

VII-K Synthesis of Compounds Having a Novel Bonding Containing Heavier Main Group Elements

Double-bond compounds of main group elements of the second row such as 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-K-1 Syntheses and Crystal Structures of the First Disulfur and Diselenium Complexes of Platinum

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[*Angew. Chem. Int. Ed. Engl.* **41**, 136 (2002)]

The chemistry of complexes with diatomic chalcogen ligands has attracted much attention due to their unique structure, biological interest, potential for hydrogen-transfer catalysis, and synthetic utility as a precursor of new metal cluster complexes. However, since sulfur and selenium ligands have a strong propensity for bridging metal atoms, it is often difficult to prepare their mononuclear diatomic complexes. To our knowledge, the disulfur and diselenium complexes of platinum remain unknown, although the dioxygen analogues, *e. g.*, [(Ph₃P)₂PtO₂], have been extensively studied.

When platinum dichlorides **1a,b** were reduced by an excess of lithium naphthalenide in THF and the resulting platinum(0) species [(ArMe₂P)₂Pt] (**2a,b**) were successively treated with elemental sulfur (3 equiv. as S) and elemental selenium, the first platinum disulfur and diselenium complexes [(ArMe₂P)₂PtE₂] (**3a,b**: E = S; **4a,b**: E = Se) were obtained, respectively. The structures of **3a,b** and **4a,b** were identified by mass spectrometry, elemental analysis, and multinuclear NMR spectroscopy, and the molecular structures of **3b** and **4b** were finally determined by X-ray crystallographic analysis. The molecular structures of **3a,b** and **4a,b** are very similar, and these complexes have a square-planar geometry and a three-membered PtE₂ (E = S, Se) ring as well as an analogous dioxygen complex [(Ph₃P)₂PtO₂].

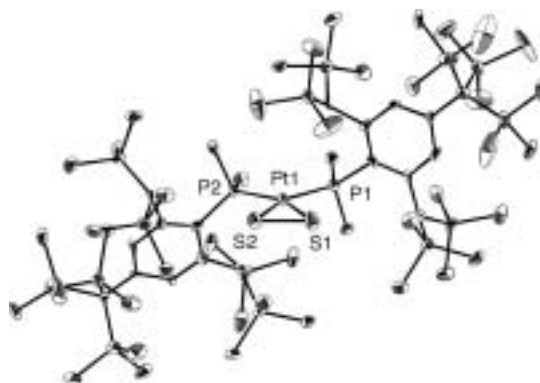
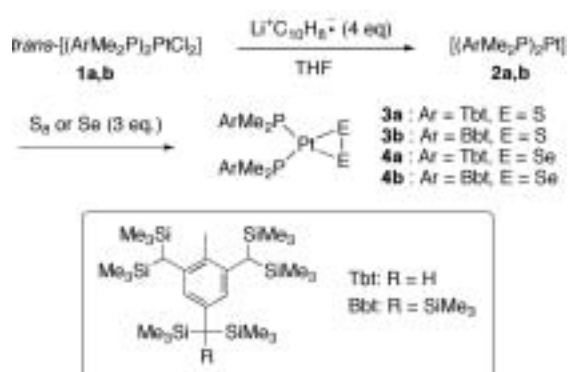


Figure 1. ORTEP drawing of a disulfur complex of platinum **3b**.

VII-K-2 Synthesis and Structure of the First Stable Phosphabismuthene

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[*Angew. Chem. Int. Ed. Engl.* **41**, 139 (2002)]

Recently, there has been much interest in doubly bonded compounds between group 15 elements, *i. e.*, heavier congeners of azo-compounds. Homonuclear

doubly bonded systems between heavier group 15 elements are no more imaginary species even in the case of bismuth, and the next target molecules are heteronuclear doubly bonded systems, which may be key compounds of great importance in the systematic elucidation of the intrinsic nature of low-coordinated compounds of heavier main group elements.

The first stable phosphabismuthene **1** was successfully synthesized by the condensation reaction of BbtBiBr_2 with Mes^*PH_2 in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in hexane at room temperature. It is noteworthy that compound **1** is not only a new member of a novel class of heteronuclear doubly bonded systems between heavier group 15 elements but also the first example of a stable species with a double bond between the third and sixth row main group elements. Phosphabismuthene **1** features a double bond between phosphorus and bismuth atom in the solid state and even in solution, as suggested by the NMR and UV/vis spectra and X-ray crystallographic analysis.

