$J(P_MP_Q)$ = 15.5 Hz. Anal. Calcd for $C_{68}H_{67}BFeP_4$: C, 75.99; H, 6.28; Fe, 5.20. Found: C, 75.82; H, 6.22; Fe, 5.07.

Catalytic Hydrogenation Reactions. Low-Pressure Experiments. The catalytic reactions were followed by measuring the hydrogen consumption as a function of time on a gas buret (Afora 516256).

The catalyst was carried with a degassed solution of the substrate in 1,2-dichloroethane (8 mL) into a 25-mL flask attached to a gas buret, which was in turn connected to a Schlenk manifold. The flask was closed by a silicone septum. The system was evacuated and refilled with dihydrogen six times, and the flask was immersed in a constant-temperature bath. The mixture was vigorously shaken during the run. Plots of the kinetic data were fitted by use of conventional linear regression programs.

Alternatively, the substrate (2 mmol), THF (12 mL), and a stirring bar were placed in a reaction vessel fitted with a reflux condenser and with a side arm with a rubber septum under a constant 1 atm of H_2. The vessel was immersed in a constant-temperature oil bath (20 or 63 °C). The catalyst (0.02 mmol) was then added. The solution was sampled after 2 h, and the samples were analyzed by GC and GC–MS.

High-Pressure Experiments. Air was evacuated from the autoclave; then, the solution containing the catalyst, the substrate, and the solvent, prepared in a Schlenk tube, was introduced by suction. Hydrogen was added up to the desired pressure, and the solution in the autoclave was stirred at the selected temperature. At the end of the reaction, the autoclave was cooled, the gas vented out, and the solution collected. The conversion was determined from the crude product by GC analysis with a 2-m packed column containing free fatty acid phase (5%) on Chromosorb G AW-DMCS.

Acknowledgment. We thank Paolo Innocenti and Fabrizio Zanobini for technical assistance. This work was supported by grants from the CNR (Rome) program "Progetti Finalizzati Chimica Fine II" and from EEC (Brussels), Contract SC1.0027.C.

Registry No. 1, 123122-81-6; 2, 54477-71-3; 3, 123054-72-8; 4, 123054-68-2; 5, 123054-70-6; 6, 123054-78-4; 7, 137436-45-4; PhC≡CH, 536-74-3; PhCH=CH_2, 100-42-5; HC≡$CSiMe_3$, 1066-54-2; PhCH=$CHSiMe_3$, 754-05-2; CH_2=CH_2, 74-85-1; *n*-C_3H_7C≡CH, 627-19-0; *n*-$C_5H_{11}C$≡CH, 628-71-7; (MeO)CH=CHC≡CH, 2798-73-4; *n*-C_3H_7CH=CH_2, 109-67-1; *n*-$C_5H_{11}CH$=CH_2, 592-76-7; (MeO)CH=CHCH=CH_2, 3036-66-6; Me_3SiCH=CHCH=$CHSiMe_3$, 13625-90-6.

Syntheses and Structures of Isopropyl- and (Bis(trimethylsilyl)methyl)antimony Rings and *catena*-Tri- and *catena*-Tetrastibanes by Reaction of Organoantimony Rings with Distibanes

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Received May 21, 1991

The syntheses and the structures of selected organoantimony rings $(RSb)_n$ and the formation of *catena*-stibanes by reaction of organoantimony rings with distibanes are reported. The syntheses include the preparation of *i*-$PrSbBr_2$ and the reaction of this intermediate with magnesium to form $(i\text{-PrSb})_4$ and $(i\text{-PrSb})_5$. The isopropylantimony rings are stable in solution but polymerize in the absence of solvent. $[(Me_3Si)_2CHSb]_4$ is, however, stable in the solid state with respect to polymerization. This four-membered ring has been obtained in the form of orange crystals from a solution of the dehalogenation products of the corresponding dichloride. The ^1H NMR data of $(i\text{-PrSb})_4$ and $(i\text{-PrSb})_5$ in solution are in accordance with the cyclic structures with the substituents adopting a maximum of trans positions. The structure of $[(Me_3Si)_2CHSb]_4$ has been determined by single-crystal X-ray diffractometry as that of a strongly folded cyclotetrastibane (115.4°) in the all-trans configuration. The Sb–Sb distances alternate between short and long (2.83, 2.87 Å), and the molecule on the whole approximates C_2 symmetry. The crystal data with Mo Kα radiation are as follows: triclinic, space group $P\bar{1}$, a = 12.361 (1) Å, b = 12.981 (1) Å, c = 17.337 (2) Å, α = 108.18 (1)°, β = 90.82 (1)°, γ = 102.82 (1)°, Z = 2, and R = 0.0362. The study of the reactivity of organoantimony rings with distibanes led to the formation of the first examples of *catena*-tri- and *catena*-tetrastibanes. The tristibanes $(Me_2Sb)_2SbR$, with R = Et, Pr, *t*-Bu, $[Me_3Si]_2CH$, and 2,4,6-$Me_3C_6H_2$, are formed by reaction of an excess of Me_4Sb_2 with the corresponding rings $(RSb)_n$. Action of an excess of Et_4Sb_2 with $(EtSb)_5$ or $(PrSb)_5$ gives $(Et_2Sb)_2SbEt$ or $(Et_2Sb)_2SbPr$. $(Ph_2Sb)_2SbEt$ and $(Ph_2SbSbEt)_2$ are formed by the reaction of Ph_4Sb_2 with $(EtSb)_5$. *catena*-Stibanes derived from difficulty accessible antimony rings are better obtained by dehalogenation of appropriate mixtures of organoantimony bromides or by salt elimination; Me_2SbBr and $MeSbBr_2$ react with magnesium to give $(Me_2Sb)_2SbMe$, and Ph_5Sb_3 is obtained by reaction of $PhSbCl_2$ and Ph_2SbLi or Ph_2SbNa in liquid NH_3. The novel *catena*-tri- and *catena*-tetrastibanes have been characterized by ^1H NMR and mass spectra. They exist in equilibrium with distibanes and cyclostibanes.

