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Journal of Organometallic Chemistry 608 (2000) 60–62

Crystal structures of tris(trimethylsilyl)stibine and pentacarbonyl(tris(trimethylsilyl)stibine)chromium

H.J. Breunig *, M. Jönsson, R. Rösler, E. Lork

Institut für Anorganische und Physikalische Chemie der Universität Bremen, Fachbereich 2, Postfach 330 440, D-28334 Bremen, Germany

Received 22 February 2000; received in revised form 10 May 2000

Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday

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Abstract

The structures of $(Me_3Si)_3Sb$ (**1**) and $(Me_3Si)_3SbCr(CO)_5$ (**2**) have been determined by single-crystal X-ray diffraction. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silicon; Antimony; Chromium; X-ray diffraction

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1. Introduction

Tris(trimethylsilyl)stibine (**1**) is an important antimony reagent featuring the excellent leaving group properties of the Me_3Si group. The compound was synthesized for the first time by Amberger and Salazar in 1967 [1] and since then it has been used as a synthon for the formation of various antimony–element bonds [2–9] and as a ligand in main group [6–10] and transition metal complexes [11,12]. The structures of tris(silyl)-stibines and other derivatives of the type $(R_3Si)_3E$ ($E =$ pnicogen; $R =$ alkyl, aryl, H, etc.) have received attention since the 1960s when controversial reports of planar or pyramidal central Si_3E cores of some of these compounds appeared [13]. Although the structural evidence is not complete, it is clear now that only the tris(silyl)amines have a planar center but all the heavier tris(silylpnicogens) have a pyramidal central core.

This was proven for $(H_3Si)_3Sb$ by electron diffraction in the gas phase [14] already in 1968 and more recently for $(Me_2PhSi)_3Sb$ by single crystal X-ray analysis by Sladek and Schmidbaur [13].

Our interest in the structures of **1** and $(Me_3Si)_3$-$SbCr(CO)_5$ (**2**) was prompted by the observation [12,15] that **2** and the analogous molybdenum and tungsten compounds act as initiators for the polymerization of THF. Common mechanistic concepts for this reaction consider a nucleophilic attack of the THF molecule on a strong Lewis acid and hence we looked for Lewis acidic sites in **2** [12,15]. Crystal structures of transition metal complexes with **1** as a ligand have not been reported before. X-ray structure analyses of related molecules feature several main group element complexes with **1** as ligand [7–10] or pentacarbonyl chromium complexes with other stibine ligands like $Ph_3SbCr(CO)_5$ [16].

2. Results and discussion

2.1. Crystal structure of tris(trimethylsilyl)stibine (1)

Single crystals of **1** were grown from the melt at −28°C. The structure was determined by single crystal X-ray diffractommetry. The crystallographic data are given in Table 1. The crystals contain two independent and slightly different molecules (**1a**, **1b**) in the unit cell. The molecular structure of one of these molecules (**1a**) is shown in Fig. 1. The Sb–Si bond lengths vary between 255.99(11) and 256.54(11) pm (**1a**) or 256.09(11) and 256.36(10) pm (**1b**). The Si–Sb–Si angles (**1a**, 98.05(4)–99.37(4)°; **1b** (98.65(4)–100.31(3)°) prove the pyramidal structure and reflect the less strained envi-

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* Corresponding author. Tel.: +49-421-2182266; fax: +49-421-2184042.

E-mail address: breunig@chemie.uni-bremen.de (H.J. Breunig).

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PII: S0022-328X(00)00366-1

ronment around the pnicogen atom, compared to the phosphorus analog (($(Me_3Si)_3P$, Si–P–Si angles 105.8(1)–106.5(1)° [17]). The C–Si–C angles range from 107.8(2)° to 109.8(2)° while the C–Si–Sb angles lie between 106.84(16)–115.59(15)°. Similar geometric parameters have been found for $(Me_2PhSi)_3Sb$ (Si–Sb 255.43(8)–256.19(8) pm; Si–Sb–Si 99.81(3), 100.76(3)° [13]).