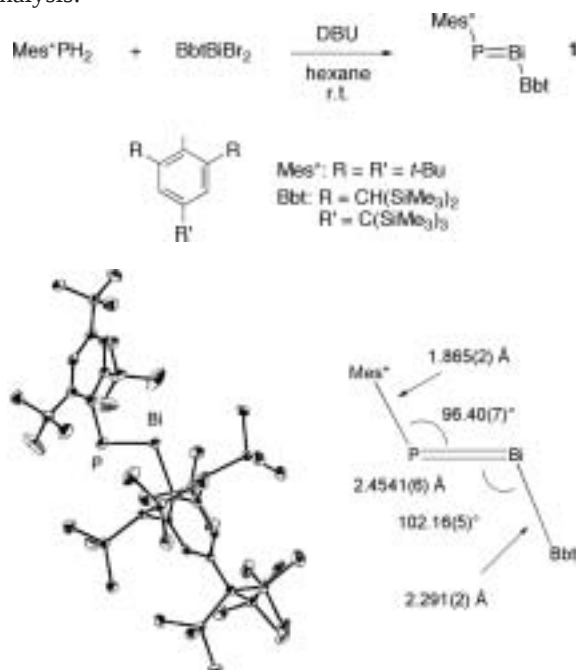


Figure 1. ORTEP drawing of phosphabismuthene **1**.

VII-K-3 Synthesis of Kinetically Stabilized Silaneselone and Silanetellone

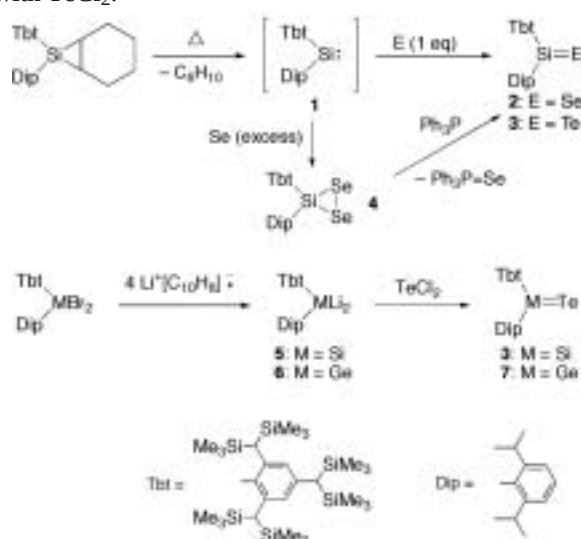
TOKITOH, Norihiro¹; SADAHIRO, Tomoyuki²; HATANO, Ken³; SASAKI, Takayo⁴; TAKEDA, Nobuhiro⁴; OKAZAKI, Renji²
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[Chem. Lett. 34 (2002)]

Since ketones play very important roles in organic chemistry, much interest has been focused on the chemistry of double-bond compounds between heavier group 14 and group 16 elements (we refer to this family of heavier congeners of ketones as “heavy ketones”). As for silicon-containing heavy ketones, only a silanethione

bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,4,6-triisopropylphenyl (Tip) groups [Tbt(Tip)-Si=S] was isolated as a stable compound. Although some examples are known for silaneselones stabilized by the intramolecular coordination of a nitrogen atom and transient silaneselones as reactive intermediates, no coordination-free examples have been synthesized yet for silaneselones and silanetellones so far.

Kinetically stabilized silaneselone **2** and silanetellone **3** were successfully synthesized by direct chalcogenation of silylene **1** with elemental chalcogen. The formation of **2** and **3** was confirmed by multinuclear NMR spectroscopy and trapping experiments. Deselenation of diselenasilirane **4**, which was generated by the reaction of **1** with an excess of selenium, also gave **2**. In addition, metallanetellones, **3** and **7**, were synthesized by a new synthetic method for heavy ketones, *i. e.*, the reaction of dilithiomethallane, **5** and **6**, with TeCl_2 .



VII-K-4 The First Stable 9-Silaanthracene

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[Organometallics **21**, 256 (2002)]

Since aromatic compounds play very important roles in organic chemistry, much attention has been also paid to silaaromatics. However, there are few reports on the synthesis and isolation of silaaromatic compounds stable at room temperature because of their high reactivity. Recently, we have succeeded in the synthesis of the first stable 2-silanaphthalene and silabenzene by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). In contrast, silaanthracenes have never been isolated as stable compounds, although there are some reports of the chemical trapping of intermediary silaanthracenes and of observation by UV/vis spectroscopy of unstable silaanthracenes in matrices at low temperature.

