Organoantimony Ring-Chain Equilibria: Trapping of *catena*-Tetrastibanes in *cyclo*-[Cr(CO)$_4$(R′$_2$Sb−SbR−SbR−SbR′$_2$)] (R′ = Me, Ph; R = Me$_3$SiCH$_2$) and Related Complexes

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Ring-chain equilibria between *cyclo*-(Me$_3$SiCH$_2$Sb)$_n$ (n = 4, 5) and R′$_4$Sb$_2$ (R′ = Me, Ph) contain the *catena*-tristibanes R′$_2$Sb−SbR−SbR′$_2$ (**1**, R′ = Me; **2**, R′ = Ph, R = Me$_3$SiCH$_2$) as the most abundant chain components. Addition of [nbdCr(CO)$_4$] (nbd = norbornadiene) to the equilibrium mixture formed from *cyclo*-(Me$_3$SiCH$_2$Sb)$_n$ (n = 4, 5) and R′$_4$Sb$_2$ (R′ = Me, Ph) gives *cyclo*-[Cr(CO)$_4$(R′$_2$Sb−SbR−SbR−SbR′$_2$)] (**3**, R′ = Me; **4**, R′ = Ph, R = Me$_3$SiCH$_2$), two complexes with *catena*-tetrastibane ligands. Reaction of **3** with [W(CO)$_5$(thf)] (thf = tetrahydrofuran) leads to *cyclo*-[Cr(CO)$_4$(Me$_2$Sb−SbR−SbR−SbMe$_2$)W(CO)$_5$] (R = Me$_3$SiCH$_2$) (**5**). The crystal structures of **3** and **5** have been determined by X-ray diffraction.
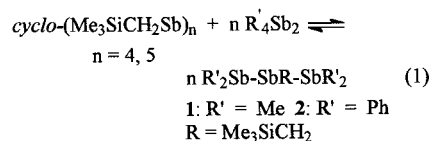
Introduction

The chemistry of organometallic antimony chains (*catena*-stibanes) has been investigated for a long time,[1] but our knowledge of this highly diverse group of compounds is still rather limited. Only three ionic trimers, [R$_2$Sb−Sb−SbR$_2$]$^-$ (R = Ph[2], t-Bu[3]) and [R$_2$Sb−SbR$_2$−SbR$_2$]$^+$ (R = Me),[4] were characterized by X-ray crystallography. Neutral *catena*-stibanes have been reported as tristibanes, R$_2$Sb−SbR′−SbR$_2$ (R = Me, Et, Ph; R′ = Me, Et, t-Bu, (Me$_3$Si)$_2$CH, Ph),[5] a tetrastibane,[5] Ph$_2$Sb−SbEt−SbEt−SbPh$_2$, and several polymers,[1] all with unknown crystal structures. The tri- and tetra-stibanes were identified by ^{1}H NMR and mass spectrometry as components in equilibria mixtures with distibanes and *cyclo*-stibanes. Complexes with homonuclear organoantimony chain ligands are presented here for the first time. However complexes with phosphorus or arsenic chains were reported before, and also a phosphorus antimony chain, Me$_2$P−SbMe−SbMe−PMe$_2$ was synthesized in the coordination sphere of a transition metal carbonyl complex.[6]

We have continued our investigations[5] of ring chain equilibria choosing the well-known and readily available distibanes Me$_4$Sb$_2$ and Ph$_4$Sb$_2$ and the reactive ring system *cyclo*-(Me$_3$SiCH$_2$Sb)$_n$ (n = 4, 5), which is not too difficult to prepare, and report here on the formation of novel *catena*-tristibanes and on trapping reactions of *catena*-tetrastibanes as ligands in metal carbonyl complexes.

Results and Discussion

The trimethylsilylmethyl antimony rings *cyclo*-(Me$_3$SiCH$_2$Sb)$_n$ (n = 4, 5)[7] react instantaneously with Me$_4$Sb$_2$[8] or Ph$_4$Sb$_2$[9] in benzene with formation of the tristibanes Me$_2$Sb−SbR−SbMe$_2$ (**1**) or Ph$_2$Sb−SbR−SbPh$_2$ (**2**) (R = Me$_3$SiCH$_2$) as major components of the equilibria mixtures. The ring-chain equilibria involving the tristibanes **1** and **2** are described in eq 1.

$$\textit{cyclo-}(Me_3SiCH_2Sb)_n + n\,R'_4Sb_2 \rightleftharpoons$$
$$n = 4, 5$$
$$n\,R'_2Sb\text{-}SbR\text{-}SbR'_2 \qquad (1)$$
$$\textbf{1}: R' = Me \quad \textbf{2}: R' = Ph$$
$$R = Me_3SiCH_2$$

Even at low temperatures the equilibria reactions are fast, and techniques allowing the isolation of **1** or **2** from the mixtures are not available. Removal of the distibanes under reduced pressure gives the antimony rings back. **1** and **2** were identified by ^{1}H NMR spectroscopy in C$_6$D$_6$ and by mass spectrometry in the case of **1**. A typical ^{1}H NMR spectrum of the equilibrium mixture obtained by the reaction of Me$_4$Sb$_2$ with *cyclo*-(Me$_3$SiCH$_2$Sb)$_n$ (n = 4, 5) in C$_6$D$_6$ is depicted in Figure 1. The most intensive signals stem from the starting materials and from the tristibane, **1**, for which the singlet signals at 0.11 ppm for the Si*Me*$_3$ protons and

