Organometallics **1998,** *17,* 5594−5595

A Cyclotristibane: Synthesis and Crystal Structure of cyclo-[$(Me_3Si)_2CH]_3Sb_3$

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Received July 8, 1998

*Summary: The reaction of $RSbCl_2$ with Li_3Sb at −40 °C gives the three-membered organoantimony ring cyclo-Sb_3R_3 (**1**; R = $(Me_3Si)_2CH$). In solution and in the crystal **1** adopts the structure of a cyclotrialkyltristibane with the substituents in the cis and trans positions.*

Monocyclic organostibanes cyclo-Sb_nR_n ($n = 3-6$)[1] for which the crystal structures are known are restricted to the ring sizes four[2] and six.[3] We report here the synthesis and the crystal structure of cyclo-Sb_3R_3 (**1**; R = $(Me_3Si)_2CH$), a monocyclic triorganotristibane.

Three-membered antimony rings are known in polycyclic systems.[4] Attempts to prepare the three-membered ring **1** were carried out in our group some years ago.[5] The reaction of $RSbCl_2$ with magnesium in tetrahydrofuran (THF) gave mixtures containing **1** as well as cyclo-$[(Me_3Si)_2CH]_4Sb_4$. However, **1** was not isolated because of difficulties with the chromatographic separation and its low tendency to crystallize from the mixture.

We have now found that **1** is formed selectively in 58% yield by reaction of $RSbCl_2$ with Li_3Sb in THF at −40 °C. During the workup **1** is first obtained as an orange, viscous liquid that solidifies slowly at low temperature to form a polycrystalline material. The preparation of orange, air-sensitive single crystals of **1** was achieved by seeding a supersaturated solution in petroleum ether. Under anaerobic conditions the crystals and also the solutions of **1** in hydrocarbons are stable for several weeks. In solution the three-membered ring also is relatively stable on exposure to UV radiation. It cannot be converted into the corresponding four-membered ring by photochemical reaction in C_6D_6. In contrast, UV irradiation of cyclo-$[(Me_3Si)_2CH]_4Sb_4$ gives **1** in quantitative yield.

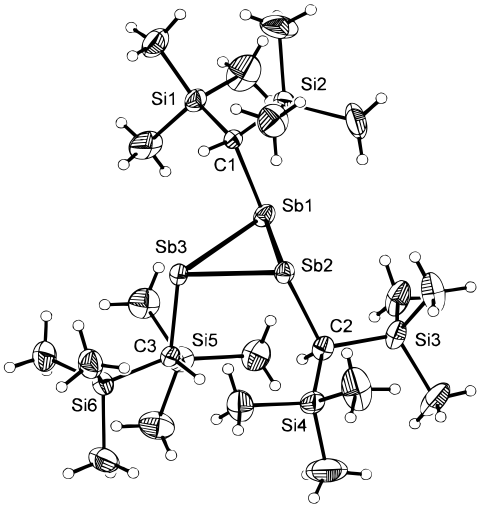

Figure 1. Molecular structure of **1** in the crystal state. The ellipsoids represent a probability of 50%. Selected bond lengths (Å) and angles (deg): Sb(1)−Sb(2) = 2.8320(5), Sb(2)−Sb(3) = 2.8453(6), Sb(1)−Sb(3) = 2.8188(6), Sb−C(mean) = 2.205(5); Sb(1)−Sb(2)−Sb(3) = 59.537(14), Sb(1)−Sb(3)−Sb(2) = 59.998(14), Sb(2)−Sb(1)−Sb(3) = 60.465(15), C(1)−Sb(1)−Sb(2) = 97.03(12), C(1)−Sb(1)−Sb(3) = 90.00(12), C(2)−Sb(2)−Sb(1) = 101.66(12), C(2)−Sb(2)−Sb(3) = 103.43(13), C(3)−Sb(3)−Sb(1) = 111.33(13), C(3)−Sb(3)−Sb(2) = 105.75(12).