The first stable 9-silaanthracene **1** was successfully synthesized by the reaction of the corresponding silyl triflate **2** with 1.0 molar amount of lithium diisopropyl-

amide. The aromaticity of **1** is discussed on the basis of the NMR, UV/vis, and Raman spectra, X-ray structural analysis, and theoretical calculations. Although 9-silaanthracene **1** is thermally stable even at 100 °C in solution, treatment of **1** with H₂O at room temperature gave the corresponding silanol (90%) via the 1,4-addition of water to the 9- and 10-positions of 9-silaanthracene ring. Furthermore, 9-silaanthracene **1** reacted with styrene and benzophenone at room temperature to give the corresponding [2 + 4] cycloadduct in good yields.

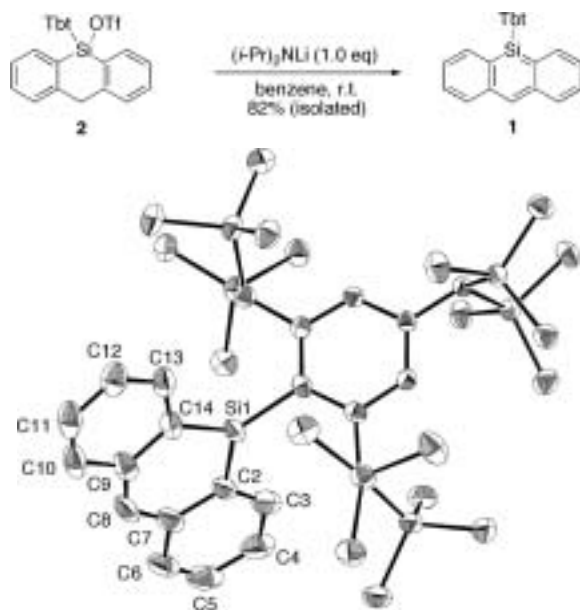


Figure 1. ORTEP drawing of 9-silaanthracene **1**.

VII-K-5 Synthesis and Characterization of an Extremely Hindered Tetraaryl-Substituted Digermene and its Unique Properties in the Solid State and in Solution

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[*Polyhedron* **21**, 563 (2002)]

During the last two decades remarkable progress has been made in the chemistry of low-coordinate compounds of heavier group 14 elements, especially in those of dimetallenes and metallylenes because of their unique structures and reactivities. In this paper, we present the synthesis and characterization of an extremely hindered digermene **1** bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group.

Digermene **1** was synthesized by the reaction of Tbt(Mes)GeCl₂ with lithium naphthalenide, and its crystal structure was determined by X-ray crystallographic analysis. An equilibrium between the digermene **1** and the corresponding germylene **2** was observed by the UV/vis spectra, and the thermodynamic parameters for the dissociation of digermene **1** to germylene **2** were obtained from temperature dependence of the absorption of **1**. Reactions of the digermene with O₂, W(CO)₅-

(THF), etc. in solution proceeded via the germylene, while, in the solid state, the digermene reacts with O₂ without the dissociation into the germylene.

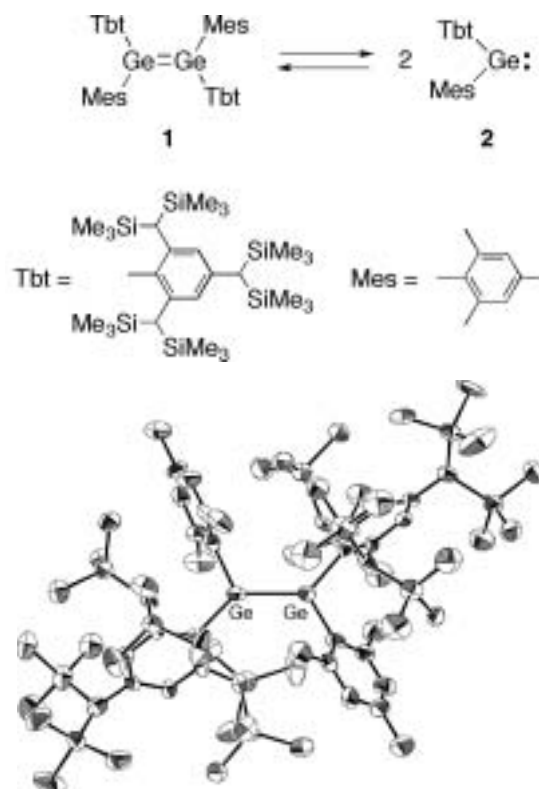


Figure 1. ORTEP drawing of digermene **1**.