Introduction

In the context with recent results on the syntheses of organoantimony rings, $(RSb)_n$ (with R = Et, Pr, Bu, Mes; n = 4, 5),[3] we reinvestigated the chemistry of isopropylantimony, which had been reported[4] as black solid polymer, and of (bis(trimethylsilyl)methyl)antimony,[5] a trimer

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Table I. ^{1}H NMR Data for 2a,b in C_6D_6

2a	H1α	H2,5α	H3,4α		
	2.702	2.442	3.200		
	H3,4βa/b	H2,5βa/b	H1β	H2,5βa/b	H3,4βa/b
	1.720	1.645	1.642	1.611	1,545
2b	Hα	Hβ			
	2.740	1.556			

and tetramer mixture. We report here on a novel synthesis of *i*-PrSbBr$_2$ (1), a starting compound for isopropylantimony, and the ^{1}H NMR and mass spectra of (*i*-PrSb)$_5$ (**2a**) and (*i*-PrSb)$_4$ (**2b**) and the spectra and the X-ray crystal structure of [(Me$_3$Si)$_2$CHSb]$_4$ (**3**).

Very little is known of the reactivity of organoantimony rings. An early result in this regard is the formation of EtSbBr$_2$ in the reaction of (EtSb)$_5$ with bromine.[6] By analogy, the reaction of cyclostibanes with distibanes should give catenatristibanes R$_5$Sb$_3$. The formation of longer chains of the type R$_2$Sb(SbR)$_n$SbR$_2$ ($n > 1$) is possible as well. These *catena*-stibanes should, however, be thermodynamically unstable and take part in ring–chain equilibria. Exchange reactions between distibanes bearing different substituents, such as tetramethyl- and tetraethyldistibanes, have been studied before.[7] We describe here the formation of *catena*-tristibanes and -tetrastibanes in equilibrium with distibanes and cyclostibanes.

Results and Discussion

Synthesis and Properties of *i*-PrSbBr$_2$ and Isopropylantimony Rings. The reaction of *i*-Pr$_2$SbBr with SbBr$_3$ at 25 °C leads to the quantitative formation of *i*-PrSbBr$_2$ (1). An earlier synthesis[4] gave 33% yield.

$$i\text{-Pr}_2\text{SbBr} + \text{SbBr}_3 \rightarrow 2i\text{-PrSbBr}_2 \quad (1)$$

Similar results also have been obtained in the synthesis of other alkylantimony dibromides.[8] Isopropylantimony dibromide reacts with magnesium in tetrahydrofuran (THF) to form the yellow ring compounds (*i*-PrSb)$_5$ (**2a**) and (*i*-PrSb)$_4$ (**2b**). Solutions of these in THF or hydro-

$$i\text{-PrSbBr}_2 + \text{Mg} \rightarrow \text{MgBr}_2 + (1/n)(i\text{-PrSb})_n \quad \begin{matrix}\mathbf{2a},\ n = 5\\ \mathbf{2b},\ n = 4\end{matrix}$$

carbons are air-sensitive. They are, however, stable for days in an inert atmosphere at room temperature but decompose over longer periods or at higher temperature with formation of *i*-Pr$_4$Sb$_2$, *i*-Pr$_3$Sb, and Sb. Attempts to crystallize the rings lead to polymerization, and black solid (*i*-PrSb)$_x$[4] is obtained.

The identification and distribution of **2a,b** follows from the mass and ^{1}H NMR spectra. In the EI mass spectrum there appear the molecular ions and characteristic fragments of the pentamer **2a** and the tetramer **2b**. Fragmentation proceeds with loss of isopropyl or isopropene and leads to the cluster ions Sb$_5^+$ or Sb$_4^+$. Experiments with variation of electron energy and the observation of

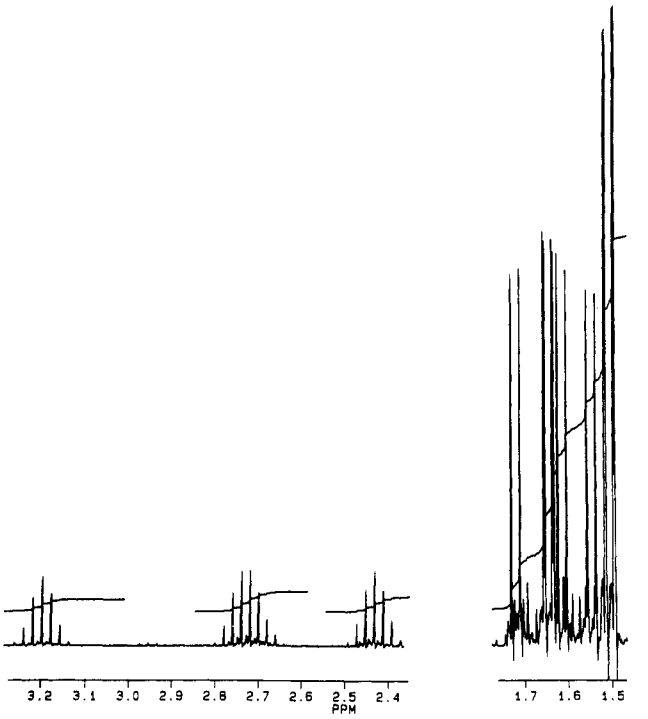
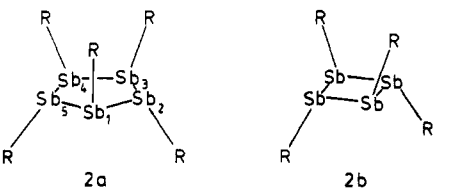
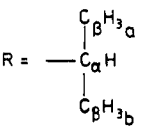


Figure 1. ^{1}H NMR spectra of **2a,b**.

Chart I





metastable signals made it unlikely that the ions of the tetramer are fragments of the pentamer. Both rings also are observed in the ^{1}H NMR spectrum (see Figure 1). The distribution of the rings in benzene at room temperature is 72% **2a** and 28% **2b**.

