Organometallics **2008,** *27,* 2169–2171

Syntheses and Structures of Ar$_3$Sb$_5$ and Ar$_4$Sb$_4$ Compounds (Ar = C$_6$H$_3$-2,6-(CH$_2$NMe$_2$)$_2$)

Libor Dostál,* Roman Jambor, Aleš Růžička, and Jaroslav Holeček

Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, nám. Čs. Legií 565, Pardubice 53210, Czech Republic

Received March 11, 2008

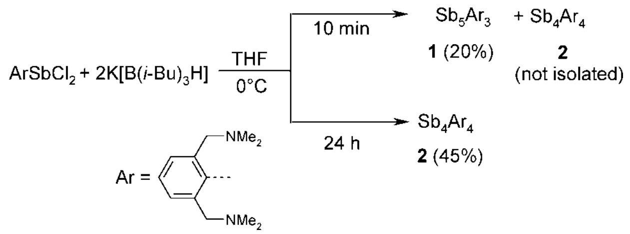
Summary: The Sb$_5$Ar$_3$ (Ar = N,C,N chelating ligand, C$_6$H$_3$-2,6-(CH$_2$NMe$_2$)$_2$) trigonal bipyramidal cluster was obtained as one of two products (along with a tetrameric Sb$_4$Ar$_4$ compound) by reduction of the parent ArSbCl$_2$ compound.

Introduction

Considerable progress has recently been achieved in the field of low-valent organoantimony compounds in formal oxidation states lower than +III, and obtained results have been reviewed.[1] Although successful isolation of "naked" monomeric stibinidenes is still lacking, dimeric distibenes, *trans*-Ar′Sb=SbAr′ (Ar′ = terphenyl-type ligands), were obtained by Okazaki, Tokitoh, and Power using effective steric protection.[2] There are many examples of monocyclic stibines R$_n$Sb$_n$ (n = 3−6), where the ring size strongly depends on the group R, and many of these compounds display ring−ring equilibrium in solution.[3] Polycyclic stibines R$_n$Sb$_m$ ($n < m$) constitute a very interesting class of low-valent organoantimony compounds. The only examples of these species, R$_4$Sb$_8$, R$_6$Sb$_8$, and R$_5$Sb$_7$ (R = (Me$_3$Si)$_2$CH), were prepared as side products by the reduction of corresponding chloride RSbCl$_2$ with Mg or by treating of RSbH$_2$ with SbCl$_3$ in the presence of pyridine. The molecular structures of the first two compounds were determined by X-ray diffraction.[4]

Dehydrocoupling reactions have recently been recognized as a convenient path to element−element bond formation.[5] Using this synthetic strategy, we report here on the synthesis of the Sb$_5$ cluster Sb$_5$Ar$_3$ (**1**) (Ar = C$_6$H$_3$-2,6-(CH$_2$NMe$_2$)$_2$). Compound **1** features a trigonal bipyramidal framework and, to our knowledge, represents the first organoantimony cluster of the general formula R$_3$Sb$_5$. This coordination arrangement of five antimony atoms is unknown even among inorganic antimony polycations and polyanions,[6] and the isolation of the stable Sb$_5^{3+}$ cation (as an analogue of the known Bi$_5^{3+}$ cation) remained unsuccessful, although its presence was proposed.[7]

Scheme 1. Preparation of Sb$_5$Ar$_3$ (1) and Sb$_4$Ar$_4$ (2)



The reaction of ArSbCl$_2$[8] with 2 equiv of K[B(i-Bu)$_3$H] in THF (Scheme 1) gives, depending on the reaction time, a mixture of two products, **1** and tetrameric Sb$_4$Ar$_4$ (**2**) (10 min), or compound **2** as a sole product (24 h).[9] Compound **1** can be isolated from the reaction mixture as red X-ray quality crystals by crystallization from hexane solution at room temperature in a low yield of 20% (**1** displayed only limited solubility in hydrocarbons after crystalization, so compound **2** could be easily washed out if necessary). It is likely that the reduction of ArSbCl$_2$ proceeds via intermediate formation of the corresponding organoantimony hydride ArSbH$_2$, which, in turn, reductively eliminates hydrogen gas and ArH and gives compound **1**.