VII-K-6 Syntheses, Structures and Properties of Kinetically Stabilized Distibenes and Dibismuthenes, Novel Doubly Bonded Systems between Heavier Group 15 Elements

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[*Bull. Chem. Soc. Jpn.* **75**, 661 (2002)]

The syntheses of stable compounds containing multiple bonds between heavier main group elements have been among the frontiers of great interest in chemical research. Nowadays, as for the heavier dipnictene series, numerous examples of kinetically stabilized diphosphenes (RP=PR), diarsenes (RAs=AsR), and phospharsenes (RP=AsR) have been isolated and fully characterized, and their various chemical properties have been revealed. However, distibene (RSb=SbR) and dibismuthene (RBi=BiR) had not been reported until our successful syntheses of the first stable distibene and dibismuthene utilizing a very effective and bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group.

Stable distibenes and dibismuthenes were successfully synthesized by taking advantage of an efficient

steric protection group, Tbt or 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) group. The crystallographic analysis and spectroscopic studies of these stable dipnictenes led to the systematic comparison of structural parameters and physical properties for all homonuclear doubly bonded systems between heavier group 15 elements. In addition to these experimentally obtained results, theoretical calculations for these doubly bonded systems also revealed the intrinsic character of dipnictenes.

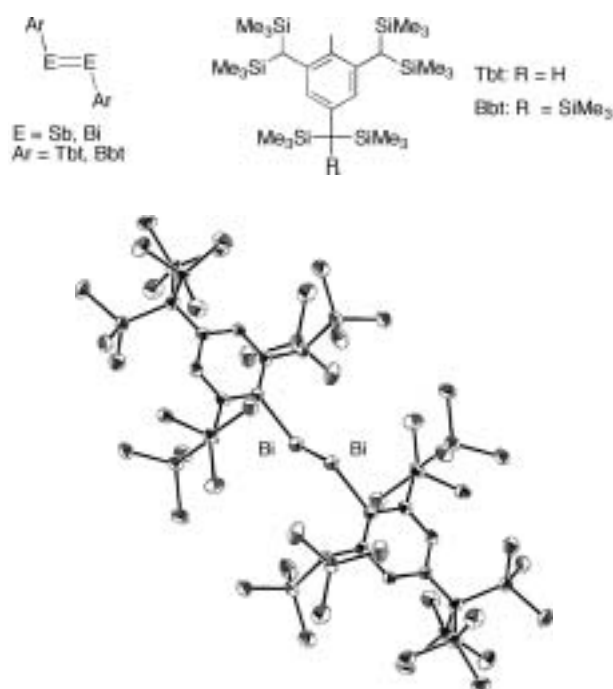


Figure 1. ORTEP drawing of BbtBi=BiBbt.

VII-K-7 Synthesis and Properties of the First Stable Germabenzene

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[*J. Am. Chem. Soc.* **124**, 6914 (2002)]

Recently, much attention has been focused on the chemistry of $[4n + 2]$ π -electron ring systems containing at least one heavier group 14 element. However, no synthesis and isolation of these compounds as stable molecules had been reported until quite recently due to their extremely high reactivity. We have recently succeeded in the synthesis and characterization of the first stable silabenzene, 2-silanaphthalene, 9-silaanthracene, and 2-germanaphthalene by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). These successful results in the sila- and germaaromatic systems naturally prompted us to extend this method to the synthesis of a germabenzene, which is the most fundamental germaaromatic compound having a simple 6 π -electron ring system.

The first stable germabenzene **1** was successfully synthesized by the reaction of the corresponding chloro-

germane **2** with lithium diisopropylamide in THF. The molecular structure and aromaticity of **1** were discussed on the basis of its NMR, UV-vis, and Raman spectra, X-ray crystallographic analysis, and theoretical calculations. Although the structural and spectroscopic data showed that **1** had aromaticity, in the reaction with various reagents, germabenzene **1** underwent 1,2- and/or 1,4-addition to the 1-germabuta-1,3-diene moiety reflecting the extremely high reactivity of the Ge-C double bond.