The assignment in Table I is based on the relative intensities and the multiplicities of the signals, which come from the cyclic molecules depicted in Chart I with the assumption of a maximum of trans positions of the groups, R.

The distribution of methyl groups, which is typical for the five-membered ring, is easily recognized in the spectrum. There are five doublet signals of equal intensity. Four of them stem from the pairs of nonequivalent methyl groups of the isopropyl substituents at the chiral atoms Sb(3), Sb(4) and Sb(2), Sb(5). The fifth doublet comes from the methyl groups of the substituent at Sb(1). The sixth doublet signal is assigned to the four-membered-ring **2b**. In the region of the methine protons there are two heptets of equal intensity at 2.44 and 3.20 ppm and a group of signals between 2.65 and 2.80 ppm. The latter is explained as a superimposition of the heptet signals for the methine groups of **2a** at Sb(1) and of **2b**. Thus, the characteristic ratio of 2:2:1 for the methine groups of the pentamer is reflected in the spectrum. The signal at 3.20

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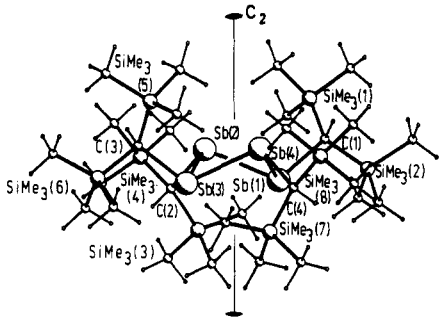

Figure 2. Molecular structure of **3** with 2-fold axis marked. Labels of atoms and groups are as given in Table V.

ppm is assigned to a pair of symmetric methine protons of the cis substituents, i.e., H3,4α. The low-field shift is explicable by the short local distance of the methine protons in cis groups. The assignment of the rest of the methine protons is then conclusive. The pair of methyl doublets with the greatest distance in the spectrum is assigned to the substituents at Sb(3) and Sb(4), because there the diastereotopic methyl groups meet very different surroundings. The remaining three doublets with similar chemical shifts then belong to the substituents on Sb(2), Sb(5), and Sb(3) with similar environments in the molecule.

The isopropylantimony system is related to the phosphorus rings $(i\text{-PrP})_n$ (n = 3–5) that are obtained by dehalogenation of i-$PrPCl_2$ with Mg in THF.[9] In the phosphorus system however, small rings are more abundant and the ring compounds are thermally much more stable than in the antimony system. These chemical differences reflect the weakness of Sb–Sb and Sb–C bonds and the smaller steric effect of the isopropyl group at antimony relative to the situation at phosphorus. Organoarsenic rings are well-known,[10] but the isopropyl derivatives have not been described. They should be more closely related to the corresponding phosphorus compounds than to **2a,b**.

Isolation, Properties, and X-ray Crystal Structure of $[(Me_3Si)_2CHSb]_4$ (3). The four-membered-ring compound **3** is formed by reaction of $(Me_3Si)_2CHSbCl_2$ with

$$4(Me_3Si)_2CHSbCl_2 + 4Mg \rightarrow \underset{\mathbf{3}}{[(Me_3Si)_2CHSb]_4} + 4MgCl_2$$

magnesium in THF. Crystallization from a mixture of petroleum ether and benzene gives **3** as red-orange crystals melting at 130–133 °C. The crystals are stable in air for a short time but very sensitive to oxygen in solution. Their solubility in hydrocarbons is good. Remarkable with reference to other known alkylantimony rings is the thermal stability of **3**. Neither 2 days at 100 °C in benzene in a sealed glass tube nor heating of the melt to 160 °C lead to decomposition of **3**. In the ^1H NMR spectrum in C_6D_6 at 360 MHz there are two singlet signals at δ = 0.34 and δ = 0.93 for the trimethylsilyl and methine protons. This shows the equivalence of the alkyl substituents and excludes the presence of four-membered rings in cis/trans configurations. In the mass spectrum the molecular ion appears with the highest mass. The most intense peak comes from the fragment $R_3Sb_4^+$. The crystal structure of **3** (see Figure 2) contains strongly folded Sb_4 rings with the alkyl groups in trans positions. Geometric data are given in Table II.

Table II. Geometric Data with Esd's for $[Sb(CH(SiMe_3)_2)]_4$

Bond Lengths (Å)[a]			
Sb(1)–Sb(2)	2.866 (1)	Sb(1)–C(1)	2.227 (4)
Sb(2)–Sb(3)	2.822 (1)	Sb(2)–C(2)	2.226 (4)
Sb(3)–Sb(4)	2.878 (1)	Sb(3)–C(3)	2.226 (5)
Sb(4)–Sb(1)	2.826 (1)	Sb(4)–C(4)	2.232 (4)
		Sb–C(av)	2.228

Bond Angles (deg)			
Sb(1)–Sb(2)–Sb(3)	80.75 (1)	Sb(2)–Sb(1)–C(1)	109.3 (1)
Sb(2)–Sb(3)–Sb(4)	80.14 (2)	Sb(4)–Sb(1)–C(1)	96.7 (1)
Sb(3)–Sb(4)–Sb(1)	80.47 (2)	Sb(1)–Sb(2)–C(2)	110.6 (1)
Sb(4)–Sb(1)–Sb(2)	80.27 (2)	Sb(3)–Sb(2)–C(2)	97.2 (1)
		Sb(2)–Sb(3)–C(3)	98.2 (1)
		Sb(4)–Sb(3)–C(3)	110.5 (1)
		Sb(1)–Sb(4)–C(4)	97.8 (1)
		Sb(3)–Sb(4)–C(4)	109.9 (1)

