Pergamon

Tetrahedron Letters 40 (1999) 5557-5560

TETRAHEDRON
LETTERS

Formation of a Borylene by Photolysis of an Overcrowded Bis(methylseleno)borane

Mitsuhiro Ito,[a] Norihiro Tokitoh,*[b] Takayuki Kawashima,[a] and Renji Okazaki[c]

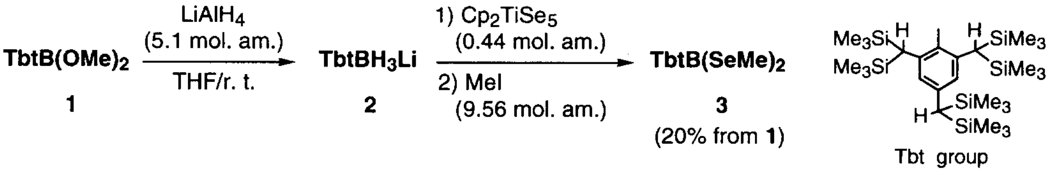
[a]*Department of Chemistry, Graduate School of Science, The University of Tokyo,*
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[b]*Institute for Fundamental Research of Organic Chemistry, Kyushu University,*
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan
[c]*Department of Chemical and Biological Sciences, Faculty of Science, Japan Women's University,*
2-8-1 Mejirodai, Bunkyo-ku, Tokyo 112-8681, Japan

Received 26 April 1999; revised 17 May 1999; accepted 21 May 1999

Abstract: A novel bis(methylseleno)borane **3** bearing a very bulky aryl group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), on the boron atom was synthesized. Photolysis of **3** gave the corresponding monovalent boron species, borylene TbtB: (**4**), the formation of which was confirmed by the trapping reactions with benzil, phenanthrenequinone, and dimethyl disulfide. Irradiation of **3** in the absence of a trapping reagent did not afford the expected diborene but a selenium-containing five-membered boracycle, 1,2,4,3,5-triselenadiborolane **9**.

Keywords: Boron heterocycles, Photochemistry, Selenium and compounds, X-ray crystal structures

Much interest has been focused on the chemistry of monovalent organoboron species, *i. e.*, borylenes (R–B:), from the viewpoints of not only a useful synthetic building block for new organoboron compounds but also one of the unexplored low valent species of boron. Although there have been several reports on intermediary borylenes, the chemistry of borylenes has not been fully investigated until now.[1-3] We chose bis(organoseleno)borane as a new precursor for a borylene, since chemical bonds involving selenium are known to be generally light-sensitive[4] and the homolytic cleavage of the two B–Se bonds of bis(organoseleno)borane may give a borylene. However, there have been very few reports on the photolysis of compounds containing a B–Se bond mainly due to their high instability. Only methyl- and phenyl-substituted bis(methylseleno)boranes have been known as examples of bis(organoseleno)boranes, *i. e.*, selenium analogs of boronic esters, but these bis(methylseleno)boranes are extremely unstable in the air and difficult to handle.[5]



Scheme 1

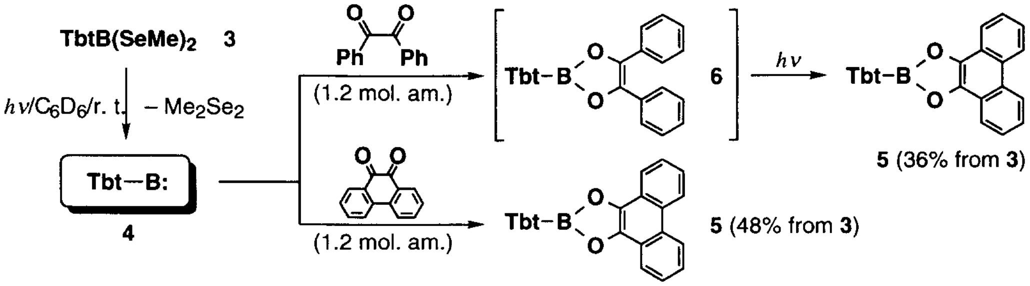
Meanwhile, we have recently succeeded in the syntheses of 1,3,2,4-dichalcogenametallaboretanes, novel four-membered boracycles, by taking advantage of the kinetic stabilization using a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter) group, and reported their thermolysis or oxidation resulting in the successful formation of novel boron–chalcogen double-bond compounds such as oxo-, thioxo-, and selenoxoboranes.[6] In this paper, we describe the synthesis of a kinetically stabilized

0040-4039/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(99)01036-9

bis(methylseleno)borane bearing a Tbt group together with its photolysis leading to a new method for the generation of a borylene.

