

VII-G Synthesis of Compounds Having a Novel Bonding Containing Heavier Main Group Element

Low-coordinate species of main group elements of the second row such as carbenes, olefins, carbonyl compounds, aromatic compounds, and azo compounds play very important roles in organic chemistry. However, the chemistry of their heavier element homologues has been undeveloped most probably due to their high reactivity and instability under ambient conditions. Since the first isolation of stable diphosphene ($P=P$), silene ($Si=C$), and disilene ($Si=Si$) in 1981 by taking advantage of steric protection, various double-bond compounds containing heavier main group elements have been synthesized and characterized.

On the other hand, we have developed an extremely bulky aromatic substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter) and 2,6-bis[bis(trimethylsilyl)methyl]-4-tris(trimethylsilyl)methylphenyl (denoted as Bbt hereafter). These substituents were found to be very effective steric protection groups for a variety of reactive species containing a heavier main group element. We have synthesized a variety of unprecedented low-coordinate compounds of heavier main group elements as stable compounds by taking advantage of kinetic stabilization using a new type of steric protection groups, Tbt and Bbt, and elucidated their properties.

VII-G-1 Separation of Orientational Disorder in the X-Ray Analysis of the Kinetically Stabilized 2-Silanaphthalene

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[*Bull. Chem. Soc. Jpn.* **73**, 2157 (2000)]

Cyclic electron delocalization of aromatic compounds distinctly appeared in their structure as bond length equalization. In view of the proximity in the periodic table, silicon analogues of aromatic compounds are expected to show similar structural features. However, sila-aromatic compounds are highly reactive and have been observed only in low-temperature matrices or in the gas phase, except for charged systems. During the course of our study on neutral sila-aromatic compounds, we have succeeded in the synthesis of the first stable 2-silanaphthalene **1** by taking advantage of an extremely bulky Tbt group. The structure of **1** was determined by X-ray crystallographic analysis, however, the severe disorder around the 2-silanaphthalene ring of **1** prevented us from discussing the detailed structure of **1** based on the X-ray analysis. Here, we report the refined crystallographic structural analysis of **1**.

The crystal structure of the stable 2-silanaphthalene **1** was refined more adequately by the separation of the disorder of overlapped two 2-silanaphthalene moieties. The bond lengths of the 2-silanaphthalene ring were in fairly good agreement with the theoretically calculated values which we previously reported.

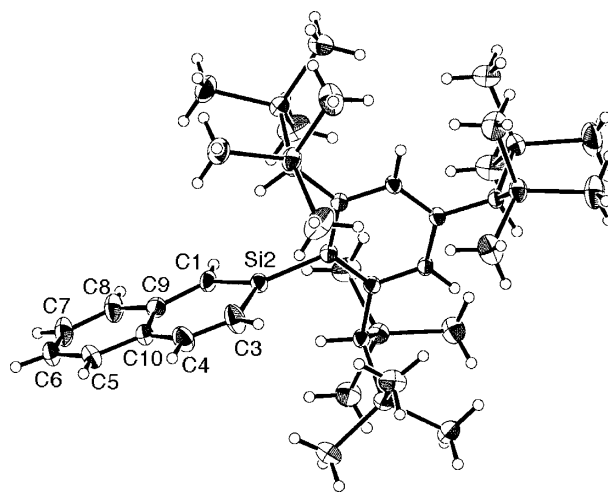


Figure 1. ORTEP drawing of 2-silanaphthalene **1** (major fragment).

VII-G-2 The First Chemical Trapping of Stibinidene, a Monovalent Antimony Compound

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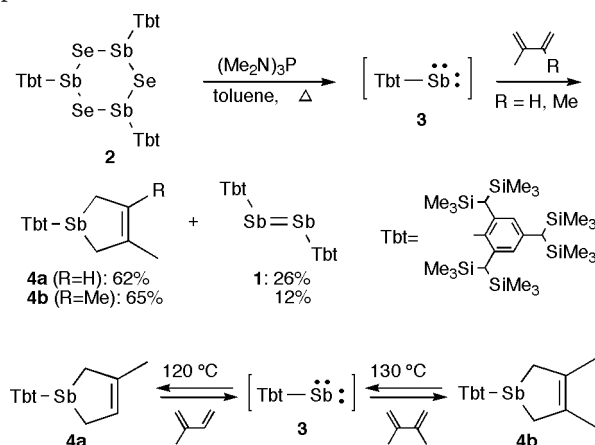
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[*Chem. Lett.* **42** (2001)]