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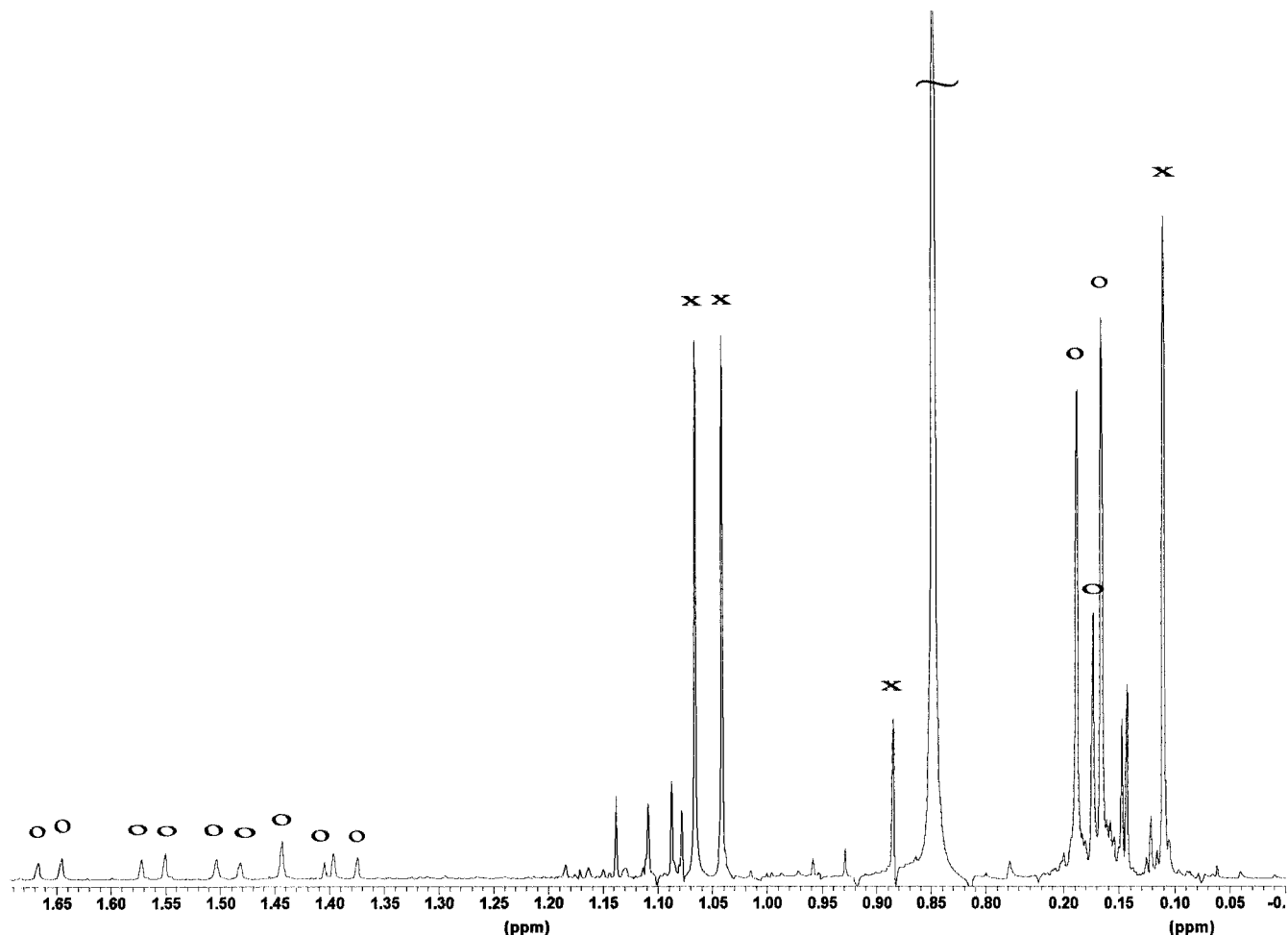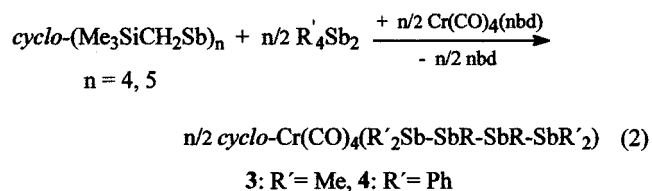
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Figure 1. ^{1}H NMR spectrum of the components of the equilibrium mixture containing $(Me_3SiCH_2Sb)_5$ (o), $-Me_4Sb_2$ ($\sim$), and $Me_2Sb-SbCH_2SiMe_3-SbMe_2$, **1**, (x).

at 0.89 ppm for the methylene protons of the central Me$_3$SiCH_2Sb group and two singlet signals of equal intensity for the diastereotopic methyl substituents of the terminal SbMe_2 groups are characteristic. The low-intensity signals probably result from *catena*-Me$_2$Sb−SbR−SbR−SbMe$_2$ (R = Me$_3$SiCH$_2$) and from longer antimony chains. They disappear with excess distibane.

