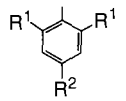
Synthesis of the First Stable Selenadistibirane and Its Molecular Structure

Norihiro Tokitoh,* Takahiro Sasamori, and Renji Okazaki#
Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033

(Received April 27, 1998; CL-980313)

Treatment of an extremely hindered 1,3,5-triselena-2,4,6-tristibane derivative with excess amount of hexamethylphosphorous triamide in toluene at 130 °C resulted in the formation of the first stable selenadistibirane derivative as orange crystals. The molecular geometry of this novel heavy atom-containing three-membered ring system was definitively determined by X-ray structural analysis.

The syntheses, structures, and reactivities of multiple bonds between atoms of heavier main group elements have attracted wide interest as one of the active areas of chemical research.[1] As for the case of group 15 elements, several examples of stable diphosphenes,[2] phosphaarsenes,[3] and diarsenes[3b,4] have been synthesized by taking advantage of steric protection with bulky substituents since the first isolation of a stable diphosphene (RP=PR; R = 2,4,6-tri-*tert*-butylphenyl).[5] Very recently we have also succeeded in the synthesis and characterization of the first stable examples of distibene **1** and dibismuthene **2** [TbtE=ETbt (**1**; E = Sb,[6] **2**; E = Bi[7])], *i. e.* long-sought, much heavier congeners of azo compounds, by utilizing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt).[8]

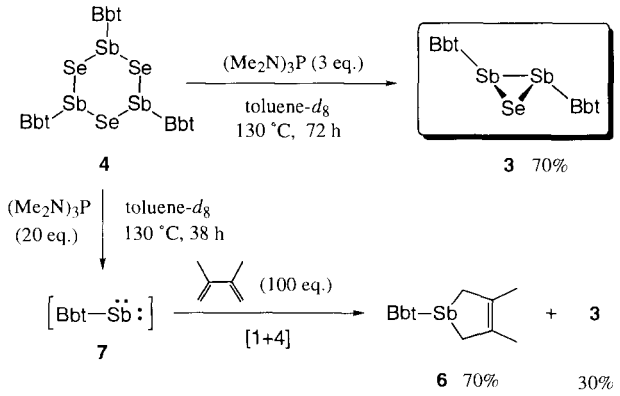


Tbt; $R^1 = R^2 = CH(SiMe_3)_2$
Bbt; $R^1 = CH(SiMe_3)_2$, $R^2 = C(SiMe_3)_3$

On the other hand, in the course of our studies on the synthesis of sterically congested molecules we have developed another bulky aromatic substituent, 2,6-bis[bis(trimethylsilyl)-methyl]-4-[tris(trimethylsilyl)methyl]phenyl group (denoted as Bbt group),[9] which is expected to be a potentially more useful steric protection group than Tbt group. In this paper, we wish to present the successful application of this Bbt group to the synthesis of the first stable selenadistibirane derivative **3** together with its X-ray structural analysis.

When an extremely hindered 1,3,5-triselena-2,4,6-tristibane bearing three Bbt groups on the antimony atoms **4** (50.8 mg, 0.02 mmol)[10] was treated with hexamethylphosphorous triamide (HMPT; 0.01 ml, 0.06 mmol, 3 equiv.) in toluene-d_8 (0.6 ml) at 130 °C in a sealed tube for 72 h, the color of the reaction mixture turned deep red. Although the UV-vis spectrum of this reaction mixture showed two characteristic absorption maxima at 490 (ε, ca. 4000) and 600 (ε, ca. 200) nm attributable to the π–π* and n–π* transitions of the expected distibene **5** (Bbt–Sb=Sb–Bbt), concentration of the reaction mixture followed by purification with gel permeation liquid chromatography afforded selenadistibirane **3** as air-stable orange crystals in 70% of isolated yield together with the recovered starting material **4** (30%) (Scheme 1).

Selenadistibirane **3** was found to be thermally very stable even in solution up to 180 °C and showed satisfactory ^1H and



Scheme 1.