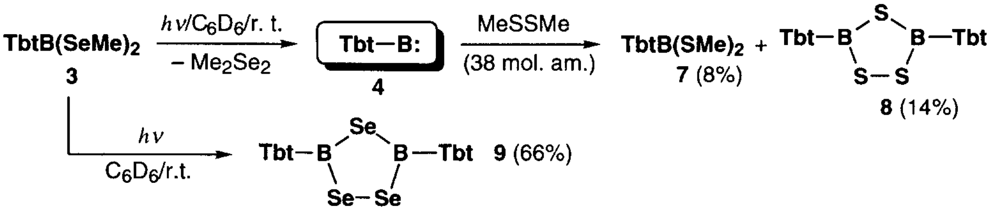
Bis(methylseleno)borane 3[7] was synthesized as colorless crystals in 20% yield from 1 by the reaction of an overcrowded trihydroborate 2[6a] with titanocene pentaselenide followed by treatment with methyl iodide (Scheme 1). When elemental selenium was used as a selenium source instead of titanocene pentaselenide, only a trace amount of 3 was obtained. Compound 3 showed a singlet signal in ^{11}B NMR (δ_B 76.6) attributable to that of the boron atom connecting two selenium atoms. It was stable in air in the solid state but slowly decomposed in solution.

A benzene-d_6 solution of bis(methylseleno)borane 3 and a trapping reagent in a sealed Pyrex tube was irradiated by means of a 400 W medium pressure mercury lamp at room temperature. The reaction was monitored by ^{1}H NMR. The irradiation of 3 in the presence of benzil gave compound 5,[7] which might have resulted from photocyclization-oxidation of dioxaborolene 6, *i. e.*, the [1+4]cycloadduct of initially generated borylene 4 with benzil (Scheme 2). The intermediacy of borylene 4 was more directly evidenced by the formation of the same cycloadduct 5 in the photolysis of 3 in the presence of phenanthrenequinone (Scheme 2). The selenium-containing photolyzates except for a small amount of precipitated elemental selenium were dimethyl diselenide and dimethyl selenide, the formation of which was confirmed by ^{77}Se NMR.



Scheme 2

The irradiation of 3 in the presence of dimethyl disulfide gave bis(methylthio)borane 7,[6c] an insertion product of borylene 4, along with 1,2,4,3,5-trithiadiborolane 8[6c] (Scheme 3).



Scheme 3

Since the results of the above-mentioned trapping reactions are most likely interpreted in terms of the formation of borylene 4 by the photolysis of bis(methylseleno)borane 3, we were prompted to examine the photolysis of 3 without a trapping reagent in the hope of the formation of boron–boron double-bond compound (diborene) by the dimerization of borylene 4. When a benzene-d_6 solution of 3 was irradiated alone, pale yellow crystals of 9 precipitated as the photolysis proceeded (Scheme 3). The spectroscopic data of the crystals were not obtained due to their marked insolubility in common organic solvents. However, the crystals were finally found to have the structure of 1,2,4,3,5-triselenadiborolane 9 by X-ray crystallographic analysis.

In contrast to the preceding studies on the synthesis and structures of boron–sulfur heterocycles, those for the selenium analogues have been rather scarce. Although the crystallographic structural analysis of 3,5-diphenyl- and 3,5-diiodo-1,2,4,3,5-triselenadiborolanes was recently reported,[8] the intrinsic structural features of this unique heterocyclic system have not been fully investigated. The ORTEP drawing and selected bond lengths and angles of **9** are shown in Figure 1.[9] The facts that the sum of interior angles of the five-membered ring of **9** is 540.1° and the maximum distance between least squares plane defined by the B(1), B(2), Se(1), Se(2), and Se(3) and the individual atoms is only 0.02 Å [for B(2)] clearly indicate the complete planarity of the triselenadiborolane ring of **9**, which is in sharp contrast to the envelope structure of 3,5-diphenyl derivative but similar to that of 3,5-diiodo-substituted system.[8] Since there was not observed any short contacts less than 3.50 Å between the molecules of **9** in the crystalline-state, the molecular structure of **9** here revealed may provide us with an intrinsic information for the 1,2,4,3,5-triselenadiborolanes ring system. The angles between the five-membered ring and the aromatic ring planes of the two Tbt groups are 90.43 and 90.99°, respectively, suggesting no essential conjugative interaction of π-electrons on the Tbt group with the boron atom. The geometries around the boron atoms in their five-membered ring of **9** were found to be perfectly trigonal planar ($\Sigma\angle B = 360°$), indicating that these boron centers are not so strained in spite of bearing an extremely bulky Tbt group.