---

* Corresponding author. E-mail: libor.dostal@upce.cz. Fax: +420 466037068. Tel.: +420 466037163.

(1) (a) Balázs, L.; Breunig, H. J. *Coord. Chem. Rev.* **2004**, *284*, 603. (b) Tokitoh, N. *Pure Appl. Chem.* **1999**, *71*, 495. (c) Breunig, H. J.; Rösler, R. *Chem. Soc. Rev.* **2000**, *29*, 403. (d) Sasamori, T.; Tokitoh, N. *Dalton Trans.* **2008**, 1395.

(2) (a) Tokitoh, N.; Arai, Y.; Sasamori, T.; Okazaki, R.; Nagase, S.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 433. (b) Twamley, B.; Solfield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 3357.

(3) For examples see: (a) Balázs, G.; Balázs, L.; Breunig, H. J.; Lork, E. *Organometallics* **2003**, *22*, 2919. (b) García, F.; Hopkins, A. D.; Kowenicki, R. A.; McPartlin, M.; Tesa, Y. *Dalton Trans.* **2004**, 2051. (c) Breunig, H. J.; Balázs, L. *Organometallics* **2004**, *23*, 304.

(4) (a) Balázs, G.; Breunig, H. J.; Lork, E.; Mason, S. *Organometallics* **2003**, *22*, 576. (b) Breunig, H. J.; Rösler, R.; Lork, E. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2237.

(5) (a) Waterman, R.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2006**, *45*, 2926. (b) Rivard, E.; Steiner, J.; Fettinger, J. C.; Guiliani, J. R.; Augustine, M. P.; Power, P. P. *Chem. Commun.* **2007**, 4919. (c) Jambor, R.; Kašná, B.; Kirschner, K. N.; Schürmann, M.; Jurkschat, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 650.

(6) (a) Lindsjö, M.; Fischer, A.; Kloo, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 2540. (b) Kuznetsov, A. N.; Popovnik, B. A.; Stahl, K.; Lindsjö, M.; Kloo, L. *Eur. J. Inorg. Chem.* **2005**, 4907. (c) Adolphson, D. G.; Corbett, J. D.; Merryman, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 7234. (d) Bolle, U.; Tremel, W. *J. Chem. Soc. Chem. Commun.* **1992**, 91.

(7) Ulvenlund, S.; Stahl, K.; Kloo, L. *Inorg. Chem.* **1996**, *35*, 223.

(8) Atwood, D. A.; Cowley, A. H.; Ruiz, J. *Inorg. Chim. Acta* **1992**, *198−200*, 271.