^{13}C NMR spectral data and its molecular composition was confirmed by elemental analysis.[11] ^{77}Se NMR of **3** was also measured in toluene-d_8 to show a signal at δ -181.5, which is within a characteristic region for those of previously reported selenirane derivatives.[12]

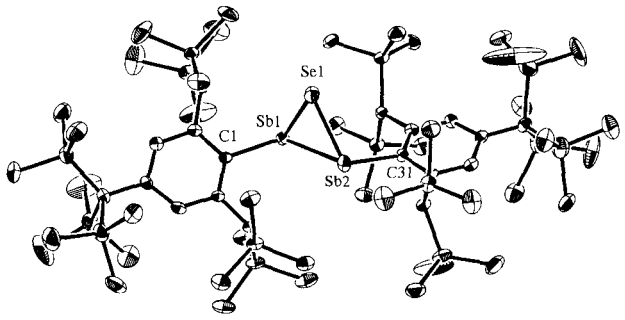


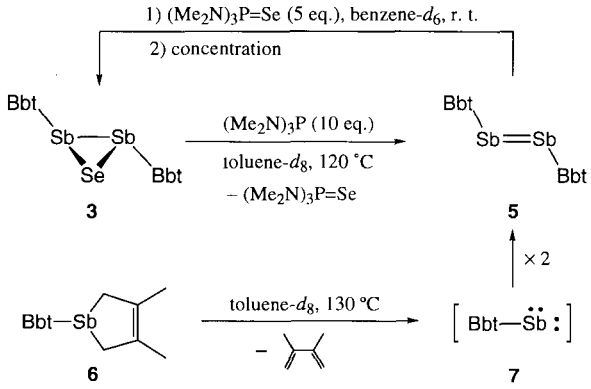
Figure 1. ORTEP drawing of **3** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (deg); Sb(1)-Sb(2) 2.852(2), Sb(1)-Se(1) 2.565(1), Sb(2)-Se(1) 2.562(2), Sb(1)-C(1) 2.187(9), Sb(2)-C(31) 2.179(9), Sb(1)-Se(1)-Sb(2) 67.60(5), Se(1)-Sb(1)-Sb(2) 56.15(4), Se(1)-Sb(2)-Sb(1) 56.25(4).

The formation of **3** is worthy of note as the first example of this ring system and the molecular geometry of **3** was definitively determined by X-ray structural analysis.[13] In Figure 1 is shown the ORTEP drawing of **3** together with some selected intramolecular structural parameters. The selenadistibirane ring skeleton of **3** is an almost isosceles triangle with the normal Sb–Sb bond length [2.852(2) Å][14] and the two Bbt groups are oriented in trans configuration with regard to the central selenadistibirane ring.

On the other hand, treatment of **4** with an excess amount of HMPT (20 equiv.) in the presence of 2,3-dimethyl-1,3-butadiene (100 equiv.) gave the stibolene derivative **6** (70%) as a major product together with **3** (30%) (Scheme 1). The formation of **6** strongly suggests the involvement of the stibinidene inter-

mediate **7** in the deselenation of **4**, since selenadistibirane **3** is almost inert toward 2,3-dimethyl-1,3-butadiene even at 130 °C in toluene-d_8 for a long time.

The diene adduct **6** here obtained was found to undergo ready thermal retrocycloaddition in toluene-d_8 at 130 °C for 64 h to give the deep-red solution of distibene **5**, the electronic spectrum of which was identical with that obtained from the direct deselenation of **4** with HMPT (*vide supra*). The reaction of distibene **5**, prepared from **6**,[15] with an excess amount of $(Me_2N)_3P$=Se in benzene-d_6 at room temperature followed by concentration resulted in the almost quantitative formation of **3**, while the reaction of isolated **3** with HMPT (ca. 10 equiv.) in toluene-d_8 at 120 °C gave only the deselenated distibene **5** in solution as judged by ^{1}H NMR.



Scheme 2.

The above-mentioned selenation reaction of the isolated distibene **5** with $(Me_2N)_3P$=Se under high concentration giving selenadistibirane **3** is important not only as a new reaction for a distibene but also as the experimental evidence of the final step for the formation of **3** in the deselenation of **4**.

In summary, we have succeeded in the synthesis and isolation of the first stable selenadistibirane derivative **3** by taking advantage of a new steric protection group Bbt. The formation of selenadistibirane **3** in the deselenation of Bbt-substituted triselenatristibane derivative **4** in contrast to that of distibene **1** in the Tbt-substituted system is most likely interpreted in terms of the remarkable insolubility of **1** in common organic solvents, which may prevent further transformation of **1** into its selenadistibirane derivative via redistribution of a selenium atom between the initially formed distibene and the phosphine selenide on concentration.

Further investigation on physical and chemical properties of the newly obtained, overcrowded selenadistibirane **3** is currently in progress.

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 09239208) from the Ministry of Education, Science, Sports, and Culture of Japan. We are also grateful to Shin-etsu Chemical Co., Ltd., and Tosoh Akzo Co., Ltd., for the generous gift of chlorosilanes and alkyllithiums, respectively.

References and Notes

Present address: Department of Chemical and Biological Sciences, Faculty of Science, Japan Women's University.