Table 1
Crystallographic data and measurements for **1** and **2**

	1	**2**
Empirical formula	$C_9H_{27}Si_3Sb$	$C_{14}H_{27}O_5Si_3CrSb$
Formula weight	341.33	533.38
Crystal sytem	Triclinic	Trigonal
Space group	$P\bar{1}$	$P3(2)$
Unit cell dimensions		
a (pm)	963.5(2)	948.90(10)
b (pm)	1233.10(10)	948.90(10)
c (pm)	1590.0(2)	2286.7(3)
α (°)	111.060(10)	90
β (°)	96.280(10)	90
γ (°)	90.430(10)	120
Unit cell volume (nm^3)	1.7501(4)	1.7831(4)
Z	4	4
F(000)	696	804
Crystal size (mm^3)	$1.0 \times 0.7 \times 0.5$	$0.7 \times 0.4 \times 0.4$
Color	Colorless	Yellow
D_{calc} (g cm^{-3})	1.295	1.490
Absorption coefficient (mm^{-1})	1.753	1.762
Absorption correction	Empirical [24]	None
θ Range (°)	2.61–27.50	2.63–27.51
Index range (°)	$-12 \leq h \leq 1$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$	$-1 \leq h \leq 12$, $-12 \leq k \leq 11$, $-29 \leq l \leq 29$
Reflections collected	8410	9079
Independent reflections	6905 ($R_{int} = 0.0387$)	5026 ($R_{int} = 0.0646$)
Refinement method	Full-matrix least-squares on F^2 [21]	Full-matrix least-squares on F^2 [21]
Data/restraints/ parameters	6905/0/255	5026/1/228
GOF	1.058	1.008
Final R values [$I > 2\sigma(I)$]	$R_1 = 0.0307$, $wR_2 = 0.0838$	$R_1 = 0.0332$, $wR_2 = 0.0807$
R Values (all data)	$R_1 = 0.0347$, $wR_2 = 0.0862$	$R_1 = 0.0374$, $wR_2 = 0.0829$
Absolute structural parameter		$-0.02(2)$
Absorption coefficient	0.0059(3)	0.0026(4)
Largest difference peak and hole (e Å^{-3})	0.800 and -0.749	0.622 and -0.608

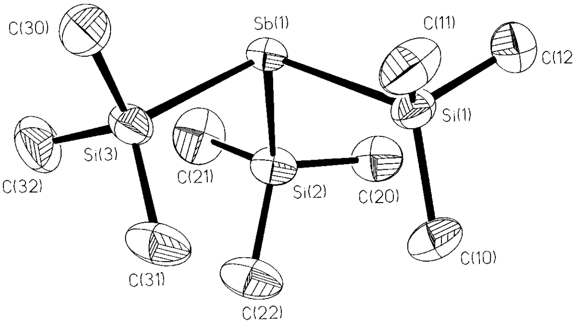

Fig. 1. Structure of **1** (molecule A). Selected bond lengths (pm) and angles (°). Molecule A: Sb(1)–Si(1) 256.54(11), Sb(1)–Si(2) 256.63(11), Sb(1)–Si(3) 255.99(11), Si(1)–C 186.6(4)–187.3(4), Si(2)–C 186.3(5)–187.3(4), Si(3)–C 186.9(4)–187.0(4), Si(1)–Sb(1)–Si(2) 98.05(4), Si(3)–Sb(1)–Si(1) 99.29(4), Si(3)–Sb(1)–Si(2) 99.37(4), C–Si(1)–Sb(1) 106.84(16)–115.59(15), C–Si(1)–C 107.8(2)–109.0(2), C–Si(2)–Sb(1) 107.78(16)–114.94(14), C–Si(2)–C 108.0(3)–109.3(2), C–Si(3)–Sb(1) 107.60(14)–115.11(15), C–Si(3)–C 108.0(2)–109.8(2). Molecule B: Sb(2)–Si(4) 256.36(10), Sb(2)–Si(5) 256.62(11), Sb(2)–Si(6) 256.09(11), Si(4)–C 186.4(4)–187.0(4), Si(5)–C 186.4(4)–188.4(4), Si(6)–C 186.9(4)–187.4(4), Si(4)–Sb(2)–Si(5) 100.31(3), Si(6)–Sb(2)–Si(4) 98.97(4), Si(6)–Sb(2)–Si(5) 98.65(3), C–Si(4)–Sb(2) 106.47(14)–114.68(14), C–Si(4)–C 108.26(19)–109.7(2), C–Si(5)–Sb(2) 106.44(16)–114.80(14), C–Si(5)–C 108.0(2)–109.5(2), C–Si(6)–Sb(2) 106.77(16)–115.78(14), C–Si(6)–C 108.4(2)–109.2(2).

*2.2. Crystal structure of tris(trimethylsilyl)stibine pentacarbonyl chromium (**2**)*