(9) Preparation of Sb$_5$Ar$_3$ (**1**): A solution of K[B(i-Bu)$_3$H] (2.35 mL, 2.35 mmol, 1 M solution in THF) was added to a precooled (0 °C) solution of ArSbCl$_2$[8] (0.450 g, 1.17 mmol) in 20 mL of THF, immediately warmed to rt, and stirred for an additional 10 min. The color of the solution turned to red-orange, and evolution of hydrogen was obvious. Then the solvent was evaporated *in vacuo* and the remaining mixture was extracted with 30 mL of hexane. The suspension was filtered, and the volume of the filtrate was reduced to ca. 10 mL. After 5 h, compound **1** was isolated as red crystals after filtration and washing with hexane (0.056 g, 20%), mp 167 °C (dec). ^{1}H NMR (C$_7$D$_8$; 500.13 MHz): δ (ppm) 2.14 (s, 12H, N(CH_3)$_2$), 3.96 (s, 4H, CH_2N), 6.95 (d, 2H, Ar-H3,5), 7.02 (t, 1H, Ar-H4). ^{13}C NMR (C$_7$D$_8$; 125.77 MHz): δ (ppm) 44.0 (N(CH$_3$)$_2$), 66.7 (CH$_2$N), 126.6 (Ar-C4), 127.7 (Ar-C3,5), 146.8 (Ar-C1), 148.5 (Ar-C2,6). UV−vis (hexane, nm): 338 (shoulder) and 435 (shoulder). Preparation of Sb$_4$Ar$_4$ (**2**): Procedure similar as for **1**: THF solution of K[B(i-Bu)$_3$H] (3.24 mL, 3.24 mmol, 1 M solution); ArSbCl$_2$[8] (0.620 g, 1.61 mmol) in 40 mL of THF, 24 h. Compound **1** was isolated as yellow-orange crystals from a saturated hexane solution at 0 °C (0.228 g, 45%), mp 156 °C (dec). Anal. Calcd for C$_{48}$H$_{76}$N$_8$Sb$_4$: C, 46.0; H 6.1. Found: C, 46.3; H 6.4. ^{1}H NMR (C$_7$D$_8$; 500.13 MHz): δ (ppm) 2.00 (s, 12H, N(CH_3)$_2$), 3.86 (s, 4H, CH_2N), 7.11 (t, 1H, Ar-H4), 7.28 (d, 2H, Ar-H3,5). ^{13}C NMR (C$_7$D$_8$; 125.77 MHz): δ (ppm) 45.2 (N(CH$_3$)$_2$), 69.9 (CH$_2$N), 126.2 (Ar-C4), 128.3 (Ar-C3,5), 140.6 (Ar-C1), 147.7 (Ar-C2,6). UV−vis (hexane, nm): 368 (shoulder).

10.1021/om800227m CCC: $40.75

Similar ligand and hydrogen elimination from an organotin(II) hydride was detected previously.[5b]

Indeed, ^{1}H and ^{13}C NMR spectra of the mother liquor after isolation of **1** indicate the presence of a significant amount of free ArH ligand together with the second product, **2**. Compound **2** was preferably isolated after prolonged reaction time as the only product in the form of orange crystals in 45% yield.[9] These findings point to a limited stability of **1** in the reaction mixture, and only an immediate isolation leads to compound **1** in reasonable yield. Both compounds **1** and **2** were characterized by a combination of ^{1}H and ^{13}C NMR, elemental analysis (for **2**), UV–vis spectroscopy, and X-ray crystallography.[10]

The molecular structure of **1** was unambiguously determined by X-ray diffraction (Figure 1) and shows a trigonal-bipyramidal framework of five antimony atoms. Each of the antimony atoms Sb(1) to Sb(3) in the equatorial plane carry one N,C,N chelating ligand, and the other two antimony atoms, Sb(4) and Sb(5), forming axial positions, remain "naked", or ligand free. The distances within the equatorial plane (Sb(1) to Sb(3)) lie between 3.7658(7) and 3.8558(7) Å. The Sb–Sb distances describing connection between the vertices (Sb(4), Sb(5) atoms) and the antimony atoms (Sb(1–3)) in the equatorial plane fall within the narrow interval 2.8459(6)–2.8699(7) Å. The distance between both axial atoms Sb(4)$\cdots$Sb(5) is 3.6664(8) Å, still shorter than $\sum_{\text{vdW}}$(Sb–Sb) = 4.52 Å. The internal ring angles in the equatorial plane are in the range 118.9(1)–121.9(2)°, close to the ideal value of 120°. The virtual angle Sb(4)–centroid of TBP–Sb(5) is 179.0(2)°, and although it deviates from linearity, the overall geometry of the Sb_5 core is very close to D_{3h} symmetry.

The Sb–C(ligand) distances are 2.181(6)–2.202(7) Å, resembling expected values for covalent bonds. Regarding the six Sb–N intramolecular coordinations, they are in the region 2.826(7)–3.143(6) Å, approaching the limit of the weakest intramolecular interactions, which can be taken into account ($\sum_{\text{vdW}}$(Sb–N) = 3.74 Å). Thus, one can only tentatively assume that stabilization of the Sb_5 framework can be rationalized only by intramolecular dative Sb–N bonds. Most probably, the stabilization is based on synergic steric and electronic influences of the pincer ligands.