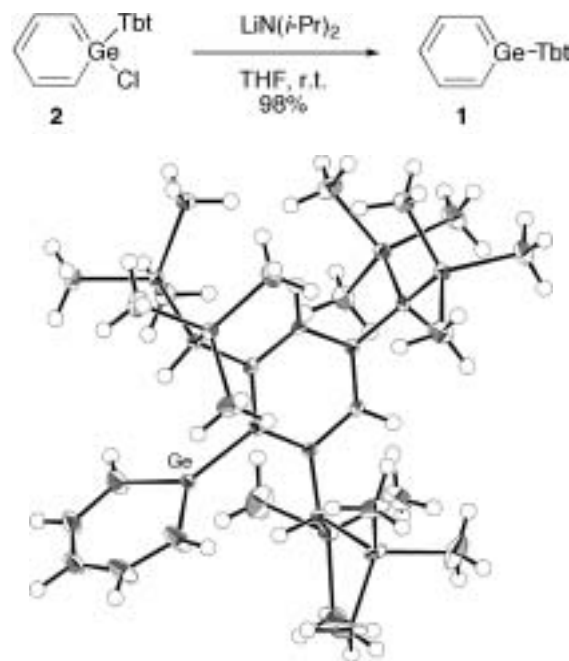


Figure 1. ORTEP drawing of germabenzene **1**.

VII-K-8 Reactions of 2-Germanaphthalene with Elemental Sulfur and Selenium: Synthesis of Novel Cyclic Polychalcogenides Containing a Germanium, Trichalcogenagermolanes

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[*Chem. Lett.* 818 (2002)]

The chemistry of cyclic polychalcogenides has attracted much interest because of their unique structures, reactivities and biological activities. Among them, however, cyclic polychalcogenides containing a germanium atom have been little known. Herein, we present the synthesis of novel Ge-containing cyclic polychalcogenides by the reactions of the first stable 2-germanaphthalene **1** bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) with elemental sulfur and selenium.

The reactions of a kinetically stabilized 2-germanaphthalene **1** with elemental sulfur and selenium resulted in the formation of novel five-membered cyclic trichalcogenides, **2** and **3**, containing a germanium, and the molecular structure of the triselenide was determined by X-ray crystallographic analysis. Desulfurization of **2** with 3 equivalent of Ph₃P resulted in the

formation of **1** (76%), while deselenation of **3** with 3 equivalent of Ph_3P gave a novel heterocycle, 1-selena-2,5-digermacyclopentane **4** (82%).

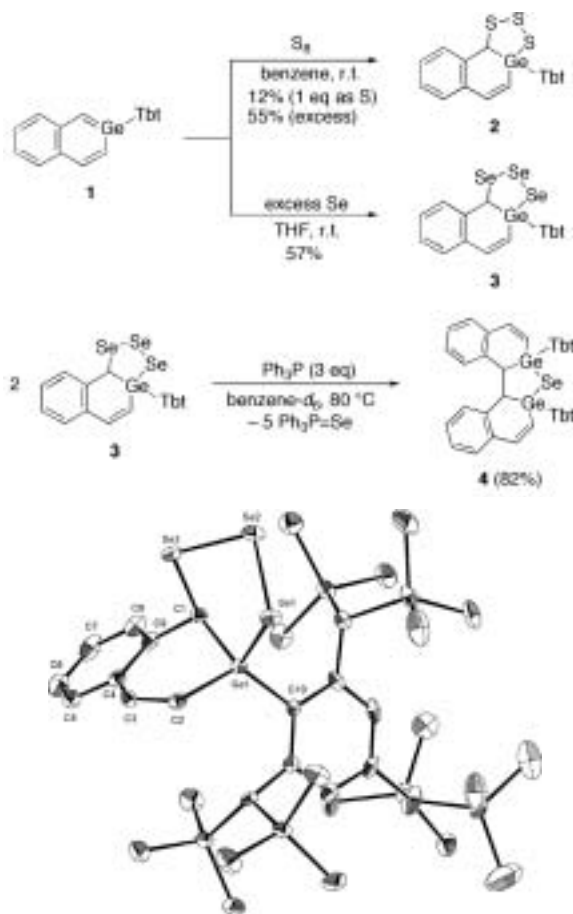


Figure 1. ORTEP drawing of triselenagermolane **3**.

