 2H], 507 (8) [M$^+$ − 3CO − 2H − Me], 494 (45) [M$^+$ − 4CO − 2H], 478 (15) [M$^+$ − 4CO − 2H, − Me], 466 (4) [M$^+$ − 5CO − 2H], 450 (40) [M$^+$ − 5CO − 2H − Me], 433(20) [M$^+$ − 5CO − 2H − 2Me], 418 (18) [M$^+$ − 5CO − 2H − 3Me], 403 (5) [M$^+$ − 5CO − 2H − 4Me], 280 (30) [RSb$^+$], 73 (100) [Me$_3$Si$^+$]; HR MS [M$^+$] calcd 603.944 82, found 603.946 77 (*R* = 10 000). **6**: ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS) δ 0.14 (s, 18H; CH_3); IR (petroleum ether) ν 1950, 2048 cm^{-1} (CO); lit.[13] IR (CH_2Cl_2) ν 1965, 2045 cm^{-1} (CO); MS (EI, 70 eV) *m*/*z* (relative intensity, %): 928 (20) [M$^+$], 885 (10) [M$^+$ − CO − Me], 788 (5) [M$^+$ − 5CO], 769 (50) [M$^+$ − R], 760 (15) [M$^+$ − 6CO], 741 (12) [M$^+$ − R − CO], 732 (5) [M$^+$ − 7CO], 713 (45) [M$^+$ − R − 2CO]; lit.[13] EI-MS 745 [M$^+$ − 6CO − Me].

Synthesis of [RSb=SbR]W(CO)$_5$ (5; R = $(Me_3Si)_2CH$). (a) A solution of $W(CO)_5THF$ obtained from 1.47 g (4.18 mmol) of $W(CO)_6$ in 120 mL of THF was added to 1.07 g (1.90 mmol) of **1** in THF. The reaction mixture was stirred for 16 h. The solvent was removed in vacuo and the residue extracted with toluene. The resulting solution was stirred with reflux for 1.5 h. After filtration and column chromatography on Al_2O_3 (2.2 × 14 cm) a broad yellow fraction was eluted with petroleum ether. Cooling at −28 °C gave 0.33 g (14.6%) of orange-red crystals of **5** (mp 99 °C). Anal. Calcd for $C_{19}H_{38}O_5Sb_2Si_4W$: C, 25.75; H, 4.32. Found: C, 26.04; H, 4.49. ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 0.22 (s, $^2J_{SiH}$ = 6.2 Hz, $^1J_{CH}$ = 118.6 Hz, 9H; CH_3), 0.30 (s, $^2J_{SiH}$ = 6.2 Hz, $^1J_{CH}$ = 118.9 Hz, 9H; CH_3), 1.00 (s, $^2J_{SiH}$ = 8.1 Hz, $^1J_{CH}$ = 115.5 Hz, 1H; CH). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ 2.43 (s, $^1J_{SiC}$ = 57.1 Hz; CH), 3.01 (s, $^1J_{SiC}$ = 50.9 Hz; CH_3), 4.03 (s, $^1J_{SiC}$ = 50.8 Hz; CH_3), 196.94 (s, $^1J_{WC}$ = 118.7 Hz; *cis*-CO), 201.85 (s; *trans*-CO). IR (Nujol): ν 1962, 1976, 2066 cm^{-1} (CO). MS (EI, 70 eV) *m*/*z* (relative intensity, %) 885 (65) [M$^+$ − H], 871 (5) [M$^+$ − Me], 856 (5) [M$^+$ − 2Me], 841 (10) [M$^+$ − 3Me], 699 (25) [M$^+$ − R − CO], 671 (12) [M$^+$ − R − 2CO], 643 (15) [M$^+$ − R − 3CO], 615 (20) [M$^+$ − R − 4CO], 587 (15) [M$^+$ − R − 5CO], 73 (100) [Me$_3$Si$^+$].

(b) Ca. 30 mg of *d,l*-**3** was dissolved in C_6D_6 in an NMR tube. The tube was sealed under argon and heated at 105 °C for 1 h. **5** formed in quantitative yield.