1 F. G. A. Stone and R. West, Eds., *Adv. Organomet. Chem.*, **39** (1996).

2 For reviews, see: L. Weber, *Chem. Rev.*, **92**, 1839 (1992). M. Yoshifuji, in "Multiple Bonds and Low Coordination in Phosphorus Chemistry", ed by M. Regitz and O. J. Scherer, Thieme, Stuttgart, Germany, (1990) p 321. A. H. Cowley, J. Kilduff, M. Pakulski, and C. Stewart, *J. Am. Chem. Soc.*, **105**, 1655 (1983). M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita, and K. Nishimoto, *J. Am. Chem. Soc.*, **105**, 2495 (1983). H. Ranaivonjatovo, J. Escudié, C. Couret, and J. Satgé, *Phosphorus Sulfur*, **31**, 81 (1987).

3 a) A. H. Cowley, J. Kilduff, J. G. Lasch, S. Mehrotra, N. C. Norman, M. Pakulski, B. Whittlesey, J. Atwood, and W. Hunter, *Inorg. Chem.*, **23**, 2582 (1984). b) J. Escudié, C. Couret, H. Ranaivonjatovo, and J.-G. Wolf, *Tetrahedron Lett.*, **24**, 3625 (1983).

4 A. H. Cowley, J. G. Lasch, N. C. Norman, and M. Pakulski, *J. Am. Chem. Soc.*, **105**, 5506 (1983).

5 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, **103**, 4587 (1981).

6 N. Tokitoh, Y. Arai, T. Sasamori, R. Okazaki, S. Nagase, H. Uekusa, and Y. Ohashi, *J. Am. Chem. Soc.*, **120**, 433 (1998).

7 N. Tokitoh, Y. Arai, R. Okazaki, and S. Nagase, *Science*, **277**, 78 (1997).

8 R. Okazaki, N. Tokitoh, and T. Matsumoto, in "Synthetic Methods of Organometallic and Inorganic Chemistry", ed by N. Auner and U. Klingebiel, Thieme, New York, (1996) Vol. 2, p 260.

9 For the synthesis and application of Bbt group, see: N. Kano, N. Tokitoh, and R. Okazaki, *Organometallics*, **17**, 1241 (1998).

10 The starting material **4** was readily prepared by a method similar to that for the Tbt analogue, see ref. 6.

11 Compound **3**: orange crystals, mp 215-220 °C (decomp). ^{1}H-NMR (500 MHz, C_6D_6) δ 0.37 (s, 54H), 0.41 (s, 72H), 3.00 (s, 4H), 6.99 (s, 4H). ^{13}C-NMR (125 MHz, C_6D_6) δ 2.01 (q), 2.13 (q), 5.65 (q), 22.30 (s), 36. 98 (d), 127. 00 (d), 142. 19 (s), 146. 05 (s), 150.89 (s). ^{77}Se-NMR (95 MHz, C_6D_6) δ -181.5. Anal. Found: C, 46.13; H, 8.37; Se, 4.56%. Calcd for $C_{60}H_{134}Sb_2Si_{14}Se$: C, 45.86; H, 8.60; Se, 5.02%. All the other products described here showed satisfactory spectral and analytical data.

12 For example, tetramesitylselenadisilirane showed a signal (singlet) at -287.1 ppm in ^{77}Se-NMR (95.4 MHz, $CDCl_3$); see, R. P.-K.Tan, G. R. Gillette, D. R. Powell, and R. West, *Organometallics*, **10**, 546 (1991).

13 The crystal data of **3** are as follows; **3**: $C_{60}H_{134}Sb_2Si_{14}Se$, M = 1571.38, a = 33.88(4), b = 9.293(3), c = 48.37(3) Å, β = 92.27(6)°, V = 17017(15) Å^3, monoclinic, space group C2/c (#15), Z = 8, D_c = 1.227 gcm^{-3}, μ = 12.90 cm^{-1}, final R = 0.070, R_w = 0.076 for 9918 [$I > 3\sigma(I)$] observed reflections and 694 variable parameters. Intensity data for **3** (20748 unique reflections) were collected at -80 °C.

14 H. Bürger and R. Eujen, *J. Mol. Struct.*, **98**, 265 (1983).

15 Thermolysis of **6** in toluene-d_8 at 130 °C for 64 h in a sealed tube followed by the slow evaporation of the reaction mixture at room temperature in a glovebox filled with argon gave distibene **5** as red paste in an almost pure form. Since the characteristic red color of **5** immediately disappeared on exposure to the open air, distibene **5** seems to be highly sensitive to moisture and/or oxygen. **5**: ^{1}H-NMR (270 MHz, C_6D_6) δ 0.37 (s, 72H), 0.46 (s, 54H), 2.55 (s, 4H), 7.24 (s, 4H).