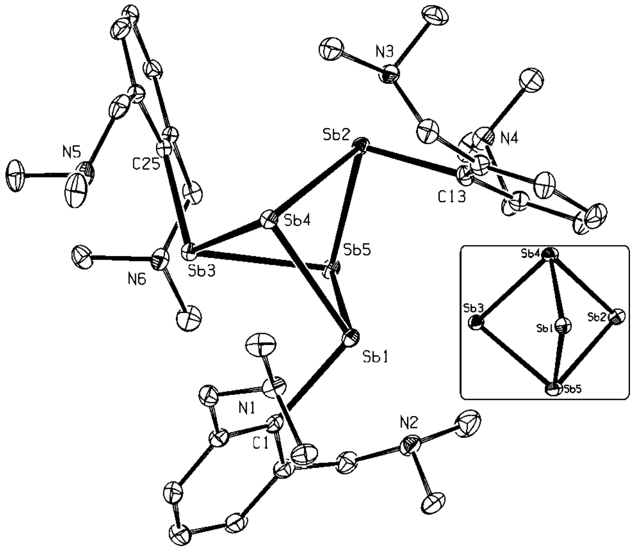


Figure 1. ORTEP plot of a molecule of **1** showing 30% probability displacement ellipsoids and the atom-numbering scheme and view of the central Sb_5 framework. Hydrogen atoms were omitted for clarity. Selected bond lenghts (Å) and angles (deg): Sb(1)–Sb(2) 3.7658(7), Sb(1)–Sb(3) 3.7811(7), Sb(2)–Sb(3) 3.558(7), Sb(4)–Sb(1) 2.8584(7), Sb(4)–Sb(2) 2.8459(6), Sb(4)–Sb(3) 2.8699(7), Sb(5)–Sb(1) 2.8512(6), Sb(5)–Sb(2) 2.8667(7), Sb(5)–Sb(3) 2.8655(6), Sb(4)$\cdots$Sb(5) 3.6664(8), Sb(1)–C(1) 2.202(7), Sb(2)–C(13) 2.195(6), Sb(3)–C(25) 2.181(6), Sb(1)–N(1) 3.143(6), Sb(1)–N(2) 2.826(7), Sb(2)–N(3) 2.859(7), Sb(2)–N(4) 3.146(6), Sb(3)–N(5) 2.967(6), Sb(3)–N(6) 2.834(6); the internal angle in the equatorial Sb_3 plane, Sb(1)–centroid–Sb(2) 118.9(1), Sb(1)–centroid–Sb(3) 119.2(1), Sb(2)–centroid–Sb(3) 121.9(2), angle between axial positions Sb(4)–centroid–Sb(5) 179.0(2), average angle of N–Sb–N angles 115.4(2).

Wade's rules have proven to be a convenient tool for estimation of the geometries of main group clusters.[11] The Sb_5^{3+} cation obeys these rules and should possess a trigonal-bipyramidal geometry. If we take N,C,N chelating ligands as monoanionic substituents $[C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]^-$, the central trigonal-bipyramidal Sb_5 core of **1** obeys Wade's rules.

In general, compound **1** represents only the second example (and the first neutral and organometallic) of a trigonal-bipyramidal cluster within the group 15 elements and, to our knowledge, a very rare example of a neutral trigonal-bipyramidal organometallic cluster in the field of all main group elements[12] (a few inorganic charged Zintl-type compounds with this shape have recently been isolated[7,13]).

