Reviews

Sila- and Germacyclopropabenzenes

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Received February 18, 2006

This review article describes the initial work on the sila- and germacyclopropabenzenes, the heavier congeners of cyclopropabenzenes that have a silicon or germanium atom instead of a carbon atom as the bridging atom of its cyclopropabenzene skeleton. The key factor in their successful preparation is the development of a synthetic method that is effective under mild conditions, i.e., the reaction of a dilithio compound (Tbt(Dip)MLi$_2$ (M = Si, Ge)) that has effective steric protective groups, 2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl (denoted as Tbt) and 2,6-diisopropylphenyl (denoted as Dip), with 1,2-dibromobenzene at −78 °C. These were successfully applied to the synthesis of not only sila- and germacyclopropabenzenes but also stable bis(sila- and germacyclopropa)benzenes with two sila- and germacyclopropene rings fused to one benzene ring. These compounds are the heavier congeners of the unknown bis(cyclopropa)benzene derivative.

1. Introduction

The chemistry of cycloproparenes has fascinated organic chemists, due to the balance of the aromatic character of the arene moiety and the angular strain in the three-membered ring, which result in their unique properties.[1] The history of cyclopropabenzene dates back to the 1960s, when Anet et al. reported the cycropropabenzene derivative **1**.[2] The successful preparation of the parent cyclopropabenzene **2** by Vogel, Grimme, and Korte followed soon thereafter.[3] Now, a variety of synthetic methods for cycloproparenes have been established and reported.[1a,b] The chemistry of cycloproparenes has been expanded through the concept of strain-induced bond localization (SIBL),[4,5] which has been controversial since the introduction of the hypothesis of the Mills−Nixon effects.[6] Although many studies (X-ray crystallographic analyses, physical properties, chemical reactivities, and theoretical calculations) have been devoted to the question of the presence or absence of the Mills−Nixon effect (or reverse Mills−Nixon effect),[5,7] no clear conclusion has been reached as yet.[5,8] This review does not cover the details of the chemistry of the all-carbon cycloproparenes, since the historical accounts

by B. Halton,[1] one of the authorities on such chemistry, are quite adequate.

On the other hand, the chemistry of heterocyclopropabenzenes, which have a heteroatom as the bridging atom of their cyclopropabenzene skeletons instead of a carbon atom, has also been an important touchstone for the SIBL effect in cycloproparene derivatives.[4c] Although a few transition metal cyclopropabenzene analogues such as **3**[9] and **4**[10] have been reported as stable compounds, their structures and properties strongly indicate that they are closer to being benzyne complexes rather than metallacyclopropabenzenes. Despite many theoretical predictions,[4,5,7,11,12] no stable example of a heterocyclopropabenzene other than the benzyne complexes (the formal metallacyclopropabenzens) has been reported. It may be that they might undergo ready polymerization or isomerization due to their extremely high reactivity and/or inherent instability.[12] The generation of benzothiirene **5**[13−15] and benzoselenirene **6**[15] (thia- and selenacyclopropabenzene derivatives) was postulated as reactive intermediates of photochemical reactions of the corresponding 1,2,3-benzochalcogenadiazoles **7** and **8** in low-temperature matrixes based on the IR spectra. However, the final products of these reactions were **9** and **10**, formed by the isomerization of **5** and **6**, respectively. On the other hand, it was reported that benzothiirene **5**, generated by the thermal