Estimations of the equilibrium constants for the reaction according to eq 1 are based on the intensity of the ^{1}H NMR signals of the most abundant components using the C$_6$H$_6$ peak as internal standard. For $K =$ [Me$_2$-SbSbRSbMe$_2$]^5/[R$_5$Sb$_5$][Me$_4$Sb$_2$]^5, R = Me$_3$SiCH$_2$, we find $K = 26$. Analogous values for R = Et or n-Pr are $K = 120$ or $K = 46$.[5] For $K =$ [Ph$_2$SbSbRSbPh$_2$]^5/[R$_5$Sb$_5$][Ph$_4$-Sb$_2$]^5, R = Me$_3$SiCH$_2$, we find $K = 8$. These data reflect a partial shift of the equilibria toward *catena*-stibanes when bulkier substituents at the end and less bulky groups in the center of the antimony chains are used. A complete shift of the equilibria is achieved when antimony chains are trapped as ligands in transition metal carbonyl complexes.

The equilibrium mixtures obtained by combining solutions of Me$_4$Sb$_2$ or Ph$_4$Sb$_2$ with *cyclo*-(Me$_3$SiCH$_2$Sb)$_n$ (n = 4, 5) in toluene react with [Cr(CO)$_4$(nbd)] (nbd = norbornadiene) to give the tetrastibane complexes *cyclo*-[Cr(CO)$_4$(R'$_2$Sb−SbR−SbR−SbR'$_2$)] (**3**, R' = Me; **4**, R' = Ph, R = Me$_3$SiCH$_2$). Best yields (**3**, 69%; **4**, 62%) are obtained when the exact stoichiometry of eq 2 is used. Variations of molar ratios reduce the yields of **3** and **4**

but do not lead to complexes of other *catena*-stibanes. The highly selective formation of **3** and **4** is remarkable in view of the complexity of the initial mixture, which contains the free tetrastibane at best as a minor component. It reflects the high thermodynamic stability of five-membered ring systems and the good fit between the bite of the tetrastibane ligand and the chromium center.

$$cyclo\text{-}(Me_3SiCH_2Sb)_n \; + \; n/2 \; R'_4Sb_2 \xrightarrow[- \; n/2 \; nbd]{+ \; n/2 \; Cr(CO)_4(nbd)}$$

$$n = 4, 5$$

$$n/2 \; cyclo\text{-}Cr(CO)_4(R'_2Sb\text{-}SbR\text{-}SbR\text{-}SbR'_2) \quad (2)$$

$$\textbf{3: } R' = Me, \; \textbf{4: } R' = Ph$$

Further complexation of **3** with [W(CO)$_5$(thf)] gives the complex *cyclo*-[Cr(CO)$_4$(Me$_2$Sb−SbR−SbR−SbMe$_2$)W-(CO)$_5$] (R = Me$_3$SiCH$_2$) (**5**) according to eq 3 in 79% yield as orange crystals, soluble in aromatic and aliphatic solvents. For a short time the complexes **3**, **4**, and **5** are stable in air.

$$\textbf{3} + W(CO)_5(thf) \xrightarrow{- \; thf}$$

$$cyclo\text{-}Cr(CO)_4(Me_2Sb\text{-}SbR\text{-}SbR\text{-}SbMe_2)W(CO)_5 \quad (3)$$

$$\textbf{5: } R = Me_3SiCH_2$$
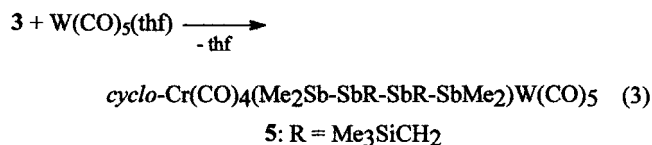
The NMR spectra of **3**−**5** are consistent with the structures established by X-ray diffraction. They correspond also to the spectra of analogous phosphorus compounds.[6a,d,f] ^{1}H NMR spectra of **3** and **4** exhibit one singlet signal for the Si*Me*₃ protons and two doublet signals (AB spin system) for the methylene groups bonded to one of the central antimony atoms, which are both chiral. The organo groups bonded to the terminal antimony atoms of the ligand are not equivalent, and therefore two signals are observed for the Sb*Me*₂ groups in **3**. In the case of **4** the nonequivalency of the phenyl groups is best reflected in the ^{13}C NMR spectra, which exhibit two singlet signals for each kind of carbon atom of the phenyl rings. In **5** all the organic groups are nonequivalent. The ^{1}H NMR spectra of **5** show two singlet signals for the Si*Me*₃ groups, two AB spin systems for the methylene groups, and four singlet signals for the Sb*Me*₂ groups. The EI mass spectra of **3**−**5** contain molecular ions at highest mass and in the case of **3** also with highest intensity. Fragmentation occurs mainly by loss of the CO groups. The IR spectra of **3** and **4** show in the region of the CO-stretching vibrations the common pattern for complexes of the type *cis*-L₂Cr(CO)₄. In the case of **5** instead of a strong signal at 1945−1950 cm⁻¹, which is common for complexes of the type LW(CO)₅, a shoulder was observed at 1952 cm⁻¹. The composition of **3**−**5** has been proven by high-resolution mass spectrometry and by elemental analyses.

