

Synthesis of a Stable Stibabismuthene; the First Compound with an Antimony-Bismuth Double Bond

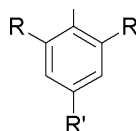
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Condensation reaction of an overcrowded dihydrostibine with dibromobismuthine using 1,8-diazabicyclo[5.4.0]undec-7-ene as a base afforded the first stable stibabismuthene, the formation of which was evidenced by the UV-vis and Raman spectra and its chemical reactivity.

Keywords: stibabismuthene/steric protection/antimony/bismuth/double bond

In recent years there has been much interest in compounds with a double bond between heavier group 15 elements. Since the first isolation of a stable diphosphene ($\text{Mes}^*\text{P}=\text{PMes}^*$; $\text{Mes}^* = 2,4,6\text{-}i\text{-butylphenyl}$) in 1981, a number of examples of kinetically stabilized diphosphenes ($\text{RP}=\text{PR}$) and diarsenes ($\text{RAs}=\text{AsR}$) have been isolated and fully characterized.[1] Recently, we have succeeded in the synthesis and characterization of the first stable distibene ($\text{TbtSb}=\text{SbTbt}$)[2] and dibismuthene ($\text{TbtBi}=\text{BiTbt}$)[3] even heavier congeners of azo compounds, by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group. Very recently, Power *et al.* also synthesized another type of stable distibene and dibismuthene substituted by bulky 2,6- $\text{Ar}_2\text{C}_6\text{H}_3$ groups ($\text{Ar} = \text{mesityl}$ or 2,4,6-triisopropylphenyl).[4] As for the case of heteronuclear double-bond compounds between heavier group 15 elements, several phospharsenes and phosphatibenes have been synthesized as stable compounds.[1,5] However, there is no examples of a heteronuclear doubly bonded system between antimony and bismuth, *i. e.* stibabismuthene. Although the successful results on the kinetic stabilization of distibene and dibismuthene

($\text{TbtE}=\text{ETbt}$; $\text{E} = \text{Sb, Bi}$) naturally prompted us to apply the Tbt group to the synthesis of stable stibabismuthene, we were apprehensive that the extremely low solubility of the Tbt-substituted doubly bonded system of heavier group 15 elements may prevent us from the examination of the possible synthetic approaches and also the spectroscopic detection of the reaction products. On the other hand, during the course of our investigation on the kinetic stabilization of low-coordinated highly reactive species we have developed another bulky aromatic substituent, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) group,[6] which is expected to be a potentially more useful steric protection group than Tbt group. In fact, a new distibene and dibismuthene substituted by Bbt groups, which have relatively high solubility compared with $\text{TbtE}=\text{ETbt}$ ($\text{E} = \text{Sb, Bi}$), were successfully synthesized and characterized. We now report the successful application of the Bbt group to the synthesis of the first stable stibabismuthene, $\text{BbtSb}=\text{BiBbt}$ (**1**).



Tbt: $\text{R} = \text{R}' = \text{CH}(\text{SiMe}_3)_2$

Bbt: $\text{R} = \text{CH}(\text{SiMe}_3)_2$, $\text{R}' = \text{C}(\text{SiMe}_3)_3$

BIOORGANIC CHEMISTRY — Organoelement Chemistry —

Scope of research

Major research interests of our laboratory are in the chemistry of the compounds having a novel bonding containing heavier main group elements and/or transition metals, such as aromatic compounds containing heavier group 14 elements, double-bond compounds containing heavier main group elements and/or transition metals, and metallacyclopropabenzene containing group 14 elements. These compounds are synthesized as stable compounds by taking advantage of bulky substituents and their properties are investigated in detail. Mechanism of biochemical reactions and organic synthesis mediated by biocatalysts are also studied.



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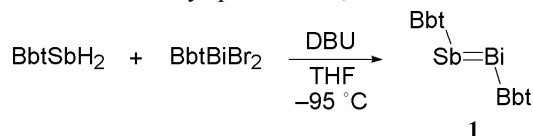
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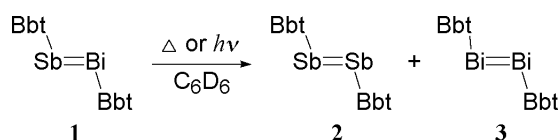
Condensation reaction of BbtBiBr_2 with BbtSbH_2 , which was prepared by the reaction of BbtSbBr_2 with LiAlH_4 , in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in THF at -95°C afforded stibabismuthene **1** as red-purple crystals quantitatively. Stibabismuthene **1** showed satisfactory spectral data, as discussed below.