The structure of **1** in the solid state was determined by single-crystal X-ray diffraction. The molecular structure is depicted in Figure 1. The three antimony atoms form an almost equilateral triangle. The alkyl substituents are in cis and trans positions. The bulky Me_3Si groups of all substituents are directed outward and shield the molecules from each other. Consequently, close intermolecular contacts between the antimony atoms are not observed in the crystalline **1**. The Sb−Sb bond lengths vary between 2.8188(6) and 2.8453(6) Å. This is not unusual; note in comparison cyclo-Sb_4R_4 (Sb−Sb = 2.822(1)−2.878(1) Å)[2d] and Sb_8R_4 (Sb−Sb = 2.784(4)−2.861(4) Å)[6] with R = $(Me_3Si)_2CH$ and Sb_3R' (Sb−Sb = 2.796(3), 2.817(3) Å)[4b] with R′ = $MeC(CH_2)_3$. A slightly shorter Sb−Sb distance has been reported for the iron complex $(CO)_4Fe(SbR)_2$ with R = $(Me_3Si)_2CH$ (Sb−Sb = 2.774(1) Å).[7] The C−Sb−Sb angles of **1** vary between 90 and 112°, with larger angles at the antimony atoms with substituents in cis positions. A close relation exists between the structure of **1** and the analogous phosphorus ring compound.[8]

The cis−trans arrangement of the substituents also is recognized in the ^1H and ^{13}C NMR spectra of solutions

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10.1021/om980575t CCC: $15.00

of **1** in C_6D_6. There are three singlets of equal intensity for the methyl protons, as expected, due to the diastereotopy of the Me_3Si groups of the substituents in cis positions. The methine protons appear in the correct ratio of intensities of 1:2 between each other. The strong high-field shift of the methine proton at the substituents in trans positions is remarkable.

Experimental Section. The reactions and manipulations were performed under an inert atmosphere of dry argon.

Li_3Sb was prepared in liquid ammonia (50 mL) from 86 mg (12.4 mmol) of lithium and 500 mg (4.11 mmol) of antimony powder.[9] After removal of NH_3 the reagent was suspended in 50 mL of THF. With strong stirring, a solution of $(Me_3Si)_2CHSbCl_2$[10] (2.17 g, 6.16 mmol) in THF (25 mL) was added dropwise at −70 °C to this suspension. Afterward, the reaction mixture was stirred for 4 h at −40 °C and 60 h at ambient temperature. The solvent was removed under reduced pressure, and the residue was washed with 2 × 250 mL of petroleum ether. The petroleum ether extracts were combined, reduced to 10 mL, and loaded onto a chromatography column (Al_2O_3, activity level II, 15 × 2 cm). With petroleum ether an intense orange fraction was obtained. The first 25 mL contained pure **1**. This solution was collected. Removal of the solvent under reduced pressure gave 1.00 g (58% yield) of **1** as a viscous oil that solidified within several days at −28 °C to an orange microcrystalline solid; mp 94−96 °C.