In an NMR-tube experiment we have also studied the reactivity of **3** with tetramethyldistibane. The spectra reveal that excess distibane leads to the formation of the tristibane **1** and probably to [*cis*-(Me₂SbSbMe₂)₂Cr-(CO)₄], a compound showing two singlet signals of equal intensity in the region of the Sb*Me*₂ protons (0.87, 1.01 ppm).

Single crystals for X-ray diffraction studies have been obtained by cooling solutions of **3** in petroleum ether to −28 °C and solutions of **5** in petroleum ether/toluene (5/1) to 7 °C. The crystal structures of **3** and **5** consist of five-membered CrSb₄ rings in which the Me₂Sb−SbR−SbR−SbMe₂ (R = Me₃SiCH₂) chain functions as a chelating bidentate four-electron donor via lone pair donation through the terminal Sb atoms. The structures of **3** and **5** are depicted in Figures 2 and 3. In both complexes the five-membered rings are nonplanar, the Sb(2)−Sb(3) unit being twisted out of the Sb(1)−Cr(1)−Sb(4) plane by 22.4° in the case of **5** and by 26.3° in the case of the main conformer of **3**. The trimethylsilylmethyl groups bound to Sb(2) and Sb(3) occupy *trans* positions. For a *catena*-tetrastibane the *meso* and *d,l* forms are possible; however only the *d,l* forms act as ligand in **3** and **5**.

The Sb−Cr bond lengths (2.596(8), 2.588(8) Å in **3** and 2.593(19), 2.575(15) Å in **5**) lie in the usual range for Sb−Cr distances ((*cyclo*-[(Me₂SbOSbMe₂Cr(CO)₄]₂, 2.566-(3), 2.573(4) Å; *cis*-[(Me₂SbSSbMe₂)₂Cr(CO)₄], 2.5986-(12), 2.5838(9) Å).[10] The angles around the antimony atoms (Sb(1) 96.52(17)−118.39(17)° in **3** and 100.0(5)− 118.73(4)° in **5**, Sb(4) 97.6(3)−121.55(2)° in **3** and 95.9-(5)−121.19(4)° in **5**, Sb(2) 89.14(14)−98.05(16)° in **3** and 99.1(2)−118.49(3)° in **5**, and Sb(3) 90.06(14)−95.24(15)°
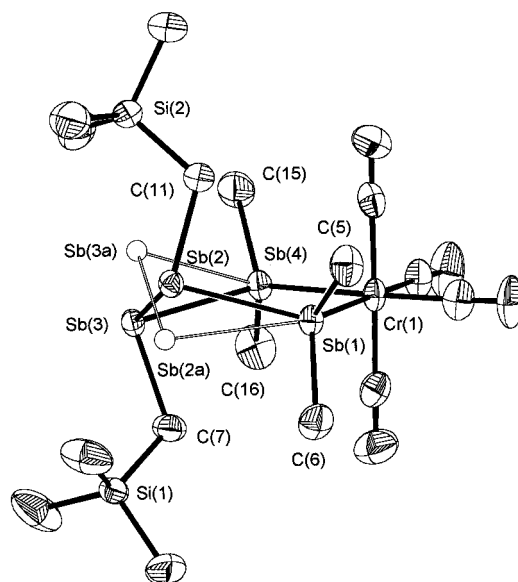

Figure 2. ORTEP representation at 50% probability of the two possible conformers of **3** (ball-and-stick representation of Sb(2a) and Sb(3a)) and atom numbering scheme for one of the *d,l* forms of **3**. Important bond lengths (Å) and angles (deg) are as follows: Sb(2)−Sb(3) 2.813(5), Sb(2)−Sb(1) 2.828(5), Sb(4)−Sb(3) 2.822(5), Sb(2a)−Sb(3a) 2.800-(2), Sb−Cr(1), 2.588(8)−2.596(8), Sb(1)−C 2.137(5)−2.144-(5), Sb(2)−C(11) 2.189(5), Sb(3)−C(7) 2.178(5), Sb(4)−C 2.130(6)−2.139(6), Sb(4)−Cr(1)−Sb(1) 92.11(3), Cr(1)−Sb-(4)−Sb(3) 121.55(2), Cr(1)−Sb(1)−Sb(2) 118.88(2), Sb(3)−Sb(2)−Sb(1) 95.805(13), Sb(2)−Sb(3)−Sb(4) 94.947(13), C(11)−Sb(2)−Sb(3) 98.05(16), C(11)−Sb(2)−Sb(1) 89.14-(14), C(15)−Sb(4)−C(16) 97.6(3), C−Sb−Cr(1) 113.6(2)− 118.39(17), C−Sb(4)−Sb(3) 99.46(19)−102.86(18), C(6)−Sb(1)−C(5) 98.5(3), C−Sb(1)−Sb(2) 96.52(17)−104.27(17), C(7)−Sb(3)−Sb(2) 95.24(15), C(7)−Sb(3)−Sb(4) 90.06(14).

