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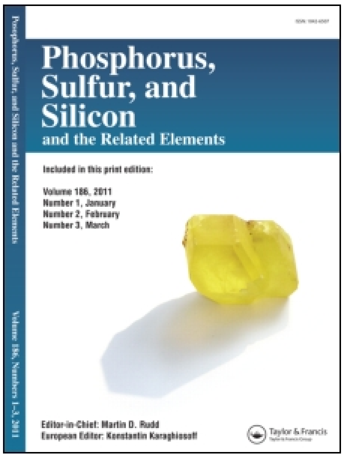

Phosphorus, Sulfur, and Silicon and the Related Elements

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To cite this Article Tokitoh, Norihiro , Arai, Yoshimitsu and Okazaki, Renji(1997) 'Deselenation of Overcrowded Triselenane Derivatives Containing Bismuth: Synthesis and Structure of the First Stable Dibismuthene', Phosphorus, Sulfur, and Silicon and the Related Elements, 124: 1, 371 — 378

To link to this Article: DOI: 10.1080/10426509708545643

URL: http://dx.doi.org/10.1080/10426509708545643

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Phosphorus, Sulfur, and Silicon, 1997, Vol. 124 & 125, pp. 371-378
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DESELENATION OF OVERCROWDED TRISELENANE DERIVATIVES CONTAINING BISMUTH: SYNTHESIS AND STRUCTURE OF THE FIRST STABLE DIBISMUTHENE

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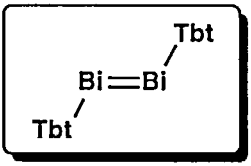
Deselenation of an overcrowded triselenatribismane, 2,4,6-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,5-triselenatribismane, with hexamethylphosphorous triamide resulted in the formation of the first stable dibismuthene {TbtBi=BiTbt; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}, *i. e.* the doubly bonded compound consisting of the heaviest stable element in the periodic table, as deep purple crystals. X-ray crystallographic structural analysis, UV-vis and Raman spectra, and the theoretical calculations revealed the unique bonding character of the unprecedented Bi–Bi double bond.

Keywords: deselenation; steric protection; triselenatribismane; dibismuthene; X-ray structural analysis

INTRODUCTION

The synthesis of doubly bonded compounds containing heavier main group elements has stimulated wide interest[1–5] because of their unusual structure and properties. Although there have been several examples of stable doubly bonded compounds of heavier group 14–16 elements such as $R_2E{=}ER_2$ (E = Si,[6] Ge,[7] Sn[8,9]), RE=ER (E = P,[10] As[11]), and $R_2E{=}X$ (E = Si, Ge; X = S, Se, Te)[12–15], no stable examples containing 6th-raw element(s) have been reported so far. Here we report the first synthesis of a stable dibismuthene, TbtBi=BiTbt (**1**), *i. e.* the long-sought doubly bonded compound consisting of the heaviest stable element in the periodic table, by utilizing a novel synthetic methodology and an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter) developed by us.[16]



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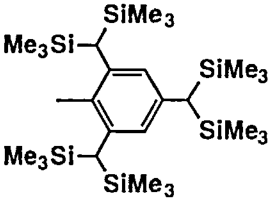
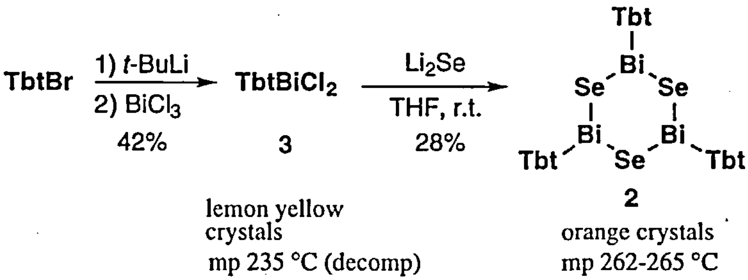


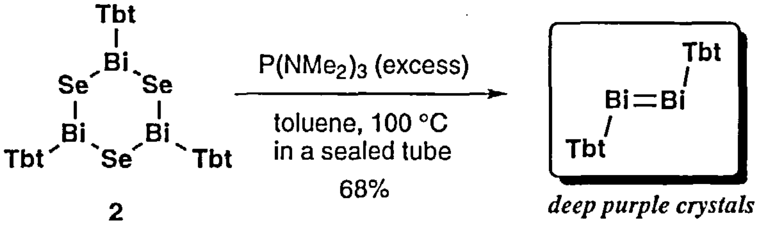
RESULTS AND DISCUSSION

For the preparation of **1** we have developed a new synthetic method, *i. e.* deselenation reaction of triselenatribismane **2** with a phosphine reagent. As shown in Scheme 1, the precursor **2** was readily synthesized by the nucleophilic substitution of bismuth trichloride with TbtLi giving the corresponding bismuth dichloride, $TbtBiCl_2$ (**3**), followed by treatment of **3** with Li_2Se in tetrahydrofuran.