In recent decades, there has been much interest in the chemistry of monovalent species of heavier group 15 elements. Phosphinidenes ($R-P:$), phosphorus analogues of nitrenes, have long been postulated as reactive intermediates. Stibinidenes ($R-Sb:$) are also interesting monovalent species of group 15 elements, but no stibinidene has been detected or trapped so far probably due to its extremely high reactivity. On the other hand, we have recently succeeded in the synthesis and characterization of the first stable distibene ($TbtSb=SbTbt$, **1**) and dibismuthene ($TbtBi=BiTbt$) by taking advantage of an efficient steric protection group, Tbt. In the final step for the synthesis of distibene **1**, that

is, deselenation reaction of $(\text{TbtSbSe})_3$ (**2**) with hexamethylphosphorous triamide (HMPT), it is rational to postulate the initial formation of a stibinidene (Tbt-Sb: , **3**) as an intermediate. In this paper we wish to present the first successful trapping reaction of the intermediary stibinidene.

Deselenation of 1,3,5-triseleno-2,4,6-tristibane **2** in the presence of 1,3-butadienes resulted in the formation of the corresponding [1+4]cycloadducts **4a,b** of a sterically hindered stibinidene **3**, a monovalent species of antimony. Thermal generation of **3** from **4a,b** via retro [1+4]cycloaddition reaction was suggested by the diene-exchange reaction in thermolysis of **4a,b** in the presence of another butadiene derivative.



VII-G-3 Formation of Antimony-Sulfur Double-Bond Compounds and Their Trapping with Nitrile Oxides

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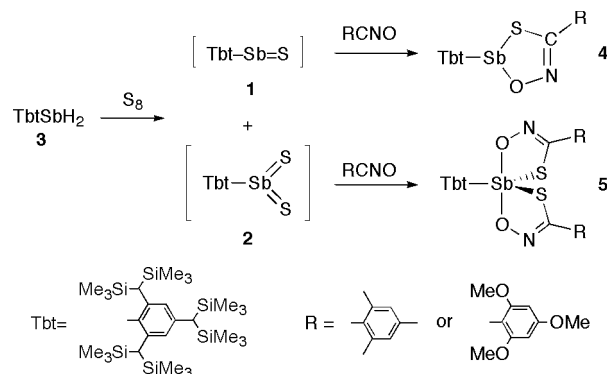
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[*Heteroatom Chem.* **12**, 244 (2001)]

The chemistry of compounds featuring double-bond containing heavier group 15 elements has attracted attention in recent years. As for the low-coordinated double-bond compounds between group 15 and group 16 elements, dithioxophosphorane $[\text{RP}(\text{S})=\text{S}]$ and diselenoxophosphorane $[\text{RP}(\text{Se})=\text{Se}]$ have been synthesized as stable compounds, and thioxophosphines $[\text{RP}=\text{S}]$ and selenoxophosphines $[\text{RP}=\text{Se}]$ stabilized by the coordination of an amino group have been observed in solution by NMR spectroscopy. However, there are no reports about the double bond of antimony with sulfur. In this paper, we describe the formation of thioxostibine $[\text{TbtSb}=\text{S}$ (**1**)] and dithioxostiborane $[\text{TbtSb}(\text{S})=\text{S}$ (**2**)] intermediates, which is confirmed by trapping reactions with nitrile oxides.

The reaction of a highly crowded dihydrostibine **3** with elemental sulfur in the presence of nitrile oxides resulted in the formation of [2+3]cycloaddition reaction products of a thioxostibine $[\text{TbtSb}=\text{S}$ (**1**)] and a dithioxostiborane $[\text{TbtSb}(\text{S})=\text{S}$ (**2**)], which are among a novel class of antimony-sulfur double bond

compounds. The structures of the [2+3]cycloadducts of dithioxostiborane **2** with nitrile oxides were determined by X-ray structural analysis. Desulfurization of highly crowded antimony-containing cyclic polysulfides $[\text{TbtSbS}_x$ ($x = 5$ or 7)] with phosphine reagents also resulted in the formation of **1** and **2**.



