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Synthesis of a stable stibabismuthene; the first compound with an antimony–bismuth double bond

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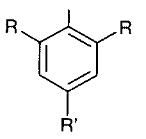
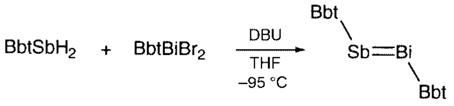
The condensation reaction of an overcrowded dihydrostibine with dibromobismuthine using 1,8-diazabicyclo[5.4.0]undec-7-ene as a base afforded the first stable stibabismuthene, the formation of which was evidenced by UV–VIS and Raman spectra and its chemical reactivity.

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 (Mes*P=PMes*; Mes* = 2,4,6-tri-*tert*-butylphenyl) in 1981,[1] a number of examples of kinetically stabilized diphosphenes (RP=PR)[2] and diarsenes (RAs=AsR)[2c,3] have been isolated and fully characterized. Recently, we have succeeded in the synthesis and characterization of the first stable distibene (TbtSb=SbTbt)[4] and dibismuthene (TbtBi=BiTbt),[5] even heavier congeners of azo compounds, by taking advantage of an efficient steric protection group, Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl.[6] Very recently, Power and coworkers also synthesized another type of stable distibene and dibismuthene substituted by bulky 2,6-$Ar_2C_6H_3$ groups (Ar = mesityl or 2,4,6-triisopropylphenyl).[7] As for the case of heteronuclear double-bond compounds between heavier group 15 elements, several phosphaarsenes[3a,8] and phosphastibenes[8,9] have been synthesized as stable compounds. However, there are 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 (TbtE=ETbt; E = 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 utilising the possible synthetic approaches or spectroscopically detecting 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),[10] which is expected to be a potentially more useful steric protecting group than TbT. In fact, a new distibene and dibismuthene substituted by Bbt groups, which have relatively high solubility compared with TbtE=ETbt (E = Sb, Bi), have been successfully synthesized and characterized.[11] We now report the successful application of the Bbt group to the synthesis of the first stable stibabismuthene, BbtSb=BiBbt **1**.



Tbt: R = R′ = $CH(SiMe_3)_2$
Bbt: R = $CH(SiMe_3)_2$, R′ = $C(SiMe_3)_3$

The 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 (Scheme 1). Stibabismuthene **1** showed satisfactory spectral data, as discussed below.



1

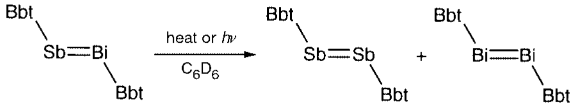
Scheme 1

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 wavenumber lies between the value of the Sb–Sb stretching vibration in TbtSb=SbTbt (207 cm^{-1})[4] and that of the Bi–Bi stretching vibration in TbtBi=BiTbt (135 cm^{-1}),[5] and is higher than the Sb–Sb and Bi–Bi stretching frequencies for $Ph_2E–EPh_2$ (E = Sb, Bi).[12] The UV–VIS spectrum of **1** in hexane shows two absorption maxima at 709 nm (ε 200 dm^3 mol^{-1} cm^{-1}) and 516 (7500), which are most likely assignable to the forbidden $n \rightarrow \pi^*$ and the allowed $\pi \rightarrow \pi^*$ transitions of the Sb=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 the $\pi \rightarrow \pi^*$ transition of **1** lies between those of BbtSb=SbBbt **2** [λ_{max} 490 nm (ε 6000 dm^3 mol^{-1} cm^{-1})][11] and BbtBi=BiBbt **3** [λ_{max} 537 nm (ε 6000 dm^3 mol^{-1} cm^{-1})].[11] These spectral data suggest that **1** features a double bond between antimony and bismuth in solution as well as in the solid state. The reason for the additional red-shift 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 X-ray crystallographic analysis, but definite structural parameters for **1** have not been obtained yet owing to the inevitable disorder of the antimony and bismuth atoms, which cannot be solved by 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



1 **2** **3**

Scheme 2

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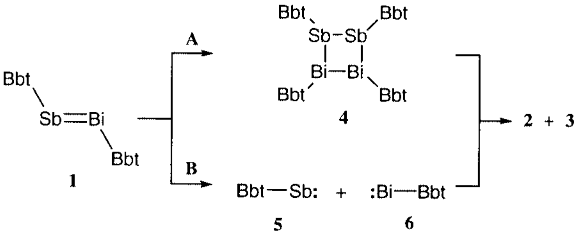
(Scheme 2). Heating a solution of **1** at 80 °C for 20 days led to the formation of a mixture of **1**, **2** and **3** with the ratio of 1 : 1.4 : 1.1, respectively. On the other hand, when a solution of **1** in benzene-d_6 was irradiated with a medium pressure mercury lamp (100 W) in a sealed Pyrex NMR tube at room temperature, the disproportionation reaction was complete 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 chemical evidence for the formation of stibabismuthene **1**.

Taking the previous reports on the reactivities of diphosphenes[2,13] into consideration, two different pathways can be postulated for the disproportionation reactions of stibabismuthene **1** (Scheme 3). The first is the dimerization of **1** by heating or irradiation followed by decomposition of the resulting four-membered dimer **4** into the homonuclear double-bond species **2** and **3** (path A), while the other 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).



Scheme 3

Although we have examined the thermolysis and photolysis of **1** in the presence of 2,3-dimethylbuta-1,3-diene 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-dimethylbuta-1,3-diene to give the stable stibinidene adduct,[10,11] the disproportionation reaction of stibabismuthene is 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 protecting group, Bbt. Further investigations on the physical and chemical properties of stibabismuthene and syntheses of other variations of heteronuclear doubly bonded systems between heavier main group elements are currently in progress.

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Notes and references

‡ *Spectral data* for **1**: red–purple crystals, mp 259–260 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6) δ 0.31 (s, 36H), 0.34 (s, 36H), 0.39 (s, 27H), 0.40 (s, 27H), 1.98 (s, 2H), 2.07 (s, 2H), 7.19 (s, 2H), 7.53 (s, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 1.37 (q), 2.42 (q), 2.82 (q), 5.76 (q), 21.42 (s), 22.15 (s), 41.35 (d), 43.64 (d), 124.23 (d), 128.95 (d), 145.48 (s), 148.54 (s), 151.81 (s), 152.20 (s), 153.70 (s), 195.34 (brs). FT-Raman (Nd : YAG laser 1064 nm) 169 cm^{-1} ($\nu_{\mathrm{Sb=Bi}}$). UV–VIS (hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 709 (200), 516 (7500). FAB-MS: *m*/*z* 880 ([BbtBiSb − Si(CH$_3$)$_3$]$^+$), 832 ([BbtBi]$^+$), 745 ([BbtSb + H]$^+$).

§ *Crystal data* for **1**: $C_{60}H_{134}Si_{14}BiSb$, M = 1579.64, triclinic, space group $P\bar{1}$ (no. 2), a = 12.574(2), b = 18.056(2), c = 9.318(1) Å, α = 92.756(3), β = 98.623(4), γ = 88.678(8)°, V = 2088.9(5) Å^3, Z = 1, D_c = 1.256 g cm^{-3}, Mo-Kα (λ = 0.71069 Å) radiation, μ(Mo-Kα) = 26.54 cm^{-1}, T = −180 °C, 13387 reflections measured, 8279 unique (R_{int} = 0.048).

CCDC 182/1683. See http://www.rsc.org/suppdata/cc/b0/b001900n/ for crystallographic files in .cif format

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