Synthesis of *meso*- and *d,l*-R(Me)Sb−Sb(Me)R (7; R = $(Me_3Si)_2CH$). Dropwise addition of 0.42 g (2.95 mmol) of MeI in 30 mL of Et_2O and 0.45 g (2.9 mmol) of DBU to a solution of 0.69 g (1.23 mmol) of **1** in 30 mL of Et_2O gave a white solid of DBU·HI. After stirring and filtration of the mixture the solvent was removed in vacuo and the remaining yellow oil subjected to column chromatography (Al_2O_3, 15 × 2.2 cm). With petroleum ether a yellowish fraction was eluted. After the removal of the solvent 0.50 g (68.5%) of **7** was obtained as a yellow oil. Anal. Calcd for $C_{16}H_{44}Sb_2Si_4$: C, 32.44; H, 7.49. Found C, 32.33; H, 7.43. ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 0.12 (s, $^2J_{SiH}$ = 7.6 Hz, 1H; CH *d,l*), 0.14 (s, $^2J_{SiH}$ = 7.6 Hz, 1H; CH *meso*), 0.18 (s, $^2J_{SiH}$ = 6.06 Hz, $^1J_{CH}$ = 118.4 Hz, 9H; $SiCH_3$ *d,l*), 0.19 (s, $^2J_{SiH}$ = 6.5 Hz, $^1J_{CH}$ = 118.4 Hz, 9H; $SiCH_3$ *meso*), 0.22 (s, $^2J_{SiH}$ = 6.28 Hz, $^1J_{CH}$ = 118.64 Hz, 9H; $SiCH_3$ *d,l*), 0.24 (s, $^2J_{SiH}$ = 6.28 Hz, $^1J_{CH}$ = 118.64 Hz, 9H; $SiCH_3$ *meso*), 1.07 (s, 3H; $SbCH_3$ *meso*), 1.19 (s, 3H; $SbCH_3$ *d,l*). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ −8.38 (s; $SbCH_3$ *meso*), −8.29 (s; $SbCH_3$ *d,l*), −2.95 (s, $^1J_{SiC}$ = 40.89 Hz; CH *d,l*), −2.66 (s, $^1J_{SiC}$ = 40.9 Hz; CH *meso*), 3.02 (s, $^1J_{SiC}$ = 50.87 Hz; $SiCH_3$ *d,l*), 3.06 (s, $^1J_{SiC}$ = 50.87 Hz; $SiCH_3$ *meso*), 3.52 (s, $^1J_{SiC}$ = 49.87 Hz; $SiCH_3$ *meso*), 3.76 (s, $^1J_{SiC}$ = 49.88 Hz; $SiCH_3$ *d,l*). MS (EI, 70 eV) *m*/*z* (relative intensity, %) 592 (15) [M$^+$], 577 (10) [M$^+$ − Me], 295 (60) [(Me$_3$Si)$_2$CH(Me)Sb$^+$], 207 (20) [Me$_3$SiCHSb$^+$], 73 (100) [Me$_3$Si$^+$].

Synthesis of R(Me)SbH (8; R = $(Me_3Si)_2CH$). Dropwise addition of 1.86 g (13.1 mmol) of MeI in 30 mL of Et_2O and 2.0 g (13.1 mmol) of DBU to a solution of 3.7 g (13.1 mmol) of **2** in 30 mL of Et_2O gave DBU·HI as a white solid. Stirring, filtration, and removal of the solvent at 20 mbar gave 3.17 g (81.6%) of **8** as a colorless liquid (bp 45 °C, 0.8 mbar). Anal. Calcd for $C_8H_{23}SbSi_2$: C, 32.33; H, 7.80. Found: C, 32.41; H, 7.70. ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ −0.24 (d, $^3J_{HH}$ = 2.22 Hz, $^2J_{SiH}$ = 8.62 Hz,1H; CH), 0.12 (s, $^2J_{SiH}$ = 6.68 Hz, $^1J_{CH}$ = 118.54 Hz, 9H; $SiCH_3$), 0.14 (s, $^2J_{SiH}$ = 6.40 Hz, $^1J_{CH}$ = 118.40 Hz, 9H; $SiCH_3$), 0.75 (d, $^3J_{HH}$ = 6.00 Hz, $^1J_{CH}$ = 126.34 Hz, 3H; $SbCH_3$), 2.64 (dq, $^3J_{HH}$ = 5.98 Hz (CH_3), $^3J_{HH}$ = 2.22 Hz (CH), 1H; SbH). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ −9.53 (s; $SbCH_3$), −1.34 (s, $^1J_{SiC}$ = 43.62 Hz; CH), 2.04 (s, $^1J_{SiC}$ = 51.22 Hz; $SiCH_3$), 2.12 (s, $^1J_{SiC}$ = 50.70 Hz; $SiCH_3$). IR (petroleum ether): ν 1846 cm^{-1} (Sb−H). MS (EI, 70 eV): *m*/*z* (relative intensity, %) 296 (30) [M$^+$], 281 (30) [M$^+$ − Me], 207 (45) [M$^+$ − Me$_4$Si], 73 (100) [Me$_3$Si$^+$].