Torsion Angles (deg)	
Sb(1)Sb(2)–Sb(3)Sb(4)	+43.97 (1)
Sb(2)Sb(3)–Sb(4)Sb(1)	−44.81 (1)
Sb(3)Sb(4)–Sb(1)Sb(2)	+43.90 (1)
Sb(4)Sb(1)–Sb(2)–Sb(3)	−44.98 (1)
C(1)Sb(1)–Sb(2)Sb(3)	−138.8 (1)
C(1)Sb(1)–Sb(4)Sb(3)	+152.4 (1)
C(2)Sb(2)–Sb(3)Sb(4)	+153.7 (1)
C(2)Sb(2)–Sb(1)Sb(4)	−139.2 (1)
C(3)Sb(3)–Sb(4)Sb(1)	−139.9 (1)
C(3)Sb(3)–Sb(2)Sb(1)	+153.5 (1)
C(4)Sb(4)–Sb(1)Sb(2)	+152.9 (1)
C(4)Sb(4)–Sb(3)Sb(2)	−139.7 (1)

Folding of the Four-Membered Ring (deg)	
Sb(1)Sb(2)Sb(3)–Sb(1)Sb(4)Sb(3)	115.27 (2)
Sb(2)Sb(1)Sb(4)–Sb(2)Sb(3)Sb(4)	115.48 (2)

[a] Shortest intermolecular Sb···Sb contacts 8.20 and 8.38 Å.

The rings are isolated from each other. The shortest intermolecular distance between antimony atoms is 8.20 Å. The fold angle of **3** (115.4°) is narrow compared to $(\sigma\text{-}Me_5C_5Sb)_4$ (144°).[11] $(t\text{-BuSb})_4$ (133°),[12] or $(MesSb)_4$ (119.8, 125.2°).[3] As a consequence, the torsion angles in the Sb_4 ring (interval of absolute values from 43.9 to 44.8°) are relatively wide. The Sb–Sb bond lengths are not equal. There are two longer and two shorter distances (2.82, 2.87 Å) opposite each other. Hence the symmetry is close to C_2, and this approximate 2-fold symmetry extends to the substituents. Phosphorus or arsenic rings with the $(Me_3Si)_2CH$ substituent have not been described. Compounds with P=P or As=As bonds are, however, stabilized by this bulky group that was also used for the synthesis of $RSb{=}PC_6H_2(t\text{-Bu})_3$[13,14] and complexes with the RSb=SbR and RSb ligands (R = $(Me_3Si)_2CH$).[15]

Reaction of Organoantimony Rings with Distibanes and Formation of *catena*-Stibanes. For a ^1H NMR study of the reactions of organoantimony rings with distibanes in C_6D_6 we chose the pentamers $(EtSb)_5$ and $(PrSb)_5$ and the tetramers $(t\text{-BuSb})_4$ **3**, and $(MesSb)_4$ as examples of rings and Me_4Sb_2, Et_4Sb_2, and Ph_4Sb_2 as examples of distibanes. The isopropylantimony rings **2a** and **2b** were not considered due to their low thermal stability relative to the other organoantimony rings. We found that the tristibanes **4**–**11** and the tetrastibane **12** are formed and

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$$5Me_2SbSbMe_2 + (RSb)_5 \rightleftharpoons 5Me_2SbSb(R)SbMe_2$$
4, R = Et
5, R = Pr

$$4Me_2SbSbMe_2 + (RSb)_4 \rightleftharpoons 4Me_2SbSb(R)SbMe_2$$
6, R = *t*-Bu
7, R = $(Me_3Si)_2CH$
8, R = Mes

$$5Et_2SbSbEt_2 + (RSb)_5 \rightleftharpoons 4Et_2SbSb(R)SbEt_2$$
9, R = Et
10, R = Pr

$$2Ph_2SbSbPh_2 + {}^3/_5(EtSb)_5 \rightleftharpoons Ph_2SbSb(Et)SbPh_2 + (Ph_2SbSbEt)_2$$
11 12

exist in equilibrium with excess distibane. Elimination of the distibanes gives back the parent cyclostibanes, and therefore, attempts to isolate **4–12** have not been successful, even at low temperature. The kinetic stabilization of the novel tri- and tetrastibanes is not sufficient for isolation, and equilibrium is reached in minutes. The decomposition of **4–12** with formation of distibanes and cyclostibanes is favored thermodynamically, because there is an increase in the number of molecules. In the presence of an excess of the corresponding distibanes, however, the tristibanes form stable yellow solutions in benzene or other organic solvents and are easily handled in an inert atmosphere.

Chains of more than four antimony atoms are not observed as major components of the equilibria even at low distibane concentrations, and only one tetrastibane, **12**, could be identified unambiguously. The formation of longer chains should, however, be expected on the basis of mechanistic considerations. The most plausible mechanism for the reactions of cyclostibanes and distibanes is a four-center metathesis between antimony atoms. The formation of a *catena*-heptastibane should be the first step of a reaction of a distibane with a cyclopentastibane. Our results imply that longer chains are unstable in presence of excess distibane and form tristibanes.

An estimation of the equilibrium constants is based on the intensity of the NMR signals using the C_6H_6 peak as internal standard: For $K = [Me_2SbSbRSbMe_2]^5/[Me_4Sb_2]^5[(RSb)_5]$ we find $K = 120$ with R = Et and $K = 46$ with R = Pr. For $K = [Me_2SbSbRSbMe_2]^4/[Me_4Sb_2]^4[(RSb)_4]$ we find $K = 3$ with R = *t*-Bu and $K = 1$ with R = $(Me_3Si)_2CH$. The relative concentrations of the tristibanes in the equilibria reflect the steric requirements of the substituents at the central antimony atom. Tristibane formation is favored by sterically less demanding groups such as the ethyl or propyl substituents. Bulky groups, *t*-Bu and $(Me_3Si)_2CH$, favor the rings. Constants of equilibria containing **8–12** could not be determined due to overlap of NMR signals.