Anal. Calcd for $C_{21}H_{57}Sb_3Si_6$ (843.45): C, 29.90; H, 6.81. Found: C, 29.82; H, 6.71. MS (CI+, NH_3; *m/z*, ion, relative intensity (%)): 1125 $[[(Me_3Si)_2CHSb]_4^+ + H]$ (3), 843 $[M^+ + H]$ (100), 601 $[[(Me_3Si)_2CH]_3Sb^+ + H]$ (47), 458 $[[(Me_3Si)_2CH]_2Sb^+ + NH_4]$ (19), 441 $[[(Me_3Si)_2CH]_2Sb^+ + H]$ (20). ^1H NMR (200 MHz, C_6D_6, 25 °C): δ −0.09 (s, $^2J(Si,H) = 8.1$ Hz, 1H, *trans*-CH), 0.27 (s, $^2J(Si,H) = 6.3$ Hz, 18H, *trans*-CH_3), 0.31 (s, $^2J(Si,H) = 6.4$ Hz, 18H, *cis*-CH_3^a), 0.32 (s, 2H, *cis*-CH), 0.33 (s, $^2J(Si,H) = 6.4$ Hz, 18 H, *cis*-CH_3^b). ^{13}C NMR (50 MHz, C_6D_6, 25 °C): δ −5.5 ($^1J(Si,C) = 40.4$ Hz, *cis*-CH), −2.7 ($^1J(Si,C) = 41$ Hz, *trans*-CH), 3.0 ($^1J(Si,C) = 51$ Hz, *cis*-CH_3^b), 3.7 ($^1J(Si,C) = 51$ Hz, *trans*-CH_3), 4.1 ($^1J(Si,C) = 51$ Hz, *cis*-CH_3^a). C,H correlation with use of HSQC and HMBC spectra, and the superscripts a and b refer to the diastereotopic methyl groups.

The second part of the fraction (500 mL) contained 0.18 g of an orange solid consisting of **1**, cyclo-Sb_4R_4, and unidentified products. From a supersaturated solution of **1** in petroleum ether, even after 4 weeks at −28 °C no solid precipitated. Needle-shaped single crystals grew from this solution only after seeding with solid polycrystalline **1**.

Photochemical Experiment. In an NMR tube (5 mm diameter) a solution of cyclo-$[(Me_3Si)_2CH]_4Sb_4$ (38 mg) in C_6D_6 (1 mL) was exposed to UV radiation (TQ 150 mercury lamp Original Hanau, distance to light source 20 mm) for 30 min. After this experiment the formation of pure **1** was shown by NMR spectroscopy.

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

formula	$C_{21}H_{57}Sb_3Si_6$
fw	843.5
color	orange
cryst size, mm	0.5 × 0.4 × 0.4
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	9.2000(10)
b, Å	35.765(3)
c, Å	12.357(2)
α, deg	90
β, deg	110.760(10)
γ, deg	90
V, Å^3	3801.9(8)
Z	4
d_{calcd}, g cm^{-3}	1.474
μ(Mo Kα), mm^{-1}	2.314
scan method	$\omega/2\theta$
$F(000)$	1680
scan range (deg)	$2.6 \le \theta \le 27.5$
no. of measd data	9867
no. of unique data	8120 ($R_{int} = 0.0439$)
no. of params	292
no. of data with $I > 2\sigma(I)$	4684
wR2(all data)[a]	0.0985
R1(all data)[a]	0.0589
wR2($I > 2\sigma(I)$)[a]	0.0903
R1($I > 2\sigma(I)$)[a]	0.0408
GOF on F^2	1.028
residual density, e Å^{-3}	+0.938, −0.847

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

NMR data for cyclo-$[(Me_3Si)_2CH]_4Sb_4$: ^1H NMR (200 MHz, C_6D_6, 25 °C) δ 0.34 (s, $^2J(Si,H) = 6.3$ Hz, 18 H, CH_3), 0.92 (s, 1 H, CH); ^{13}C NMR (50 MHz, C_6D_6, 25 °C) δ 1.37 (CH), 4.13 (CH_3).

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 ($\lambda = 0.710\,73$ Å). For this purpose a crystal was attached with Kel-F oil to a glass fiber and cooled under a nitrogen stream to 173 K.

The structure was solved, after Lp and absorption correction (ψ-scans), by direct methods. All non-hydrogen atoms 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.[11] The drawing was created with the XP program of the SHELXTL program system.[12]

Acknowledgment. The support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Tables of crystal data and structure refinement details, atom coordinates and *U* values, bond distances and angles, and anisotropic thermal parameters and figures giving additional views of the structure of **1** (9 pages). See any current masthead page for ordering information and Internet access instructions.

OM980575T

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