Synthesis of R_4Sb_8·*n*THF (9·*n*THF; R = $(Me_3Si)_2CH$). One-fourth of the solution of 0.76 g (3.35 mmol) of $SbCl_3$ in 20 mL of Et_2O was added dropwise to 1.42 g (5.0 mmol) of **2** and 0.87 g (11.1 mmol) of pyridine in 30 mL of Et_2O at −70 °C. A white solid (pyridine·HCl) formed. Thereafter the cooling bath was removed and the rest of the $SbCl_3$ solution was added rapidly. Stirring for 16 h at room temperature, filtration through a D4 frit covered with Kieselguhr, removal of the solvent at low pressure, and column chromatography (Al_2O_3 2.2 × 14 cm) of the residue gave an orange-yellow fraction eluted with petroleum ether. Removal of the solvent gave a yellow oil, which was dissolved in 10 mL of THF. After 3 weeks 0.434 g (ca. 32%) of **9**·*n*THF crystallized as cubic deep orange crystals (dec pt 160−180 °C). Anal. Calcd for *n* = 1, $C_{32}H_{84}OSb_8Si_8$: C, 22.83; H, 5.03. Found: C, 23.37; H, 5.15. ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 0.256 (s, $^2J_{SiH}$ = 6.18 Hz, $^1J_{CH}$ = 118.76 Hz, 9H; CH_3), 0.296 (s, $^2J_{SiH}$ = 6.70 Hz, $^1J_{CH}$ = 118.24 Hz, 9H; CH_3), 2.095 (s, $^2J_{SiH}$ = 7.74 Hz, 1H; CH). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ 2.99 (s; CH_3), 3.93 (s; CH_3), 10.28 (s; CH). MS (CI, positive, NH_3): *m*/*z* (relative intensity, %) 1648 (4) [M$^+$ + 2 NH$_4$], 1528 (2) [M$^+$ + 2 NH$_4$ − Sb], 1489 (6) [M$^+$ + 2 NH$_4$ − R], 1406 (5) [M$^+$ + 2 NH$_4$ − 2Sb], 1248 (15)

[$M^+ + 2\ NH_4 - R - 2Sb$]. MS (CI, negative): *m/z* (relative intensity, %) 1454 (20) [$M^- - 3CH_3 - Sb$], 966 (15) [$R_3Sb_4^-$], 683 (100) [$R_2Sb_3^-$].

Synthesis of *cis,trans*-R$_4$Sb$_4$ (*cis,trans*-11; R = (Me$_3$Si)$_2$CH). Addition of 0.33 g (8.62 mmol) of $LiAlH_4$ with stirring to a solution of 2.43 g (4.31 mmol) of **1** in 20 mL of Et_2O led to evolution of gas. Stirring for 2 h, evaporation of the solvent, and column chromatography on Al_2O_3 gave with petroleum ether a broad yellow fraction. The petroleum ether was evaporated, and the remaining orange oil was dissolved in diethyl ether. At −28 °C ca. 0.8 g (33%) of **10** crystallized. From the remaining solution 0.197 g (8.13%) of *cis,trans*-**11** was obtained as small orange crystals (mp 143 °C). *cis,trans*-**11** was recrystallized from THF or toluene. ^1H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 0.29 (s, $^2J_{SiH} = 6.04$ Hz, $^1J_{CH} = 118.08$ Hz, 9H; CH_3), 0.40 (s, $^2J_{SiH} = 6.52$ Hz, $^1J_{CH} = 117.6$ Hz, 9H; CH_3) 1.35 (s, $^2J_{SiH} = 7.4$ Hz, 1H; CH). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ − 0.06 (s; CH), 2.81 (s; CH_3), 4.61 (s; CH_3). MS (CI, positive, NH_3): *m/z* (relative intensity, %) 1125 (100) [$M^+ + H$], 966 (30) [$M^+ - R$], 845 (60) [$M^+ - RSb$]. MS (CI, negative): *m/z* (relative intensity, %) 1124 (8) [M^-], 965 (85) [$M^- - R$], 685 (100) [$M^- - 2\ R - Sb$]. HR MS (CI, negative): 1 120.025 39 ± 10 ppm; *R* = 5000.