VII-G-4 Synthesis, Structures, and Reactivities of Novel Silacyclic Systems: The First Stable Silabenzene and Silacyclopropabenzene

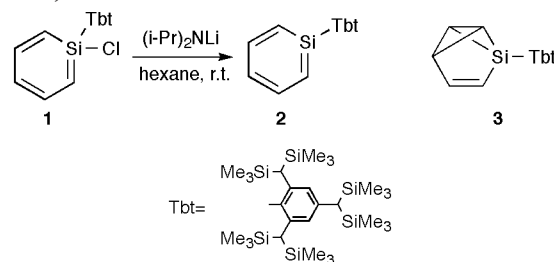
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[*Phosphorus, Sulfur Silicon Relat. Elem.* **168**, 31 (2001)]

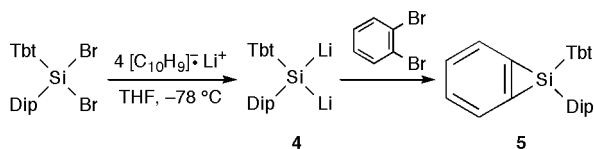
In the last two decades, kinetic stabilization has played an important role in the synthesis and isolation of a variety of heavier main group element compounds having an exotic structure and novel bonding. We have developed an extremely bulky and efficient steric protection group, Tbt, and applied it to the kinetic stabilization of highly reactive species of heavier main group elements. In this paper, the synthesis and isolation of the first stable silabenzene and silacyclopropabenzene are described as further application of Tbt group to the kinetic stabilization of novel conjugated ring systems containing a silicon atom.

The first stable silabenzene **2** was synthesized by the reaction of the corresponding chlorosilane **1** with $(i\text{-Pr})_2\text{NLi}$. The crystal structure and spectroscopic properties of **2** indicated that silabenzene **2** has a completely planar, delocalized 6π -electron ring system as in the case of benzene. Interestingly, irradiation of a benzene solution of **2** with the light of 290–350 nm resulted in the formation of an unprecedented valence isomer, silabenzvalene **3**.



On the other hand, an overcrowded diaryldithio-silane **4** was allowed to react with *o*-dibromobenzene to give the first stable silacyclopropabenzene **5**, which was

fully characterized by NMR spectra, FAB-MS, and X-ray structural analysis. The silacyclopropabenzene **5** thus obtained was found to be thermally very stable and have a completely planar geometry but a slightly squashed benzene ring. The crystallographic analysis revealed that no distinct bond localization is observed for the benzene moiety in contrast to its carbon analogue, *i.e.* cyclopropabenzene.



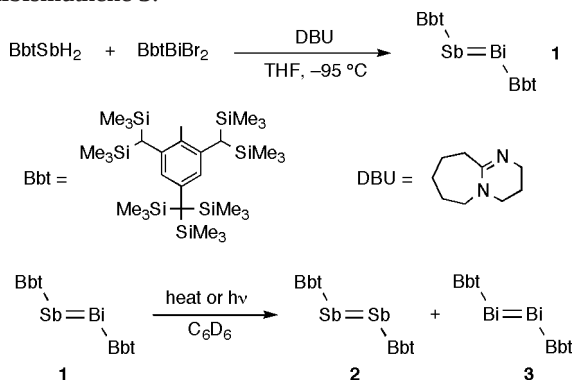
VII-G-5 Synthesis and Reactivities of the First Stable Stibabismuthene

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[*Phosphorus, Sulfur Silicon Relat. Elem.* **169**, 89 (2001)]

In recent years there has been much interest in compounds with a double bond between heavier group 15 elements. As for the case of heteronuclear double-bond compounds between heavier group 15 elements, several phospharsenes [RP=AsR] and phosphatibenes [RP=SbR] have been synthesized as stable compounds. However, there is no example of a heteronuclear doubly bonded system between antimony and bismuth, *i.e.* stibabismuthene. Recently, we have succeeded in the synthesis and characterization of the first stable distibene and dibismuthene [Ar-E=E-Ar (E = Sb, Bi; Ar = Tbt, Bbt)] by taking advantage of an efficient steric protection group, Tbt or Bbt group. We now report the successful application of the Bbt group to the synthesis of the first stable stibabismuthene, BbtSb=BiBbt (**1**).