In the series of the tristibanes **4–11** compounds with the methyl group on the central antimony atom are missing because methylantimony rings are not known. Attempts to synthesize such rings failed.[3] We obtained, however, pentamethyltristibane (**13**) by reduction of Me_2SbBr and

$$2Me_2SbBr + MeSbBr_2 + 2Mg \rightarrow Me_2SbSb(Me)SbMe_2 + 2MgBr_2$$
13

$MeSbBr_2$ with magnesium in THF. The reaction must be carried out in the presence of a large excess of Me_2SbBr and magnesium. Under these conditions **4** is formed together with Me_4Sb_2, the presence of which is necessary to stabilize **13**. Removal of this distibane gives the black solid polymer $(MeSb)_x$ even at low temperature. These results indicate an equilibrium between methylantimony and Me_4Sb_2 on one side and the tristibane, **13**, on the other.

An attempt to stabilize a tristibane by phenyl substitution in the solid state led us to study the reactions of Ph_2SbLi or Ph_2SbNa with $PhSbCl_2$ in liquid ammonia. A brown powder containing the tristibane **14** is formed.

$$2Ph_2SbM + PhSbCl_2 \rightarrow Ph_2SbSb(Ph)SbPh_2 + 2MCl$$
14

M = Li, Na

$$14 \rightarrow (1/x)(PhSb)_x + Ph_4Sb_2$$

However, the reactivity of **14** is very similar to that of the other tristibanes. It decomposes with formation of Ph_4Sb_2 and a polymeric form of phenylantimony.

The evidence for the formation of the tristibanes and the tetrastibane comes from the ^1H NMR spectra and the mass spectra of solutions with excess distibanes. Detailed data are given in the Experimental Section. In the NMR spectra the tristibanes are easily identified by the pattern and intensity ratio of the signals of the organic substituents at the different antimony atoms. The spectra are characteristic, because the peripheral antimony atoms are prochiral and, hence, the substituents are not equivalent. Therefore, all the methyl compounds **4–8** and **13** show two characteristic singlet signals for the diastereotopic methyl groups at Sb(1) and Sb(3). In the case of the ethyl compounds **9** and **10** the spectra are more complex. The diastereotopic ethyl groups at Sb(1) and Sb(3) bear diastereotopic methylene protons. This explains the 32 lines of two ABX_3 spin systems that were observed due to these substituents.

The substituents at Sb(2) give signals of a relatively simple pattern and are easily identified. Evidence for the formation of the phenyl compounds **11** and **12** comes from signals of the ethyl groups. There is a triplet quartet pattern for **11** and one ABX_3 spin system for the tetrastibane **12**. For **12** meso and d,l isomers are possible and should give rise to two sets of signals. If accidental degeneracy is excluded, the spectrum of **12** indicates that only one isomer is present. The presence of excess distibanes made it difficult to record mass spectra of the tristibanes. Nevertheless, molecular ions and characteristic fragments were obtained for **4**, **5**, **8–10**, **13** and **14**.

The chemistry of phosphorus and arsenic analogues of **4–10** and **13** is similar to that of their antimony congeners. *catena*-Phosphanes or -arsanes decompose with formation of diphosphanes or diarsanes and the corresponding ring compounds. However, some *catena*-phosphanes[16–19] or -arsanes[17] with terminal Me_3Si or phenyl substituents have been isolated as remarkably stable compounds that do not decompose readily at room temperature. The comparison with **11**, **12**, and **14** indicates that the effect of phenyl groups in stabilizing a chain vs a ring compound is smaller on Sb than on P or As systems.

Experimental Section

General Data. Proton NMR spectra were run on a Bruker WH 360 spectrometer. Mass spectra were recorded on Finnigan MAT 8222 spectrometer. The pattern of antimony-containing ions was compared with theoretical values. *i*-Pr_2SbBr,[20]

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Table III. Distribution of the Components Obtained by Reactions of Cyclostibanes with Excess Distibanes

tristibane	tetrastibane	distibane
14% **4**		86% Me_4Sb_2
11% **5**		89% Me_4Sb_2
4% **6**		96% Me_4Sb_2
8% **7**		92% Me_4Sb_2
11% **8**		89% Me_4Sb_2
12% **9**		88% Et_4Sb_2
13% **10**		87% Et_4Sb_2
10% **11**	7% **12**	82% Ph_4Sb_2

$(Me_3Si)_2CHSbCl_2$,[5] Me_4Sb_2,[21] Et_4Sb_2,[21] Ph_4Sb_2,[22] $(EtSb)_5$,[3] $(PrSb)_5$,[3] $(t\text{-}BuSb)_4$,[23] $(MesSb)_4\cdot C_6H_6$,[3] $MeSbBr_2$,[8] Me_2SbBr,[24] and $PhSbCl_2$[25] were prepared according to reported procedures. All the experiments were carried out under argon.

Isopropylantimony Dibromide (1). A mixture of 10.0 g (0.027 mol) of $SbBr_3$ and 8.0 g (0.027 mol) of $i\text{-}Pr_2SbBr$ is stirred for 4 h at 25 °C. Yellow liquid **1** is formed quantitatively. ^1H NMR (C_6D_6): δ 1.27 (d, 6 H), 1.68 (h, 1 H), ^3J = 7.3 Hz. MS (70 eV) [m/z (%)]: 324 (5), (M^+), 281 (7), 243 (2), 43 (100).

Pentaisopropylcyclopentastibane (2a) and Tetraisopropylcyclotetrastibane (2b). The reaction of isopropylantimony dibromide with Mg in THF was carried out as previously described.[4] At the end of the operation the rings were dissolved in benzene to prevent their polymerization to $(RSb)_x$. MS for **2a,b** (70 °C, 70 eV) [m/z (%), assignment]: 824 (1), R_5Sb_5; 781 (1), R_4Sb_5; 695 (1), R_2Sb_5; 609 (1), Sb_5; 660 (1), R_4Sb_4; 617 (2), R_3Sb_4; 575 (1), R_2Sb_4H; 531 (1), RSb_4; 489 (4), Sb_4H; 43 (100), R = *i*-Pr.