Scheme 1

Triselenatribismane **2** thus isolated as a stable crystalline compound was then treated with an excess amount of hexamethylphosphorous triamide in toluene at 100 °C in a sealed tube. After heating for 12 h the solution turned purple and the expected dibismuthene **1**, which precipitated from the mixture on cooling, was isolated by filtration in a glovebox filled with argon as deep purple single crystals (Scheme 2). The dibismuthene **1** has a very low solubility probably due to its high symmetry in the molecular structure, thus making its isolation quite simple.



Scheme 2

Dibismuthene **1** is the first compound containing a bismuth–bismuth double bond which is the heaviest among those which consist of stable elements in the periodic table and the molecular geometry of **1** was finally determined by X-ray crystallographic structural analysis as shown in Figure 1. Dibismuthene **1** is in the trans-form, and has a center of symmetry, the two bismuth atoms and the two ipso carbons of the Tbt groups attached to bismuth atoms all lying in the same plane. The benzene ring of the Tbt groups are placed almost perpendicular to this plane with the dihedral angle of 90.70 °. Two important parameters in the structure of **1** are the Bi–Bi bond length [2.8206(8) Å] and the Bi–Bi–C angle [100.5(2) °].

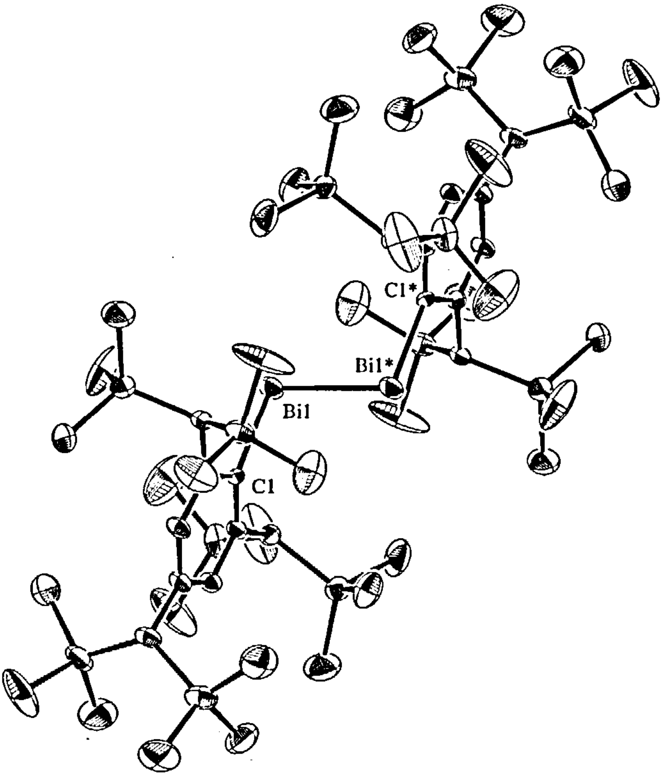
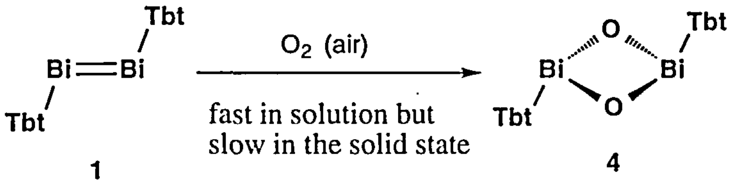


FIGURE 1. ORTEP drawing of TbtBi=BiTbt (**1**) with thermal ellipsoid plot (30% probability).