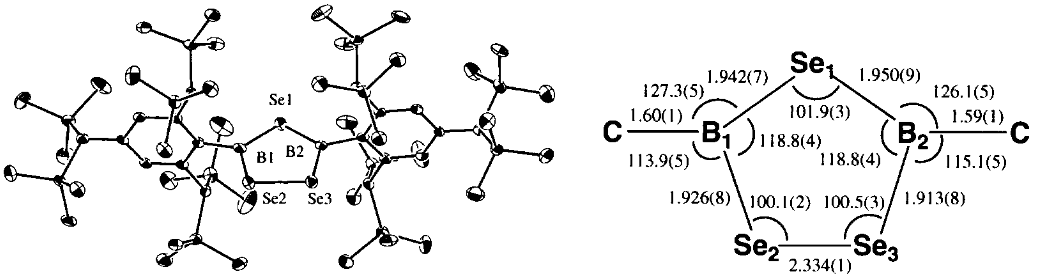
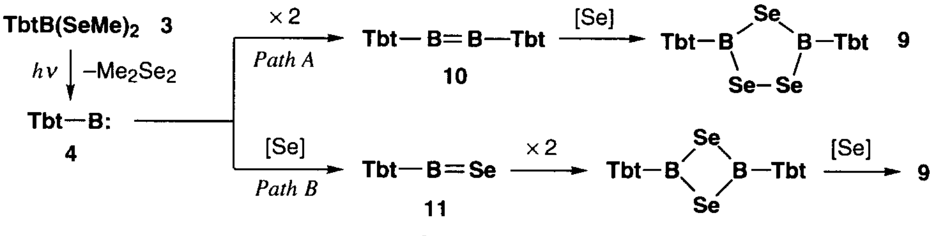


Figure 1. ORTEP drawing of **9** with thermal ellipsoid plot (30% probability) and selected bond lengths (Å) and angles (deg) for **9**.

The mechanism for the unexpected formation of 1,2,4,3,5-triselenadiborolane **9** in the photolysis of bis(methylseleno)borane **3** is not clear at present, but our plausible explanation is as follows (Scheme 4). The most straightforward reaction pathway is the dimerization of initially formed borylene **4** followed by the selenation of resulting diborene **10** (Path A), and another one is based on the selenation of borylene **4** giving selenoxoborane **11** which may undergo dimerization and successive ring expansion via selenation to give **9** (Path B). The selenium source in this mechanism should be dimethyl diselenide itself and/or elemental selenium formed by the photolysis of dimethyl diselenide.[10] Also compound **8**, which was obtained by the photolysis of **2** in the presence of dimethyl disulfide, was probably formed by the sulfur abstraction of diborene **10** or borylene **4** from co-existing dimethyl disulfide.



Scheme 4

In summary, we have found that the photolysis of an overcrowded bis(methylseleno)borane provides us with a new method for the generation of a borylene, which is among a novel class of low valent organoboron compounds. Since both intermediary borylene **4** here generated and triselenadiborolane **9** are both thought to be good precursors for the unprecedented boron–boron double-bond compound, *i. e.*, diborene **10**, further investigations are currently in progress.

Acknowledgments: This work was partially supported by Grants-in-Aid for Scientific Research (Nos. 09239208 and 09440216) from the Ministry of Education, Science, Sports, and Culture, Japan. M.I. thanks Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. The authors are grateful to Shin-Etsu Chemical and Tosoh Akzo Co. Ltds. for the generous gifts of chlorosilanes and alkyllithiums, respectively.