Synthesis of R$_6$Sb$_8$ (12; R = (Me$_3$Si)$_2$CH). To a solution of 2.53 g (4.49 mmol) of **1** in 40 mL of Et_2O were added 0.68 g (8.96 mmol) of ^tBuONa and 2.37 g (8.97 mmol) of 18-crown-6 ($C_{12}H_{24}O_6$). The reaction mixture was stirred for 2 h at room temperature and filtered through a frit covered with Kieselguhr. From the concentrated solution at −28 °C 18-crown-6 precipitated. The solution was subjected to column chromatography (Al_2O_3, 2,2 × 15 cm). With petroleum ether a broad yellow fraction was eluted. The petroleum ether was evaporated, and the orange residue was dissolved in acetone. Fractional crystallization at −28 °C gave 0.39 g of R_3Sb_3 (**10**) and 0.05 g (2.3%) of R_6Sb_8 (**12**) (mp 152−153 °C dec). The amount of **12** obtained was not sufficient for elemental analyses. ^1H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 0.366 (s, $^2J_{SiH} = 6.30$ Hz, $^1J_{CH} = 118.58$ Hz, 36H; CH_3), 0.414 (s, $^2J_{SiH} = 6.36$ Hz, $^1J_{CH} = 118.66$ Hz, 18H; CH_3), 0.863 (s, $^2J_{SiH} = 8.44$ Hz, $^1J_{CH} = 119.0$ Hz, 1H; CH), 1.137 (s, $^2J_{SiH} = 8.36$ Hz, $^1J_{CH} = 123.72$ Hz, 2H; CH).^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ 3.14 (s, CH), 3.81 (s, CH), 3.88 (s, $^1J_{SiC} = 50.86$ Hz, CH_3), 4.120 (s, $^1J_{SiC} = 50.86$ Hz, CH_3), 4.903 (s, $^1J_{SiC} = 51.35$ Hz, CH_3). MS (CI, positive, NH_3): *m/z* (relative intensity, %) 1648 (1) [$M^+ - RSb$], 1124 (5) [$R_4Sb_4^+$], 843 (98) [$R_3Sb_3^+$], 601 (30) [$R_3Sb^+ + H$], 386 (100) [$R_2Sb^+ + NH_3 - Me_3Si$]. MS (CI, negative): *m/z* (relative intensity, %) 964 (20) [$M^-/2$], 682 (100) [$R_2Sb_3^-$], 562 (15) [$R_2Sb_2^-$], 439 (25) [R_2Sb^-], 159 (85) [R^-]. HR MS (CI, negative): [$M^-/2$] calcd 960.922 91, found 960.922 50; *R* = 5000.