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 **1**, the formation of which was evidenced by UV-vis and Raman spectra and its chemical reactivity. Thermolysis or photolysis of **1** resulted in the disproportionation reaction into the homonuclear double-bond species, distibene **2** and dibismuthene **3**.



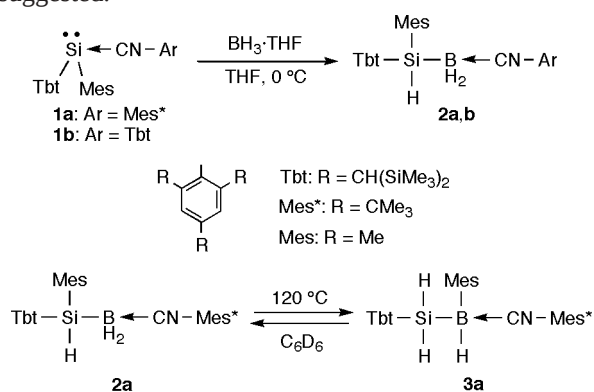
VII-G-6 Reaction of Stable Silylene–Isocyanide Complexes with BH₃·THF

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In recent decades, much attention has been paid to the chemistry of silylenes (silicon analogues of carbenes). Also, silylene complexes with Lewis bases have been extensively studied and some complexes have been synthesized in low temperature matrices so far. However, their properties have not been fully disclosed yet due to their instability at ambient temperature. On the other hand, we have recently succeeded in the synthesis of the first stable silylene–Lewis base complexes **1a,b** by taking advantage of an efficient steric protection group, Tbt group. In this paper, we describe the reactivity of **1a,b** with BH₃·THF.

Stable silylene–isocyanide complexes **1a,b** reacted with BH₃·THF to give the first stable silylborane–isocyanide complexes **2a,b**. The structures of **2a,b** were determined by NMR, IR, and mass spectrometry, elemental analysis, and X-ray crystallographic analysis. Thermolysis of **2a** at 120 °C gave a 1:5 mixture of **2a** and the corresponding migration product **3a** in contrast to the previously reported intermediary silylborane–isocyanide complexes [PhMe₂SiBX₂ ← CNR], which is known to give the corresponding (boryl)(silyl)imino-methanes [(PhMe₂Si)(X₂B)C=NR] as final products. Since the isolated compound **3a** also affords the 1:5 mixture of **2a** and **3a** by heating at 120 °C, the existence of an equilibrium between **2a** and **3a** is strongly suggested.



VII-G-7 Synthesis and Properties of the First Stable Germanaphthalene

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[*Organometallics* in press]

In recent years much attention has been focused on germaaromatic compounds, since they are among heavier congeners of aromatic hydrocarbons which play

very important roles in organic chemistry. Some ionic germaaromatic compounds have been successfully synthesized as stable compounds, while no isolation of a neutral germaaromatic compound has been reported probably due to its high reactivity. On the other hand, we have recently succeeded in the synthesis of kinetically stabilized silabenzene and 2-silanaphthalene, the first examples of stable neutral silaaromatic compounds, by taking advantage of an efficient steric protection group, Tbt group. Here, we report the synthesis and structure of 2-germanaphthalene **1** kinetically stabilized by the Tbt group, the first stable neutral germaaromatic compound.

The first stable 2-germanaphthalene **1** was synthesized by the dehydrobromination of bromogermane **2** with $(i\text{-Pr})_2\text{NLi}$ in THF at room temperature. The molecular structure of **1** was fully characterized by its ^1H and ^{13}C NMR spectra, which indicate the delocalized π -electronic structure of **1**. Moreover, the low-temperature X-ray crystallographic analysis of **1** revealed that 2-germanaphthalene ring was almost planar and the benzene ring of Tbt group was almost perpendicular to the 2-germanaphthalene ring. In addition, all the ^1H and ^{13}C NMR chemical shifts and the structural parameters of **1** experimentally obtained are in good agreement with the values theoretically calculated for some model compounds. UV-vis and Raman spectra of **1** also supported the aromatic character of the 2-germanaphthalene ring system.