REFERENCES AND NOTES

1. a) Timms, P. L. *J. Am. Chem. Soc.* **1967**, *89*, 1629-1632. b) Timms, P. L. *J. Am. Chem. Soc.* **1968**, *90*, 4585-4589. c) Timms, P. L. *Acc. Chem. Res.* **1973**, *6*, 118-123. d) van der Kerk, S. M.; Budzelaar, P. H. M.; van Eekeren, A. L. M.; van der Kerk, G. J. M. *Polyhedron* **1984**, *3*, 271-280.
2. a) van der Kerk, S. M.; Boersma, J.; van der Kerk, G. J. M. *Tetrahedron Lett.* **1976**, *51*, 4765-4766. b) van der Kerk, S. M.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1980**, *190*, C11-C13. c) van der Kerk, S. M.; Budzelaar, P. H. M.; van der Kerk-van Hoof, A.; van der Kerk, G. J. M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 48.
3. Pachaly, B.; West, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 454-455.
4. For example, dimethylgermylene was reported to be generated by the photolysis of dimethylbis(phenylseleno)germane, see; Tomoda, S.; Shimoda, M.; Takeuchi, Y.; Kajii, Y.; Obi, K.; Tanaka, I.; Honda, K. *J. Chem. Soc., Chem. Commun.* **1988**, 910-912.
5. Siebert, W.; Ospici, A. *Chem. Ber.* **1972**, *105*, 454-463.
6. a) Tokitoh, N.; Ito, M.; Okazaki, R. *Organometallics* **1995**, *14*, 4460-4462. b) Tokitoh, N.; Ito, M.; Okazaki, R. *Tetrahedron Lett.* **1996**, *37*, 5145-5148. c) Ito, M.; Tokitoh, N.; Okazaki, R. *Organometallics* **1997**, *16*, 4314-4319. d) Ito, M.; Tokitoh, N.; Okazaki, R. *Tetrahedron Lett.* **1997**, *38*, 4451-4454. e) Ito, M.; Tokitoh, N.; Okazaki, R. *Chem. Commun.* **1998**, 2495-2496.
7. All new organoboron compounds here obtained showed satisfactory spectral and analytical data except for the case of compound **9** . The spectral and analytical data for **3** were described as a representative as follows. Compound **3**: pale yellow crystals, mp 164-168 °C; ^{1}H NMR(500 MHz, C_6D_6) δ 0.22 (s, 18H), 0.31 (s, 36H), 1.53 (s, 1H), 1.99 (s, 6H), 2.07 (s, 2H), 6.53 (br s, 1H), 6.63 (br s, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ –0.78 (q), –0.20 (q), 0.24 (q), 27.83 (d), 28.19 (d), 28.80 (q), 30.20 (d), 120.01 (d), 124.39 (d), 134.02 (s), 142.79 (s), 143.08 (d), 143.78 (d); ^{11}B NMR(160 MHz, C_6D_6) δ 76.6; ^{77}Se NMR(95 MHz, C_6D_6) δ 284.4. HRMS(FAB): *m/z* Calcd for $C_{29}H_{65}BSe_2Si_6$ 752.2125. Found: 752.2174. Anal. Calcd for $C_{29}H_{65}BSe_2Si_6$: C, 46.38; H, 8.72; Se, 21.03%. Found: C, 46.32; H, 8.43; Se, 18.90%. UV-vis (hexane), 231 (ε, 51200), 262 (14400, sh) nm. Compound **9** was isolated as pale yellow crystals (mp > 300 °C), the elemental analysis of which gave not satisfactory but supporting data for the molecular structure of **9** (Found: C, 45.02; H, 8.42; Se, 18.53%; Calcd for $C_{54}H_{118}B_2Se_3Si_{12}$: C, 47.58; H, 8.73; Se, 17.38%).
8. a) Conrady-Pigorsch, R.; Müller-Warmuth, W.; Schwetlik, G.; Wienkenhöver, M.; Krebs, B. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 453-458. b) Conrad, O.; Jansen, C.; Krebs, B. *Angew. Chem., Int. Ed.* **1998**, *37*, 3208-3218.
9. Crystallographic data for **9**: $C_{54}H_{118}B_2Se_3Si_{12}$, MW = 1363.05, triclinic, space group P–1 (#2), a = 17.871(2), b = 18.489(2), c = 13.211(4) Å, α = 107.361(5)°, β = 109.889(8)°, γ = 89.105(8)°, V = 3899.6(7) Å^3, $Z = 2$, D_c = 1.161 g cm^{-3}, μ = 16.3 cm^{-1}, T = 153 K, $R(R_w)$ = 0.067(0.084). The intensity data for **1** were collected on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα radiation (λ = 0.71070 Å), and a total of 14398 reflections was measured. The structure of **1** was solved by direct methods with SIR92.[11] All the non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located in the calculated positions. The final cycles of the least square refinement were based on 8605 observed reflections [$I > 3.00\sigma(I)$] and 640 variable parameters.
10. Brown, D. H.; Cross, R. J.; Millington, D. *J. Chem. Soc., Dalton Trans.* **1977**, 159-161.
11. SIR92, Program for Crystal Structure Determination: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Cryst.* **1994**, *27*, 435.