The molecular structure of **2** is depicted in Figure 2. Compound **2** is formed as a cyclic tetramer and closely resembles the structure of the tetrameric N,C-chelated analogue Sb_4Ar_4* (Ar* = C_6H_4-2-CH_2NMe_2).[14] The presence of more

---

(10) Suitable single crystals of **1** and **2** were mounted on a glass fiber with oil and measured on a four-circle KappaCCD diffractometer with CCD area detector by monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The numerical[15] absorption correction from crystal shape was applied for crystals of **2** and multi-scan[16] for **1**. The structures were solved by the direct method (SIR92[17]) and refined by a full matrix least-squares procedure based on F^2 (SHELXL97[18]). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$(pivot atom); for the methyl moiety a multiple of 1.5 was chosen. The final difference maps displayed no peaks of chemical significance, as the highest peaks and holes are in close vicinity (~1 Å) of heavy atoms. **1**: $C_{36}H_{57}N_6Sb_5$, $M = 1182.63$, monoclinic, $P2_1/c$, red block, $a = 10.3120(8)$ Å, $b = 34.361(4)$ Å, $c = 13.8470(9)$ Å, $\beta = 117.132(6)°$, $V = 4366.5$ Å^3, $Z = 4$, $T = 150(1)$ K, 22 529 total reflections, 9180 independent ($R_{\text{int}} = 0.069$, R_1 (obs data) = 0.055, wR_2 (all data) 0.108. CCDC 679245. **2**: $C_{48}H_{76}N_8Sb_4.2C_6H_6$, $M = 1406.54$, orthorhombic, *Pnma*, yellow needle, $a = 22.9280(5)$ Å, $b = 22.6020(17)$ Å, $c = 12.2360(8)$ Å, $V = 6340.9$ Å^3, $Z = 4$, $T = 150(1)$ K, 50 512 total reflections, 7355 independent ($R_{\text{int}} = 0.085$, R_1 (obs data) = 0.043, wR_2 (all data) 0.110. CCDC 679246. There is disordered solvent (benzene) in this structure. Attempts were made to model this disorder or split it into two positions, but were unsuccessful. PLATON/SQUEZZE[19] was used to correct the data for the presence of disordered solvent. A potential solvent volume of 702 Å^3 was found. 337 electrons per unit cell worth of scattering were located in the void. The stoichiometry of the solvent was calculated to be eight molecules of benzene per unit cell, which results in 336 electrons per unit cell. The crystals of **2** with no solvent were also obtained, and their structure was determined in hexagonal point group $P3_221$, orange block, $a = 13.2623(18)$ Å, $b = 13.2623(9)$ Å, $c = 52.515(6)$ Å, $V = 7999.2$ Å^3, $Z = 6$, but the low quality of the data collected resulted in a large disorder of two of the ligands present.

(11) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Kuznetsov, A. N.; Kloo, L.; Lindsjö, M.; Rosdahl, J.; Stoll, H. *Chem.–Eur. J.* **2001**, *7*, 2821.

(12) A similar propellane-like organotin Sn_5 cluster was prepared and characterized by X-ray diffraction: Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 6454.

(13) (a) For example see: Cordier, G.; Ludwig, M.; Stahl, D.; Schmidt, P. C.; Kniep, R. *Angew. Chem., Int. Ed.* **1995**, *34*, 1761. (b) Goicoechea, J. M.; Sevov, S. C. *J. Am. Chem. Soc.* **2004**, *126*, 6860.

(14) Opris, L. M.; Silvestru, A.; Silvestru, C.; Breunig, H. J.; Lork, E. *Dalton Trans.* **2004**, 3575.

(15) Coppens, P. In *Crystallographic Computing*; Ahmed F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; pp 255–270.

(16) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421.

(17) Altomare, A.; Cascarone, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 1045.