Tetrakis(bis(trimethylsilyl)methyl)cyclotetrastibane (3). The reaction of $(Me_3Si)_2CHSbCl_2$ with Mg in THF was carried out as previously described.[5] The crude product was dissolved in 1:1 petroleum ether/benzene. Cooling the solution gave crystals of **3**. MS (150 °C, 20 eV) [m/z (%), assignment]: 1124 (20), R_4Sb_4; 965 (80), R_3Sb_4; 73 (100), Me_3Si; R = $(Me_3Si)_2CH$.

Reactions of Cyclostibanes with Distibanes. Solutions of distibanes in various concentrations in C_6D_6 were added at room temperature to saturated solutions of the respective cyclostibane in NMR tubes. The catenastibanes **4–12** were formed immediately in equilibrium with the distibanes and cyclostibanes. **4** and **5** were also obtained by heating Me_4Sb_2 and the solid polymers $(EtSb)_x$ or $(PrSb)_x$ in sealed glass tubes at 60 °C for 3 h. The molar ratio of the components was determined by integration of the NMR signals. The compositions of mixtures that were used for the ^1H NMR analyses are given in Table III. Components of low relative concentrations (<1%) have not been considered.

1,1,3,3-Tetramethyl-2-ethyltristibane (4). ^1H NMR (C_6D_6): δ 1.03 (s, 6 H, CH_3Sb), 1.04 (s, 6 H, CH_3Sb), 1.38 (t, 3 H, CH_3), 1.786 (q, 2 H, CH_2); ^3J = 7.99 Hz. MS (70 eV, 20 °C) (m/z): 454 (M^+), 425 ($M^+ - C_2H_5$), 424 ($M^+ - 2CH_3$) 409 ($M^+ - 3CH_3$), 379 ($Sb_3C_2H_5$), 365 (Sb_3).

1,1,3,3-Tetramethyl-2-propyltristibane (5). ^1H NMR (C_6D_6): δ 0.906 (t, 3 H, CH_3), 1.042 (s, 6 H, CH_3Sb), 1.043 (s, 6 H, CH_3Sb), 1.56–1.72 (m, 2 H, CH_2), 1.84–1.99 (m, 2 H, CH_2Sb).

1,1,3,3-Tetramethyl-2-*tert*-butyltristibane (6). ^1H NMR (C_6D_6): δ 1.0 (s, 6 H, CH_3), 1.01 (s, 6 H, $t\text{-}C_4H_9Sb$), 1.04 (s, 6 H, CH_3).

1,1,3,3-Tetramethyl-2-(bis(trimethylsilyl)methyl)tristibane (7). ^1H NMR (C_6D_6): δ 0.25 (s, 18 H, $(CH_3)_3Si$)), 0.99 (s, 6 H, CH_3Sb), 1.01 (s, 1 H, CH), 1.06 (s, 6 H, CH_3Sb).

1,1,3,3-Tetramethyl-2-mesityltristibane (8). ^1H NMR (C_6D_6): δ 0.9 (s, 6 H, CH_3), 1.1 (s, 6 H, CH_3), 2.08 (s, 3 H, *p*-CH_3), 2.65 (s, 6 H, *o*-CH_3), 6.78 (s, 2 H, C_6H_2). MS (70 eV, 60 °C) (m/z): 544 (M^+), 529 ($M^+ - CH_3$), 514 ($M^+ - 2CH_3$).

Pentaethyltristibane (9). ^1H NMR (C_6D_6): C_2H_5Sb═, δ 1.428 (t, 3 H, CH_3), 1.901 (q, 2 H, CH_2); $[(C_2H_5)_2Sb]_2Sb$–, two spin systems ABX_3 and $A'B'X'_3$ with δ 1.328 (X) (t, 6 H, CH_3), 1.332 (X′) (t, 6 H, CH_3), 1.638 (A), 1.658 (A′), 1.789 (B), 1.764 (B′) (8 H, CH_2) (^3J = 7.71 Hz, ^2J = 12.1 Hz). MS (70 eV, 90 °C) (m/z): 510 (M^+), 481 ($M^+ - C_2H_5$), 453.

1,1,3,3-Tetraethyl-2-propyltristibane (10). ^1H NMR (C_6D_6): PrSb═, δ 1.34 (t, 3 H, CH_3), 1.65–1.75 (m, 2 H, CH_2), 1.95–2.00 (m, 2 H, CH_2); $(Et_2Sb)_2Sb$–, two spin systems ABX_3 and $A'B'X'_3$

Table IV. Crystallographic Data for $[Sb(CH(SiMe_3)_2)]_4$ and Structure Determination Details

Crystal Data (Mo Kα_1, λ = 0.709 26 Å)	
formula, M_r	$C_{28}H_{76}Sb_4Si_8$, 1124.61
cryst habit	parallelogram-shaped plate
cryst color	yellow (thick layers are red)
cryst system, space group	triclinic $P\bar{1}$ (No. 2)
unit cell dimens	a = 12.361 (1) Å, α = 108.18 (1)°
	b = 12.981 (1) Å, β = 90.82 (1)°
	c = 17.337 (2) Å, γ = 102.82 (1)°
least-squares fit	75 reflections, θ = 23–25°
packing: V, Z	2567 (1) Å^3, 2
D_{calcd}, D_{exptl}	1.455, 1.48 g cm^{-3}
Intensity Data Collection (Mo K$\bar{\alpha}$, λ = 0.710 69 Å, graphite monochr)	
temp, θ range, (sin θ_{max})/λ	22 °C, 1.5–29.5°, 0.692 Å^{-1}
range of hkl	+17,±18,±24
ref reflctns	three, every 4000 s
loss of intensity (time), corr	10.1% (16 days), linear
reflcns: no. measd, no. indep (R_{int})	14 855, 14 231 (0.0163)
no. of reflcns used, limit	10 133 with $I > 3\sigma(I)$
μ, abs corr	23.0 cm^{-1}, by face indices
range of transm	0.6211–0.1312
Refinement	
no. of var, ratio reflctns/var, last shifts	365, 27.8, <0.06σ
final R, R_w	0.0362, 0.0554
weighting scheme w^{-1}	$\sigma^2(F)$ + 0.003811F^2
final diff Fourier max	1.6–1.2 e/Å^3 near Sb