in **3** and 88.6(3)−116.4(3)° in **5**) correspond to p³ configurations for the three-coordinate antimony atoms and to sp³ hybridization for the four-coordinate antimony atoms. This view is also supported by the Sb−C bond lengths of **3** and **5** (Sb(4-coordinate)−C 2.130(6)− 2.154(10) Å and Sb(3-coordinate)−C 2.149(8)−2.189(5) Å). Close to the Sb(2) and Sb(3) atoms of **3** we found two additional electron densities representing approximately 1.5 electron each. These electron densities were assigned to antimony atoms from another conformation of the five-membered CrSb₄ ring. The crystal of **3** contains 98% of the main conformer and 2% of the second conformer, the latter being formed by a ring inversion process. Conformational effects of this kind are not unusual for five-membered metal-containing rings.[11]

Experimental Section

General Comments. NMR spectra were run on Bruker DPX 200 and AVANCE DRX-600 spectrometers. Chemical shifts are reported in δ units (ppm) referenced to C₆D₅H (7.15 ppm, ^{1}H) and C₆D₆ (128.0 ppm, ^{13}C). The C, H correlation was performed with the use of HSQC spectra. Mass spectra were recorded on Finnigan MAT CH7 (A) and Finnigan MAT 8222 spectrometers. The pattern of antimony-containing ions was compared with theoretical values. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller in Göt-

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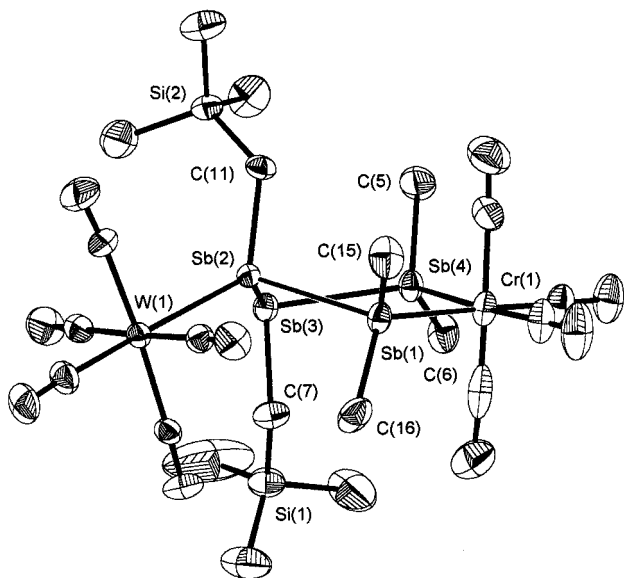(11) Corey, E. J.; Bailar, J. C. *J. Am. Chem. Soc.* **1959**, *81*, 2620.

Figure 3. ORTEP representation at 25% probability of **5** and atom-numbering scheme for one of the enantiomers of **5**. Important bond lengths (Å) and angles (deg) are as follows: Sb(3)−Sb(2) 2.811(9), Sb(3)−Sb(4) 2.845(9), Sb-(1)−Sb(2) 2.832(11), Sb−Cr(1) 2.576(15)−2.593(19), Sb(2)−W(1) 2.791(6), Sb(4)−C 2.142(10)−2.145(10), Sb(2)−C(11) 2.149(8), Sb(3)−C(7) 2.177(9), Sb(1)−C 2.134(11)−2.154-(10), Sb(1)−Cr(1)−Sb(4) 94.21(5), Cr(1)−Sb(1)−Sb(2) 118.73-(4), Cr(1)−Sb(4)−Sb(3) 121.19(4), Sb(2)−Sb(3)−Sb(4) 94.780-(3), Sb(3)−Sb(2)−Sb(1) 99.17(3), W(1)−Sb(2)−Sb(1) 99.17(3), W(1)−Sb(2)−Sb(3) 118.49(3), C(11)−Sb(2)−Sb(3) 107.7(2), C(11)−Sb(2)−Sb(1) 99.1(2), C(11)−Sb(2)−W(1) 116.4(3), C(15)−Sb(1)−C(16) 100.0(5), C(6)−Sb(4)−C(5) 95.9(5), C−Sb-(1)−Cr(1) 114.9(3)−118.5(3), C−Sb(4)−Cr(1) 114.0(4)−117.3(3), C−Sb(1)−Sb(2) 100.4(3)−101.1(3), C−Sb(4)−Sb(3) 101.5(3)−102.9(3), C(7)−Sb(3)−Sb(2) 88.6(3), C(7)−Sb(3)−Sb(4) 95.3(3).

tingen. The reactions and manipulations were performed under an inert atmosphere of dry argon. (Me$_3$SiCH$_2$Sb)$_5$,[7] Me$_4$-Sb$_2$,[8] Ph$_4$Sb$_2$,[9] and [Cr(CO)$_4$(nbd)] (nbd = norbornadiene)[13] were prepared according to reported procedures.

Reactions of *cyclo*-(Me$_3$SiCH$_2$Sb)$_n$ (*n* = 4, 5) with Distibanes. Solutions of distibanes in various concentrations in C$_6$D$_6$ were added at room temperature to saturated solutions of (Me$_3$SiCH$_2$Sb)$_5$. The *catena*-stibanes **1** and **2** were formed immediately in equilibria with the distibanes and the cyclostibane. The molar ratio of the components was determined by integration of the NMR signals.