Synthesis of R(D)Sb−Sb(D)R (*deuterio*-1; R = (Me$_3$Si)$_2$CH). A 0.10 g (2.38 mmol) portion of $LiAlD_4$ was added to a solution of 1.65 g (16.07 mmol) of $RSbCl_2$ in 30 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 1.11 g (84.1%) of yellow crystals of *deuterio*-**1** (mp 70−71 °C) formed. ^1H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 0.175 (s, $^2J_{SiH} = 6.24$ Hz, $^1J_{CH} = 118.88$ Hz, 18H; CH_3 *d,l*), 0.185 (s, $^2J_{SiH} = 6.20$ Hz, $^1J_{CH} = 116.72$ Hz, 18H; CH_3 *meso*), 0.190 (s, $^2J_{SiH} = 6.0$ Hz, $^1J_{CH} = 114.56$ Hz, 18H; CH_3 *d,l*), 0.46 (2H; CH *d,l*), 0.48 (1H; CH *meso*). ^2H NMR (92 MHz, C_6H_6, 25 °C, TMS): δ 1.78 (s, 2D; SbD_2 *d,l*), 2.45 (s, 2D; SbD_2 *meso*). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ −5.6 (s; CH *meso*), −5.53 (s; CH *d,l*), 2.03 (s; CH_3 *meso*, CH_3 *d,l*). IR (Nujol): ν 1329 cm^{-1} (Sb−D). MS (EI, 70 eV): *m/z* (relative intensity, %) 566 (15) [M^+], 564 (8) [$M^+ - 2D$], 551 (4) [$M^+ - Me$].

Synthesis of RSbD$_2$ (*deuterio*-2; R = (Me$_3$Si)$_2$CH). A 3.99 g (11.34 mmol) portion of $(Me_3Si)_2CHSbCl_2$ in 30 mL of diethyl ether was added dropwise to 0.48 g (11.43 mmol) of $LiAlD_4$ in 40 mL of diethyl ether at −60 °C. The mixture was warmed to room temperature, and 0.5 mL of D_2O was added. The solution was filtered through a D4 frit covered with Kieselguhr. Removal of the solvent at 20 mbar and distillation at 1 mbar, bp 43−44 °C, gave 1.99 g (61.53%) of *deuterio*-**2** as a colorless liquid. ^1H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ −0.28 (q, $^3J_{DH} = 1.1$ Hz, $^2J_{SiH} = 8.4$ Hz, 1H; CH), 0.06 (s, $^2J_{SiH} = 6.44$ Hz, $^1J_{CH} = 118.38$ Hz, 18H; CH_3). ^2H NMR (92 MHz, C_6H_6, 25 °C, TMS): δ 2.16 (s; SbD_2). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ −8.80 (s; $^1J_{SiC} = 41.9$ Hz; CH), 1.63 (s, $^1J_{SiC} = 51.25$ Hz; CH_3). IR (film): ν 1335 cm^{-1} (Sb−D). MS (EI, 70 eV): *m/z* (relative intensity, %) 284 (10) [M^+], 269 (20) [$M^+ - Me$].

Synthesis of R(Me)SbD (*deuterio*-8; R = (Me$_3$Si)$_2$CH). To a solution of 1.56 g (5.48 mmol) of $RSbD_2$ in 40 mL of Et_2O was added dropwise 0.84 g (5.91 mmol) of MeI in 30 mL of Et_2O, and 0.90 g (5.91 mmol) DBU was added via a syringe. A white solid of DBU·HI was formed. The reaction mixture was stirred for 2 h. After the filtration the solvent was removed at 20 mbar. The remaining colorless oil distilled at 46 °C, 1 mbar (1.31 g, 80.5% yield). ^1H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ −0.24 (s, $^2J_{SiH} = 8.6$ Hz, 1H; CH), 0.11 (s, $^2J_{SiH} = 6.48$ Hz, $^1J_{CH} = 118.38$ Hz, 9H; $SiCH_3$), 0.13 (s, $^2J_{SiH} = 6.24$ Hz, $^1J_{CH} = 118.4$ Hz, 9H; $SiCH_3$), 0.75 (m, $^3J_{DH} = 0.9$ Hz, 3H; $SbCH_3$). ^2H NMR (92 MHz, C_6H_6, 25 °C, TMS): δ 2.73 (s; SbD). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ −9.42 (s; $SbCH_3$), −1.54 (s; CH), 2.03 (s, $^1J_{SiC} = 52.16$ Hz; $SiCH_3$), 2.12 (s, $^1J_{SiC} = 50.66$ Hz; $SiCH_3$). IR (film): ν 1326 cm^{-1} (Sb−D). MS (EI, 70 eV): *m/z* (relative intensity, %) 297 (5) [M^+], 282 (8) [$M^+ - Me$].

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Supporting Information Available: Tables of crystal data and structure refinement details and diagrams for *meso*-**1**, *d,l*-**3**, *meso*-**3**, **4**, **5**, **9**·2THF, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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