The Bi–Bi bond in **1** is 6% (0.169 Å) shorter than the Bi–Bi single bond length of 2.990(2) Å in $Ph_2Bi–BiPh_2$.[17] This agrees reasonably well with the calculated bond shortening of 7% (0.214 Å) from $H_2Bi–BiH_2$ (3.009 Å) to HBi=BiH (2.795 Å).[18] In addition, it is interesting that the bond shortenings are comparable with those reported for diphosphenes; the experimental value is 8% (0.183 Å) from $(PhP)_5$ [2.217(6) Å][19] to ArP=PAr [2.034(2) Å; Ar = 2,4,6-tri-*t*-butylphenyl][10], while the calculated value is 9% (0.200 Å) from $H_2P–PH_2$ (2.247 Å) to HP=PH (2.047 Å).[18] Moreover, the bond shortening observed for **1** is in sharp contrast to the considerably elongated Sn–Sn bond length in the isolated distannenes $R_2Sn=SnR_2$ [2.768(1) Å for R = $CH(SiMe_3)_2$[8] and 2.910(1)Å for R = 2-*t*-butyl-4,5,6-trimethylphenyl[20]], the bond lengths of which are almost equal to or longer than the typical Sn–Sn single bond length [*e. g.*, 2.780(4) Å for $Ph_3Sn–SnPh_3$].[21]

The observed Bi–Bi–C angle of 100.5 ° deviates greatly from the ideal sp^2 hybridized bond angle (120 °). This is due to the fact that the heavy Bi atom has the lowest tendency to form a hybrid orbital because the size-difference of the valence *s* and *p* orbitals increases upon going from N to Bi (the significant 6*s* orbital contraction originates mostly from the relativistic effect) and prefers to maintain the $(6s)^2(6p)^3$ valence electron configuration. The use of these three orthogonal 6*p* orbitals without significant hybridization leads to a bond angle of *ca.* 90 ° at Bi.[22] The Bi–Bi–C bond angle in **1**, being close to 90 °, is exactly the experimental evidence for the core-like nature of the 6*s* electrons, *i. e.* so called "inert *s*-pair effect" or "non-hybridization effect".[23]

Dibismuthene **1** is purple in hexane and shows two absorption maxima at λ_1 = 660 nm (sh, ε 100) and λ_2 = 525 nm (ε 4000), which correspond to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the Bi=Bi chromophore, respectively. These red-shifts relative to the values reported for diphosphenes[10,24,25] and diarsenes[11,26] agree with the changes in the n, π, and π* orbital levels calculated for HE=EH (E = P, As, Sb, and Bi).[22] Meanwhile, in the FT-Raman spectrum a strong band attributable to the Bi–Bi stretching was observed at 134 cm^{-1} for the dibismuthene **1** (solid; excitation, He-Ne laser 632.8 nm). This is 31 cm^{-1} higher than the Bi–Bi stretching frequency of $Ph_2Bi–BiPh_2$ (103 cm^{-1}),[27] agreeing with the frequency shift of 34 cm^{-1} calculated for HBi=BiH (153 cm^{-1}) and $H_2Bi–BiH_2$ (119 cm^{-1}).[18] Thus, the spectroscopic data here obtained indicate again that **1** features double bonding between the Bi atoms even in solution.



Scheme 3

Finally, it should be noted that dibismuthene **1** undergoes a unique reaction with oxygen (Scheme 3). Dibismuthene **1** is considerably stable in the solid state, retaining its purple color for several hours on exposure to the open air, but it undergoes slow reaction with oxygen to give quantitatively the corresponding colorless 1,3,2,4-dioxadibismuthene derivative, $(TbtBiO)_2$ **4**, the structure of which was determined by X-ray crystallographic analysis. In solution **1** reacts with oxygen quite rapidly to give **4**.

The successful isolation of dibismuthene **1** is worthy of special note because the Bi–Bi double bond is the heaviest known and changes drastically our understanding of double-bond compounds in chemistry textbooks. Future work along this line may lead us to a whole new class of multiply bonded compounds.

ACKNOWLEDGMENTS 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, Japan. We are grateful to Prof. Yukio Furukawa, the University of Tokyo, for the measurement of FT-Raman spectra. N. T. is thankful to Ciba-Geigy Foundation (Japan) for the Promotion of Science for the financial support. We are also grateful to Shin-etsu Chemical Co., Ltd. and Tosoh Akzo Co., Ltd. for the generous gift of chlorosilanes and alkyllithiums, respectively.

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