1,3,3-Tetramethyl-2-(trimethylsilylmethyl)tristiban (1). ^{1}H NMR (C$_6$D$_6$, 600 MHz): 0.11 (s, 9 H, (CH_3)$_3$Si, $^2J_{SiH}$ = 6.4 Hz), 0.89 (s, 2 H, CH_2), 1.05 (s, 6 H, CH_3Sb), 1.08 (s, 6 H, CH_3Sb). ^{13}C (C$_6$D$_6$, 50 MHz): −12.42 (*CH$_2$*), −8.40 (*CH$_3$*Sb), −8.20 (*CH$_3$*Sb), 1.33 ((*CH$_3$*)$_3$Si). MS (EI, 70 eV, 44 °C): 512 (2) [M$^+$], 497 (1) [M$^+$ − Me], 440 (3.4) [M$^+$ − Me$_3$Si], 425 (2) ([Sb$_3$-Me$_2^+$], 409 (1.4) [Sb$_3$Me$_3^+$], 395 (4.4) [Sb$_3$Me$_2^+$], 376 (1.2) [Sb$_3$-Me$^+$], 365 (1) [Sb$_3^+$].

1,3,3-Tetraphenyl-2-(trimethylsilylmethyl)tristiban (2). ^{1}H NMR (C$_6$D$_6$, 600 MHz): −0.11 (s, 9 H, (CH_3)$_3$Si, $^2J_{SiH}$ = 6.3 Hz, $^1J_{CH}$ = 115.2 Hz), 0.90 (s, 2 H, CH_2), 7.06 (m, 12 H, C$_6H_5$ − m + p), 7.72 (m, 8 H, C$_6H_5$ − o). ^{13}C (C$_6$D$_6$, 50 MHz): −9.13 (*CH$_2$*), 0.63 ((*CH$_3$*)$_3$Si), 128.56 (*C$_6$H$_5$* − p), 128.72 (*C$_6$H$_5$* − p), 129.31 (*C$_6$H$_5$* − m), 129.37 (*C$_6$H$_5$* − m), 138.08 (*C$_6$H$_5$* − o), 138.27 (*C$_6$H$_5$* − o).

[Cr(CO)$_4$(Me$_2$Sb−SbR−SbR−SbMe$_2$)] (R = Me$_3$SiCH$_2$) (3). A mixture of 0.99 g (0.94 mmol) of (Me$_3$SiCH$_2$Sb)$_5$ and 0.72

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g (2.36 mmol) of Me$_4$Sb$_2$ in 15 mL of toluene was added to 0.6 g (2.36 mmol) of nbdCr(CO)$_4$ in toluene (10 mL). The reaction mixture was stirred for 12 h at room temperature. Thereafter the solution was reduced to 10 mL, combined with Al$_2$O$_3$ (2 g), dried to a flowing powder under reduced pressure, and placed on a chromatography column (12 × 2 cm, Al$_2$O$_3$, activity level II). With petroleum ether/toluene (1/1) an intense orange fraction was eluted. Removal of the solvents under reduced pressure gave 1.44 g (69%) of **3** as a orange microcrystalline solid. Crystals were grown by keeping a solution of **3** in petroleum ether for 2 days at −28 °C; mp 107 °C. Anal. Calcd for C$_{16}$H$_{34}$Si$_2$O$_4$Cr$_1$Sb$_4$ (885.57): C, 21.70; H, 3.86. Found: C, 21.71; H, 3.82. ^{1}H NMR (C$_6$D$_6$, 200 MHz): −0.04 (s, 18 H, (CH_3)$_3$Si, $^1J_{CH}$ = 136.9 Hz, $^2J_{SiH}$ = 6.1 Hz), AB spin system with A, 0.11; B, 0.19 (4 H, CH_2, $^2J_{HH}$ = 12.9 Hz), 1.09 (s, 6 H, CH_3Sb), 1.38 (s, 6 H, CH_3Sb). ^{13}C NMR (C$_6$D$_6$, 50 MHz): −9.34 (s, *CH$_2$*), −2.56 (s, *CH$_3$*Sb), −1.95 (s, *CH$_3$*Sb), 0.62 (s, (*CH$_3$*)$_3$-Si), 221.82 (s, *CO*$_{eq}$), 234.42 (s, *CO*$_{ax}$). IR (toluene): 1998 s, 1988 sh, 1909 vs cm^{-1} (*ν* CO). HRMS (EI, 70 eV): 885.75616 (calcd 885.75617 amu, C$_{16}$H$_{34}$O$_4$Si$_2$Cr^{52}Sb$_2$121Sb$_2$123, M$^+$). MS (EI, 70 eV, 204 °C): 886 (100) [M$^+$], 802 (14) [M$^+$ − 3 CO], 774 (47) [M$^+$ − 4 CO], 740 (4) [M$^+$ − (SiMe$_3$)$_2$], 686 (14) [Sb$_4$-Me$_6$Cr(CO)$_2^+$], 670 (15) [(Me$_3$SiCH$_2$)$_4$Sb$_3^+$ − 3 Me], 540 (20) [Sb$_4$Cr$^+$], 502 (33) [CH$_2$Sb$_2$Cr$_2$(CO)$_5^+$], 446 (18) [(Me$_3$SiCH$_2$)$_4$-Sb$_2^+$ − (SiMe$_3$)$_2$], 430 (23), 417 (20) [(Me$_3$SiCH$_2$)$_4$Sb$_2^+$ − CH$_2$-(SiMe$_3$)$_2$, − Me], 295 (11) [(Me$_3$SiCH$_2$)$_2$Sb$^+$], 225 (5) [(Me$_3$-SiCH$_2$)MeSb$^+$], 139 (29) [Me$_3$SiCH$_2$Cr$^+$], 73 (58) [Me$_3$Si$^+$], 52 (18) [Cr$^+$].