VII-K-9 Synthesis and Properties of the First Stable 1-Silanaphthalene

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[Organometallics in press]

In recent decades, much interest has been paid to the chemistry of silicon analogs of aromatic compounds. However, the properties of sila-aromatic compounds have not been fully revealed yet because of the extreme instability of the low-coordinated silicon compounds. Very recently, we have succeeded in the synthesis of the first stable silabenzene, 2-silanaphthalene, and 9-silaanthracene by taking advantage of an extremely bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). On the other hand, there is no report for the synthesis of 1-silanaphthalene, which is a structural isomer of 2-silanaphthalene, although much attention has been focused on the similarities and differences between 1- and 2-silanaphthalenes.

The first 1-silanaphthalene **1** was successfully synthesized as moisture-sensitive, pale yellow crystals by taking advantage of Tbt group. The structure of **1**

was determined based on its ^1H , ^{13}C , and ^{29}Si NMR, Raman, and UV/vis spectra together with theoretical calculations. These data clearly indicated that **1** has aromaticity comparable with naphthalene as well as Tbt-substituted 2-silanaphthalene. In contrast to the thermal stability of 2-Tbt-2-silanaphthalene, 1-Tbt-1-silanaphthalene (**1**) underwent a ready [2 + 4] dimerization reaction in solution even at room temperature.



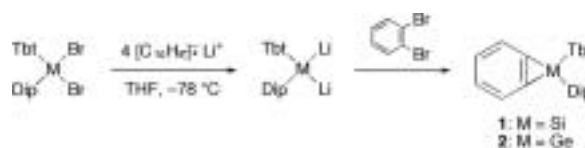
VII-K-10 Synthesis and Isolation of the First Germacyclopropabenzene: A Study to Elucidate the Intrinsic Factor for the Ring Deformation of Cyclopropabenzene Skeletons

TOKITO, Norihiro¹; HATANO, Ken²; SASAKI, Takayo³; SASAMORI, Takahiro³; TAKEDA, Nobuhiro³; TAKAGI, Nozomi; NAGASE, Shigeru
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[Organometallics in press]

Since the finding of significant deformation for the fused aromatic rings in the series of benzocycloalkanes, it has been one of the important subjects assigned to organic chemists to solve a riddle for such deformation. Cyclopropabenzene has attracted special attention because of the most severely enforced deformation in this series. Recently, we have synthesized and isolated silacyclopripabenzene **1** as the first example of a stable heteracyclopripabenzene by taking advantage of the characteristic reactivity of the sterically hindered dilithiosilane, $\text{Tbt}(\text{Dip})\text{SiLi}_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dip = 2,6-diisopropylphenyl), towards 1,2-dibromobenzene. This successful isolation of **1** naturally prompted us to examine the synthesis of germacyclopripabenzene.

The treatment of an overcrowded diaryldilithio-germane, $\text{Tbt}(\text{Dip})\text{GeLi}_2$, generated by exhaustive reduction of $\text{Tbt}(\text{Dip})\text{GeBr}_2$, with 1,2-dibromobenzene resulted in the isolation of the first stable germacyclopripabenzene **2**, which was fully characterized by ^1H and ^{13}C NMR spectra, FAB-MS, and X-ray structural analysis. As well as the case of silacyclopripabenzene **1**, the structural parameters of **2** indicated that the germacyclopripabenzene ring can enjoy annelation with much less perturbation, in contrast to the severe distortion in cyclopropabenzene rings.



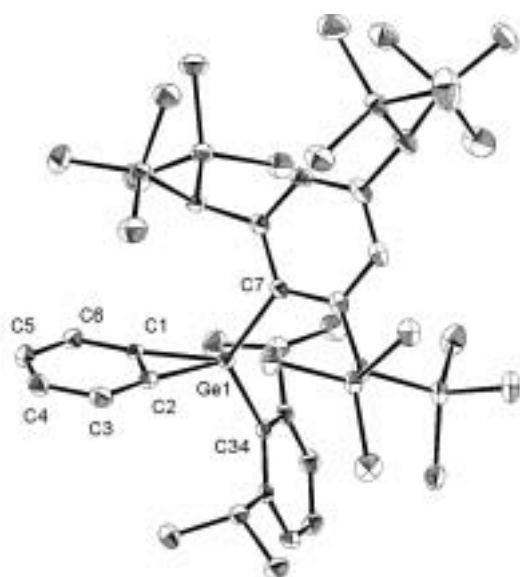


Figure 1. ORTEP drawing of germacyclopropabenzene 1.