Table V. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[Sb(CH(SiMe_3)_2)]_4$ (Esd's in Parentheses)

group	atom	x/a	y/b	z/c	U(eq),[a] Å^2
	Sb(1)	0.21494 (2)	0.10734 (2)	0.24369 (2)	0.0448 (1)
	Sb(2)	0.16235 (2)	−0.11344 (2)	0.25546 (2)	0.0447 (1)
	Sb(3)	0.36860 (2)	−0.11455 (2)	0.18788 (2)	0.0442 (1)
	Sb(4)	0.42383 (2)	0.10322 (2)	0.30954 (2)	0.0450 (1)
	C(1)	0.1707 (3)	0.2254 (3)	0.3556 (2)	0.051 (2)
$SiMe_3(1)$	Si(1)	0.0818 (1)	0.1627 (1)	0.42324 (8)	0.0636 (7)
	C(11)	0.0357 (7)	0.2671 (6)	0.5073 (3)	0.115 (5)
	C(12)	0.1631 (6)	0.0902 (6)	0.4710 (3)	0.092 (4)
	C(13)	−0.0495 (4)	0.0647 (5)	0.3638 (3)	0.078 (3)
$SiMe_3(2)$	Si(2)	0.1340 (1)	0.3384 (1)	0.32087 (9)	0.0628 (7)
	C(21)	0.0059 (5)	0.2813 (5)	0.2477 (4)	0.094 (4)
	C(22)	0.2481 (5)	0.3956 (5)	0.2679 (5)	0.110 (5)
	C(23)	0.1164 (9)	0.4585 (6)	0.4088 (4)	0.143 (7)
	C(2)	0.0550 (3)	−0.2330 (3)	0.1458 (2)	0.049 (2)
$SiMe_3(3)$	Si(3)	−0.0051 (1)	−0.1724 (1)	0.07483 (8)	0.0616 (7)
	C(31)	0.1076 (5)	−0.1038 (5)	0.0242 (3)	0.090 (4)
	C(32)	−0.0846 (4)	−0.0670 (5)	0.1307 (3)	0.080 (3)
	C(33)	−0.1042 (6)	−0.2800 (6)	−0.0082 (4)	0.116 (5)
$SiMe_3(4)$	Si(4)	−0.0349 (1)	−0.3401 (1)	0.1838 (1)	0.0670 (7)
	C(41)	0.0511 (6)	−0.3943 (6)	0.2424 (5)	0.120 (6)
	C(42)	−0.1341 (6)	−0.2799 (6)	0.2533 (5)	0.113 (6)
	C(43)	−0.1115 (9)	−0.4640 (6)	0.0998 (5)	0.167 (7)
	C(3)	0.4173 (3)	−0.2395 (3)	0.2359 (2)	0.047 (1)
$SiMe_3(5)$	Si(5)	0.4961 (1)	−0.1864 (1)	0.33875 (9)	0.0635 (7)
	C(51)	0.4035 (6)	−0.1263 (5)	0.4162 (3)	0.090 (4)
	C(52)	0.6283 (4)	−0.0806 (5)	0.3419 (3)	0.085 (3)
	C(53)	0.5360 (7)	−0.3019 (5)	0.3680 (4)	0.118 (6)
$SiMe_3(6)$	Si(6)	0.4636 (1)	−0.3397 (1)	0.14593 (8)	0.0573 (6)
	C(61)	0.5820 (5)	−0.2692 (5)	0.1035 (4)	0.092 (4)
	C(62)	0.3413 (6)	−0.4050 (5)	0.0674 (4)	0.103 (4)
	C(63)	0.5066 (7)	−0.4559 (5)	0.1690 (4)	0.107 (5)
	C(4)	0.5302 (3)	0.2257 (3)	0.2594 (2)	0.048 (2)
$SiMe_3(7)$	Si(7)	0.5767 (1)	0.1694 (1)	0.15628 (8)	0.0592 (7)
	C(71)	0.6571 (4)	0.0624 (4)	0.1512 (3)	0.076 (3)
	C(72)	0.4506 (5)	0.1110 (5)	0.0813 (3)	0.085 (4)
	C(73)	0.6662 (6)	0.2775 (5)	0.1217 (4)	0.105 (5)
$SiMe_3(8)$	Si(8)	0.6319 (1)	0.3237 (1)	0.34816 (9)	0.0601 (6)
	C(81)	0.7192 (5)	0.2480 (5)	0.3876 (4)	0.089 (4)
	C(82)	0.7234 (6)	0.4408 (5)	0.3201 (5)	0.114 (5)
	C(83)	0.5499 (6)	0.3940 (6)	0.4296 (4)	0.121 (5)

[a] U(eq) = $^1/_3$ of the trace of the isotropic U(ij) tensor.

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with δ 1.348 (X) (t, 6 H, CH_3), 1.355 (X') (t, 6 H, CH_3), 1.689 (A), 1.715 (A'), 1.759 (B), 1.785 (B') (8 H, CH_2), ^2J = 12.82 Hz, ^3J = 7.69 Hz.

1,1,3,3-Tetraphenyl-2-ethyltristibane (11). ^{1}H NMR (C_6D_6): δ 1.19 (t, 3 H, CH_3), 1.73 (q, 2 H, CH_2) (^3J = 8.0 Hz), 6.9–7.1, 7.5–7.7 (m, C_6H_5).

1,1,4,4-Tetraphenyl-2,3-diethyltetrastibane (12). ^{1}H NMR (C_6D_6): ABX_3 spin system with δ 1.153 (X) (t, 6 H, CH_3), 1.737 (A), 1.802 (B) (4 H, CH_2), 6.9–7.1, 7.5–7.7 (m, C_6H_5) (^2J = 12.5 Hz, ^3J = 8.0 Hz).