[Cr(CO)$_4$(Ph$_2$Sb−SbR−SbR−SbPh$_2$)] (R = Me$_3$SiCH$_2$) (4). The reaction of a mixture of 0.37 g (0.35 mmol) of (Me$_3$-SiCH$_2$Sb)$_5$ and 0.49 g (0.88 mmol) of Ph$_4$Sb$_2$ with 0.22 g (0.88 mmol) of nbdCr(CO)$_4$ in 20 mL of toluene and the workup procedures were performed in a manner analogous to that of the synthesis of **3**. However, after stirring for 12 h at room temperature, the reaction mixture was heated under reflux for 3 h. For the chromatography Al$_2$O$_3$, activity level III, 17 × 2 cm was used. **4** was eluted with petroleum ether/toluene (19/1) as a yellow fraction. Removal of the solvent under reduced pressure gave 0.62 g (62%) of **4** as a yellow microcrystalline solid, mp 181 °C. Anal. Calcd for C$_{36}$H$_{42}$Si$_2$O$_4$Cr$_1$Sb$_4$ (1133.86): C, 38.13; H, 3.73. Found: C, 38.36; H, 3.82. ^{1}H NMR (C$_6$D$_6$, 200 MHz): −0.02 (s, 18 H, (CH_3)$_3$Si, $^1J_{CH}$ = 122.1 Hz), AB spin system with A, 0.08; B, 0.47 (4 H, CH_2, $^2J_{HH}$ = 12.8 Hz), 6.91−7.08 (m, 12 H, C$_6H_5$ − m + p), 7.95 (d, 4 H, C$_6H_5$ − o, $^3J_{HH}$ = 7.2 Hz), 8.10 (d, 4 H, C$_6H_5$ − o, $^3J_{HH}$ = 7.2 Hz). ^{13}C NMR (C$_6$D$_6$, 50 MHz): −8.45 (s, *CH$_2$*), 0.23 (s, (*CH$_3$*)$_3$Si), 129.67 (s, *C$_6$H$_5$* − m), 129.74 (s, *C$_6$H$_5$* − p), 129.83 (s, *C$_6$H$_5$* − m), 129.87 (s, *C$_6$H$_5$* − p), 134.24 (s, *C$_6$H$_5$* − ipso), 134.70 (s, *C$_6$H$_5$* − ipso), 136.17 (s, *C$_6$H$_5$* − o), 136.61 (s, *C$_6$H$_5$* − o), 221.63 (s, *CO*$_{eq}$), 233.72 (s, *CO*$_{ax}$). IR (toluene): 2003 vs, 1970 sh, 1909 vs cm^{-1} (*ν* CO). MS (EI, 70 eV, 230 °C): 1134 (22) [M$^+$], 1022 (52) [M$^+$ − 4 CO], 658 (14) [Sb$_3$Ph(Me$_3$SiCH$_2$)$_3^+$ − 3 Me], 648 (15) [Sb$_3$Ph$_2$(Me$_3$SiCH$_2$)$_2^+$ − 3 Me], 604 (38) [Ph$_4$Sb$_2$Cr$^+$], 552 (20) [Ph$_4$Sb$_2^+$], 502 (27) [CH$_2$Sb$_2$Cr$_2$(CO)$_5^+$], 450 (26) [CH$_2$Sb$_2$Cr-(CO)$_5^+$], 327 (29) [Ph$_2$SbCr$^+$], 295 (23) [(Me$_3$SiCH$_2$)$_2$Sb$^+$], 285 (25) [(Me$_3$SiCH$_2$)SbPh$^+$], 275 (65) [Ph$_2$Sb$^+$], 205 (39) [Sb(CH$_2$-Si)$_2^+$], 154 (100) [Ph$_2^+$], 135 (96) [PhSiMe$_3^+$], 77 (20) [Ph$^+$], 73 (98) [Me$_3$Si$^+$], 52 (34) [Cr$^+$], 28 (9) [Si$^+$].

[Cr(CO)$_4$(Me$_2$Sb−SbR−SbR−SbMe$_2$)W(CO)$_5$] (R = Me$_3$-SiCH$_2$) (5). A 0.5 g (0.56 mmol) sample of **3** and 0.22 g (0.56 mmol) of W(CO)$_5$(thf) in 150 mL of THF were stirred for 12 h at room temperature. Thereafter, the solution was reduced to 10 mL, combined with Al$_2$O$_3$ (1.5 g), dried to a flowing powder under reduced pressure, and placed on a chromatography column (20 × 2 cm, Al$_2$O$_3$, activity level III). With petroleum ether/toluene (19/1) an orange fraction was eluted. Removal of the solvents under reduced pressure gave 0.54 g (79%) of **5** as an orange microcrystalline solid. Crystals were grown by storing a solution of **5** in petroleum ether/toluene (5/1) for 12 h at 7 °C, mp 146−147 °C. Anal. Calcd for C$_{21}$H$_{34}$Si$_2$O$_9$Cr$_1$W$_1$-Sb$_4$ (1209.47): C, 20.85; H, 2.83. Found: C, 21.10; H, 2.94. ^{1}H