Single crystals of **2** were obtained by cooling a solution of **2** in petroleum ether to −28°C. The crystal data and the data for the refinement of the structure are given in Table 1. The structure of the molecule that is shown in Fig. 2 has the expected geometry. It consists of the stibine ligand with a trigonal pyramidal Si_3Sb skeleton bonded to the square pyramidal $Cr(CO)_5$ unit. The Sb–Cr bond in **2** (271.67(8) pm) is longer than in other known pentacarbonyl chromium complexes with antimony ligands: $MeBr_2SbCr(CO)_5$, 255.6(2) pm [18]; $Ph_3SbCr(CO)_5$, 261.70(3) pm [16]; $Ph_2SbSbPh_2Cr(CO)_5$ 262.6(1) pm [19]; $Ph_2SbSSbPh_2Cr(CO)_5$, 259.8(3) pm [20]. The Sb–Si bond lengths in **2** (256.64(14)–257.73(14) pm) are similar to the corresponding values in **1** (255.99(11)–256.63(11) pm). The differences between the bond angles around the silicon atoms in **1** and **2**, e.g. mean C–Si–C angles **1** (108.7°), **2** (110.6°) are not significant. The main stereochemical effect of the complexation on the ligand is the increase of the mean Si–Sb–Si angles from 99.2° in the free ligand to 103.6° in the complex **2**. This effect is not unusual. It is also observed when **1** is coordinated to a main group acceptor molecule (cf. $(Me_3Si)_3Sb–AlEt_3$, mean Si–Sb–Si 103.6° [7]) and may result from a change of the character of the bonding orbitals of the antimony atom which have more p character in the free ligand and more sp^3 character in the complexes. It is tempting to correlate this structural change between **1** and **2** with the unexpected reactivity of **2** as initiator of the THF polymerization. In fact an attack of a THF molecule in the expected position opposite to the Sb–Cr bond might be facilitated by the widening of the Si–Sb–Si angles. Nevertheless the antimony atom in **2** still appears to be very well protected by the bulky Me_3Si groups and the concept of a strong electrophilic activity of the antimony center in **2** remains speculative. It is more likely that a specific trans-influence of the $(Me_3Si)_3Sb$-ligand is responsible for the unusual reactivity of the complex.

3. Experimental

Details of the crystal structure determination and refinement are given in Table 1. Data were collected at 173(2) K on a Siemens P4 four-circle diffractometer using graphite monochromated, Mo–K_α radiation (λ = 71.073 pm) and $\omega/2\theta$ scan. Reference reflections were measured every 197 reflections. Calculations were carried out with the SHELXL-97 program package [21]. The drawings were created with the program DIAMOND [22] and the XP-program of the SHELXTL program system [23].

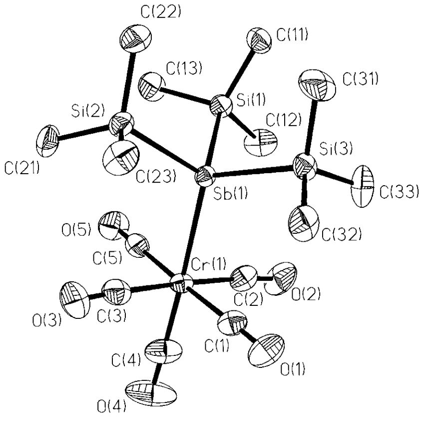

Fig. 2. Structure of **2**. Selected bond lengths (pm) and angles (°). Sb(1)–Cr(1) 271.67(8), Sb(1)–Si(1) 257.73(14), Sb(1)–Si(2) 257.13(14), Sb(1)–Si(3) 256.64(14), Cr(1)–C 188.6(6)–191.2(6), Cr(1)–C(4) 184.7(6), Si(1)–C 184.8(6)–187.0(6), Si(2)–C 186.2(6)–187.2(6), Si(3)–C 184.3(7)–186.4(6), C–O 113.6(7)–115.8(7), C(4)–O(4) 115.5(8), Si(1)–Sb(1)–Si(2) 103.42(5), Si(3)–Sb(1)–Si(1) 103.34(5), Si(3)–Sb(1)–Si(2) 103.89(5), Si(1)–Sb(1)–Cr(1) 113.59(4), Si(2)–Sb(1)–Cr(1), 116.38(4), Si(3)–Sb(1)–Cr(1) 114.67(4), C–Si(1)–Sb(1) 107.7(2)–111.8(2), C–Si(1)–C 108.4(3)–111.0(3), C–Si(2)–Sb(1) 107.7(2)–110.0(2), C–Si(2)–C 109.8(3)–110.9(3), C–Si(3)–Sb(1) 104.9(3)–111.2(2), C–Si(3)–C 108.2(4)–112.5(3), Sb(1)–Cr(1)–C 86.81(16)–93.07(17), Sb(1)–Cr(1)–C(4) 177.6(2), C–Cr(1)–C 86.6(2)–93.6(2), C–Cr(1)–C *trans*-C 176.0(2)–177.0(2), C(4)–Cr(1)–C *cis*-Sb 89.2(3)–91.0(2), O–C–Cr(1) 175.4(5)–177.6(5), O(4)–C(4)–Cr(1) 177.4(7).

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC-142408 for compound **1** and CCDC-142409 for compound **2**. Copies of this information can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)

Acknowledgements

We thank the Fonds der Chemischen Industrie for financial support.

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