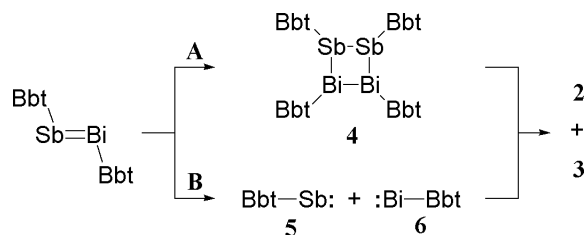
In the Raman spectrum (in the solid state) of **1**, a strong line attributable to the Sb-Bi stretching was observed at 169 cm^{-1} . This frequency lies between the value of the Sb-Sb stretching vibration in $\text{TbtSb}=\text{SbTbt}$ (207 cm^{-1})[2] and that of the Bi-Bi stretching vibration in $\text{TbtBi}=\text{BiTbt}$ (135 cm^{-1}),[3] and is higher than the Sb-Sb and Bi-Bi stretching frequencies for $\text{Ph}_2\text{E}-\text{EPh}_2$ ($\text{E}=\text{Sb, Bi}$). The UV/vis spectrum of **1** in hexane shows two absorption maxima at 709 nm (ϵ 200) and 516 nm (ϵ 7500), which are most likely assignable to the forbidden $n \rightarrow \pi^*$ and the allowed $\pi \rightarrow \pi^*$ transitions of the $\text{Sb}=\text{Bi}$ chromophore, respectively. These results are consistent with the characteristic red-shifts in the electronic spectra of previously reported heavier congeners of azo compounds, and the λ_{max} value for $\pi \rightarrow \pi^*$ transition of **1** is in the middle between that of $\text{BbtSb}=\text{SbBbt}$ (**2**) [λ_{max} 490 nm (ϵ 6000)] and that of $\text{BbtBi}=\text{BiBbt}$ (**3**) [λ_{max} 537 nm (ϵ 6000)]. These spectral data suggest that **1** features a double bond between antimony and bismuth even in solution as well as in the solid state. The reason of the superfluous red-shifts for the $n \rightarrow \pi^*$ transition of **1**, which is 39 nm longer than that of **3** [λ_{max} 670 nm (sh, ϵ 20)], is not clear at present.

The molecular structure of stibabismuthene **1** was also supported by the X-ray crystallographic analysis, but the definite structural parameters for **1** have not been obtained yet due to the inevitable disorder of the antimony and bismuth atoms, which cannot be solved by the data collection with a number of different single crystals of **1** even at low temperature (-180°C).

Stibabismuthene **1** is stable at ambient temperature in hydrocarbon solvents in the absence of air and light. When a solution of **1** in benzene- d_6 was heated at 70°C , **2** and **3** were formed very slowly as judged by ^1H NMR spectroscopy. Heating the solution of **1** at 80°C for 20 days led to the formation of a mixture of **1**, **2** and **3** with the ratio of 1:1.4:1.1, respectively. On the other hand, when a solution of **1** in benzene- d_6 was irradiated with a medium pressure mercury lamp (100 W) in a sealed Pyrex NMR tube at room temperature, the disproportionation reaction was completed in 4 h to give a 1:1 mixture of **2** and **3**. The results of the thermal and photochemical disproportionation reactions of **1** into the homonuclear double-bond species **2** and **3** can be regarded as a chemical evidence for the formation of stibabismuthene **1**.



Taking the previous reports on the reactivities of diphosphenes[7] into consideration, two different pathways can be postulated for the disproportionation reactions of stibabismuthene **1**. The first one is the dimerization of **1** by heating or irradiation followed by the decomposition of the resulting four-membered dimer **4** into the homonuclear double-bond species **2** and **3** (path A), while the other one is based on the dissociation of **1** giving the corresponding monovalent species, *i. e.*, stibinidene **5** and bismuthinidene **6**, both of which might undergo ready dimerization leading to the formation of **2** and **3**, respectively (path B).



Although we have examined the thermolysis and photolysis of **1** in the presence of 2,3-dimethyl-1,3-butadiene in expectation of trapping the intermediary monovalent species **5** and **6**, no [4+1] cycloadducts of **5** and **6** but only distibene **2** and dibismuthene **3** were obtained in high yields. Since we have already found that the stibinidene **5** generated by thermal cycloreversion of the corresponding overcrowded stibolene derivative readily undergoes [4+1] cycloaddition with 2,3-dimethyl-1,3-butadiene to give the stable stibinidene adduct,[6] the disproportionation reactions of stibabismuthene are not rationalized by the mechanism via stibinidene and bismuthinidene intermediates but most likely interpreted in terms of the association-dissociation mechanism via the head-to-head dimerization of **1**.

In summary, we have succeeded in the synthesis of the first stable stibabismuthene **1** by taking advantage of kinetic stabilization afforded by a new and effective steric protection group, Bbt. Further investigations on the physical and chemical properties of stibabismuthene and synthesis of other variations of heteronuclear doubly bonded systems between heavier main group elements are currently in progress.

References

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