Table 1. Crystal Data, Data Collection, and Structure Refinement Parameters for 3 and 5

	3	5
formula	$C_{16}H_{34}CrO_4Sb_4Si_2$	$C_{21}H_{34}CrO_9Sb_4Si_2W$
fw	885.61	1209.51
color	orange	orange
temp (K)	173(2)	298(2)
cryst size, mm	$0.5 \times 0.4 \times 0.3$	$0.7 \times 0.5 \times 0.5$
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	15.8510(10)	9.639(4)
b, Å	10.1220(10)	21.484(3)
c, Å	20.436(3)	18.414(2)
α, deg	90	90
β, deg	110.580(10)	90.56(2)
γ, deg	90	90
V, Å^3	3069.6(6)	3813.1(17)
Z	4	4
d_{calcd}, g·cm^{-3}	1.916	2.107
μ(Mo Kα), mm^{-1}	3.911	6.172
scan method	$\omega/2\theta$	$\omega/2\theta$
F(000)	1672	2248
scan range (deg)	$2.75 \leq \theta \leq 27.50$	$2.56 \leq \theta \leq 25$
no. of measd data	8799	8544
no. of unique data	7032	6654
	(R(int) = 0.0259)	(R(int) = 0.0198)
no. of params	267	356
abs corr	ψ-scans	DIFABS[12]
wR2^a (all data)	0.0753	0.0942
R1^a (all data)	0.0470	0.0530
wR2^a ($I>2\sigma(I)$)	0.0709	0.0894
R1^a ($I>2\sigma(I)$)	0.0337	0.0388
GOF on F^2	1.045	1.029
residual density, e·Å^{-3}	+0.688; −0.638	+0.975; −0.995

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

NMR (C_6D_6, 200 MHz): −0.06 (s, 9 H, $(CH_3)_3$Si), −0.04 (s, 9 H, $(CH_3)_3$Si), AB spin system with A, 0.08; B, 0.16 (2 H, CH_2, $^2J_{HH}$ = 12.7 Hz), AB spin system with A, 0.70; B, 0.82 (2 H, CH_2, $^2J_{HH}$ = 12.9 Hz), 1.13 (s, 3 H, CH_3Sb), 1.18 (s, 3 H, CH_3-Sb), 1.31 (s, 3 H, CH_3Sb), 1.40 (s, 3 H, CH_3Sb). ^{13}C NMR (C_6D_6, 50 MHz): −8.01 (s, CH_2), −4.95 (s, CH_2), −2.46 (s, CH_3Sb), −1.95 (s, CH_3Sb), −1.62, (s, CH_3Sb), −0.13 (s, $(CH_3)_3$Si), 0.79 (s, CH_3Sb), 1.16 (s, $(CH_3)_3$Si), 197.58, 198.47, 220.75, 232.21 (CO). IR (toluene): 2064 vs, 1999 s, 1977 sh, 1952 sh, 1914 s, 1900 s cm^{-1} (ν CO). HRMS (EI, 70 eV): 1203.67822 (calcd 1203.67826 amu, $C_{21}H_{34}O_9Si_2Cr^{52}Sb_4^{121}W^{182}$, M$^+$). MS (EI, 70 eV, 237 °C): 1210(29) [M$^+$], 1098 (26) [M$^+$ − 4 CO], 886 (100) [M$^+$ − W(CO)$_5$], 802 (32) [M$^+$ − W, − 8 CO], 774 (82) [M$^+$ − W, 9 CO], 742 (16) [M$^+$ − W(CO)$_5$, − (SiMe$_3$)$_2$], 686 (29) [Sb$_4$-Me$_6$Cr(CO)$_2^+$], 670 (17) [(Me$_3$SiCH$_2$)$_4$Sb$_3^+$ − 3 Me], 540 (19) [Sb$_4$Cr$^+$], 502 (29) [CH$_2$Sb$_2$Cr$_2$(CO)$_5^+$], 446 (16) [(Me$_3$SiCH$_2$)$_4$-Sb$_2^+$ − (SiMe$_3$)$_2$], 430 (18), 417 (17) [(Me$_3$SiCH$_2$)$_4$Sb$_2^+$ − CH$_2$-(SiMe$_3$)$_2$, − Me], 295 (8) [(Me$_3$SiCH$_2$)$_2$Sb$^+$], 139 (19) [Me$_3$SiCH$_2$-Cr$^+$], 73 (56) [Me$_3$Si$^+$], 52 (22) [Cr$^+$].

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 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 in the case of **3**. 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.[14] The drawings were created with the DIAMOND program.[15]

Supporting Information Available: Tables of crystal data and refinement details, atom coordinates and U values, bond distances and angles, anisotropic thermal parameters, and dihedral angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Sheldrick, G. M. *SHELX-97*; Universität Göttingen, 1997.
(15) *DIAMOND*−Visual Crystal Structure Information System; CRYSTAL IMPACT: P.O.B. 1251, D-53002, Bonn.