Pentamethyltristibane (13). A mixture of 13.4 g (0.045 mol) of $MeSbBr_2$ and 37.8 g (0.163 mol) of Me_2SbBr is added to 6.6 g (0.27 mol) of Mg filings in 300 mL of THF during 2 h. This produces an exothermic reaction, and the mixture is stirred for 12 h. After evaporation of the solvent, the residue is extracted three times with petroleum ether. Evaporation of the solvent gives 21 g of a mixture of 90 mol % Me_4Sb_2 and 10 mol % 4. Distillation of the mixture gives 18.1 g (73%) of Me_4Sb_2 and a black solid residue. ^{1}H NMR (C_6D_6): δ 1.00 (s, 6 H, $(CH_3)_2Sb$), 1.01 (s, 9 H, CH_3Sb + $(CH_3)_2Sb$). MS (70 eV, 20 °C) (m/z): 440 (M^+), 425 ($M^+ - CH_3$), 410 ($M^+ - 2CH_3$), 395 ($M^+ - 3CH_3$), 365 (Sb_3).

Pentaphenyltristibane (14). Lithium diphenylantimonide was generated by slow addition of 10.6 g (0.03 mol) of Ph_3Sb to a solution of 0.4 g (0.06 mol) of lithium in 150 mL of NH_3 at −80 °C. After the color change, from blue to red, 1.6 g (0.03 mol) of NH_4Cl and 4.0 g (0.015 mol) of $PhSbCl_2$ were added. The solution decolorized, and a brown solid formed. Evaporation of the solvent, washing the solid with water, and drying under reduced pressure gave 8.7 g (77%) of a brown powder containing **14**, $(PhSb)_x$, and Ph_4Sb_2. MS (70 eV, 140 °C) (m/z): **14**, 750 (M^+), 672 ($M^+ - Ph$), 596 ($M^+ - 2\,Ph$); $(PhSb)_x$, 796 (Ph_4Sb_4); Ph_4Sb_2, 552 (M^+). Extraction and crystallization from toluene gave 6.5 g (58%) of Ph_4Sb_2 as yellow crystals. Ph_4Sb_2 was identified by comparison of the NMR spectrum with that of an authentic[22] sample.

Structure Determination of 3. Crystal data as well as details of intensity data collection and refinement are given in Table IV. The density was obtained from neutral buoyancy in aqueous sodium polytungstate solution. The crystal was fixed by gravity and sealed in a glass capillary filled with Ar. The quality and symmetry of the crystal was examined by Weissenberg exposures. Integrated intensities were measured by means of $\omega/2\theta$ scans on a CAD4 diffractometer (Enraf-Nonius).

The structure was solved by a Patterson synthesis (Sb and Si atoms) and completed by Fourier syntheses (C atoms). The refinements were by full matrix (one block only). Hydrogen positions were considered as riding on carbon atoms. The refinement produced good convergence and an even distribution of the variances. Besides several locally written routines, local versions of SHELX-76 and SHELX-86 were used for the calculations, and that of PLUTO-78 was used for Figure 2 (HB-DPS-8/70 equipment at the Zentrum für Datenverarbeitung, Universität Mainz). Table V contains the final parameters.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, Bad Godesberg, and the Fonds der Chemischen Industrie, Frankfurt/Main, for financial support.

Registry No. 1, 73300-46-6; **2a**, 136763-69-4; **2b**, 136763-70-7; **3**, 91043-36-6; **4**, 136763-71-8; **5**, 136763-72-9; **6**, 136763-73-0; **7**, 136782-17-7; **8**, 136763-74-1; **9**, 136763-75-2; **10**, 136763-76-3; **11**, 136763-77-4; **12**, 136763-78-5; **13**, 136763-79-6; **14**, 136763-80-9; $SbBr_3$, 7789-61-9; *i*-Pr_2SbBr, 73300-44-4; $(Me_3Si)_2CHSbCl_2$, 86509-03-7; Me_4Sb_2, 41422-43-9; Et_4Sb_2, 4669-92-5; $MeSbBr_2$, 54553-06-9; Me_2SbBr, 53234-94-9; Ph_3Sb, 603-36-1; Ph_2SbLi, 55085-09-1; $PhSbCl_2$, 5035-52-9; Ph_4Sb_2, 2654-44-6; $(EtSb)_5$, 118399-63-6; $(PrSb)_5$, 118399-67-0; $(t\text{-}BuSb)_4$, 4791-73-5; $(MesSb)_4$, 118456-82-9; $(EtSb)_x$, 68781-08-8; $(PrSb)_x$, 118399-71-6; $(PhSb)_x$, 136763-81-0.

Supplementary Material Available: Tables listing anisotropic thermal parameters, H atom coordinates, complete bond distances and angles, and torsion angles (5 pages); a table of observed and calculated structure factor amplitudes (60 pages). Ordering information is given on any current masthead page.

UV Photolysis of Digermanyliron Complexes and Dynamic NMR Spectroscopy of Alkoxy-Bridged Bis(germylene)iron Products

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Received March 8, 1991

Digermanyliron complexes $[Cp(CO)_2FeGeMe_2GeMe_2R]$, with different terminal substituents (R = Me, Et, or OMe) have been synthesized and subjected to UV irradiation. Deoligomerization is observed to occur, initially generating a highly unstable germyl(germylene)iron complex. Where R is alkyl, a germylene is ejected to yield a germyliron complex. Where R is methoxy, internal base stabilization of the germylene moiety by the donor oxygen atom affords a methoxy-bridged bis(germylene)iron complex which is fluxional with a value of $\Delta G^{\ddagger}_{298}$ for the process of germanium–oxygen bond cleavage and germylene rotation of 88.9 kJ mol^{-1}.

Introduction

The coordination chemistry of divalent group 14 species is now well established in the cases of carbenes,[1-3] germylenes,[4-8] and stannylenes.[4-7] In contrast, silylene chemistry is comparatively sparsely reported, due to their lower stability and greater reactivity. Their existence as reactive intermediates or short-lived products is well-known from various reactions with trapping reagents such as 1,3-butadiene and trimethylsilane.[9] Some donor-sta-

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0276-7333/92/2311-0150$03.00/0