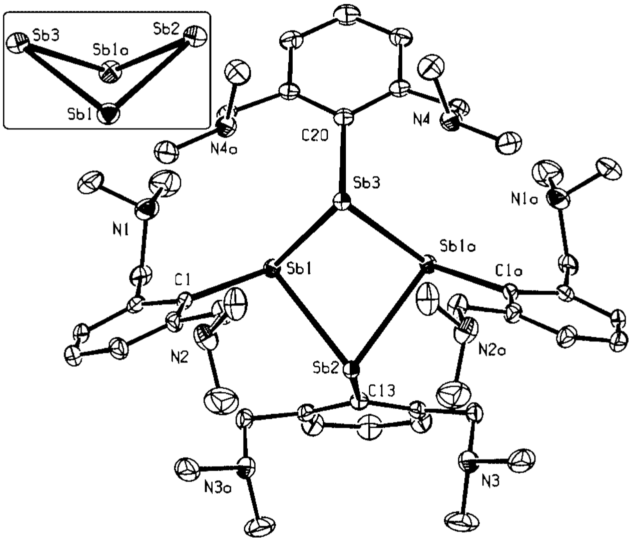


Figure 2. ORTEP plot of a molecule of **2** showing 30% probability displacement ellipsoids and the atom numbering scheme and view of the central Sb_4 framework. Hydrogen atoms were omitted for clarity. Selected bond lenghts (Å) and angles (deg): Sb(1)−Sb(2) 2.8650(5), Sb(1)−Sb(3) 2.8808(5), Sb(1)−C(1) 2.181(4), Sb(2)−C(13) 2.195(6), Sb(3)−C(20) 2.168(7), Sb(1)−N(1) 3.304(5), Sb(1)···N(2) 4.950(5), Sb(2)−N(3) 3.342(5), Sb(3)−N(4) 3.016(4); Sb(1)−Sb(2)−Sb(1a) 72.99(1), Sb(2)−Sb(1)−Sb(3) 86.13(1), Sb(1)−Sb(3)−Sb(1a) 72.53(1), N(3)−Sb(2)−N(3a) 93.38(11), N(4)−Sb(3)−N(4a) 109.09(11).

sterically demanding N,C,N ligands leads only to marginal elongation of the Sb−Sb bond within the central ring, average 2.873(2) Å compared to 2.854(3) Å. Whereas in Sb_4Ar_4* each of the four nitrogen donor atoms is coordinated to one antimony atom (range of Sb−N contacts 2.915(3)−3.040(3) Å), this situation is more complex in **2**. Both nitrogen atoms of the ligands bonded to the antimony atoms Sb(2) and Sb(3) can be regarded as coordinated, although very weakly, the range of Sb−N distances being 3.016(4)−3.342(5) Å. On the other hand, in the case of ligands on the Sb(1) and Sb(1a) atoms only one of the donor atoms (N(1) and N(1a)) remains in contact with the antimony atom (Sb−N = 3.304(5) Å), and the second donor group (N(2) and N(2a)) is unambiguously pendant (Sb···N 4.950(5) Å).

Both compounds **1** and **2** retain their structures in solution. The ^{1}H and ^{13}C NMR spectra[9] contain one set of signals for both NCH_2 and $N(CH_3)_2$ at various concentrations, ruling out the presence of any ring−ring equilibria in solution, similarly to a tetrameric Sb_4Ar_4* N,C-chelated compound.[14] The ^{1}H NMR signals corresponding to $NC\mathit{H}_2$ groups are in the case of both compounds observed as singlets at 300 K, indicating that both ligand's donor groups undergo a fluxional association/dissociation process, as is common for pincer ligands and complexes and indicating only weak Sb−N intramolecular interactions in solution of **1** and **2** (similar results were observed in the solid state).

In conclusion, a rare example of a trigonal bipyramidal main group cluster (**1**) was obtained by dehydrocoupling reaction, and its molecular structure was determined by X-ray diffraction. An investigation concerning the theoretical background of the bonding structure in **1** and the reactivity of **1** and **2** is currently underway.

Acknowledgment. The authors thank the GAČR (project 203/07/P094) and the Ministry of Education of the Czech Republic (projects MSM0021627501 and LC523) for financial support.

Supporting Information Available: ^{1}H, ^{13}C NMR spectra of **1**, all crystal data and structure refinement, atomic coordinates, anisotropic displacement parameters, and geometric data for compounds **1**and **2** (cif files) are available free of charge via the Internet at http://pubs.acs.org.

OM800227M

---

(18) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; University of Göttingen: Germany, 1997.

(19) Spek, A. L. *Acta Crystalllogr., Sect. A* **1990**, *46*, C34.