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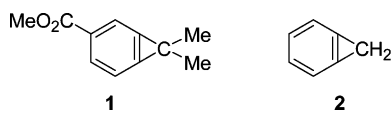
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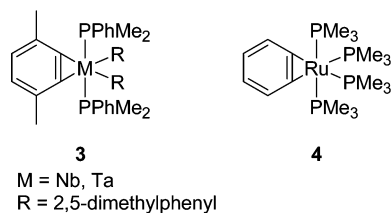
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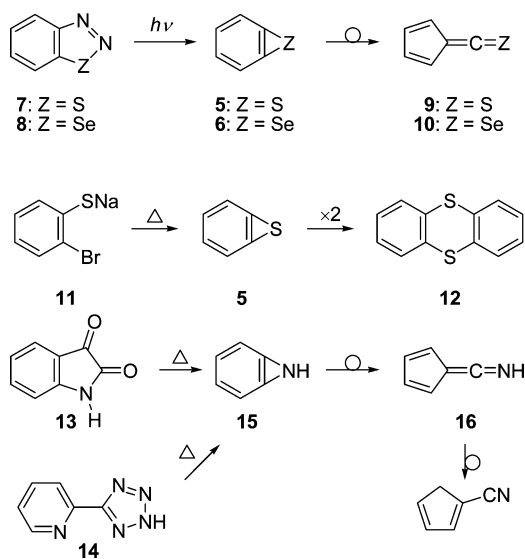
Scheme 1

1

2

Scheme 2

3

M = Nb, Ta
R = 2,5-dimethylphenyl

4

Scheme 3

hν

7: Z = S
8: Z = Se

5: Z = S
6: Z = Se

9: Z = S
10: Z = Se

△

11

5

×2

12

△

13

15

16

△

14

Scheme 4

hν
− H₂

major

17

18

Si

minor

17

18

+ :SiH₂

19

Table 1. Relative Energies[a] (kcal/mol) of Isomers and Dimer of the Heteracyclopropabenzene Derivatives [B3LYP/ 6-311G(2d,p)]

20

21

22

23

24

25

18 + **26**

27

	E =			
	a: SiPh₂	**b**: PPh	**c**: NPh	**d**: S
20[a]	0.0	0.0	0.0	0.0
21	71.1	61.7	33.7	50.2
22	81.0	88.7	58.4	109.6[k]
23	95.3	104.1[e]	−[i]	106.7
		103.1[e]		
24	37.0	13.3	−43.4	−13.7
25[b]	64.8	48.4	6.3	33.4
18+**26**	88.5[d]	78.7[f]	84.7[d]	77.8[f]
27[c]	−86.5	−85.8[g]	−171.2[j]	−118.7
		−85.7[h]		

[a] The energy of the isomer **20** is set to 0.0 kcal/mol as a standard. [b] Singlet species. [c] The energies were compared with the two molecules of **20**. [d] Singlet species is more stable than the triplet species. [e] Two isomers were found as local minimum. [f] Triplet species is more stable than the singlet species. [g] *syn* isomer. [h] *anti* isomer. [i] The local minimum was not found. [j] The N atoms showed planar geometries. [k] Transition state.

reaction of **11**, underwent ready dimerization to afford thianthrene (**12**).[16] In addition, the FVP (flash vacuum pyrolysis) of isatin (**13**) or tetrazole **14** was reported to afford the intermediary benzazirine (azacyclopropabenzene) **15**, which underwent ready isomerization leading to the formation of **16**.[17] Thus, it was found to be difficult to suppress the high tendency toward isomerization and/or dimerization of the heteracyclopropabenzenes and to isolate them as stable compounds.

Above all, silacyclopropabenzenes (benzosilirenes) are a fascinating class of organosilicon compounds, since silicon-containing three-membered silirene ring systems have been well studied and have attracted much attention from the viewpoints of their strained molecular structures and unique reactivities. Unfortunately, the conventional synthetic methods for cyclopropabenzenes or silicon-containing three-membered-ring compounds are difficult to apply to the construction of a silacyclopropabenzene skeleton. Silacyclopropabenzene **17** was postulated as a highly reactive intermediate in the photolysis of PhSiH₃.[18] It was reported to undergo dissociation into benzyne **18** and silylene **19** (Scheme 4). However, there have been no claims of a stable silacyclopropabenzene.

Tokitoh et al. performed preliminary theoretical calculations on possible valence isomers of some heteracyclopropabenzenes
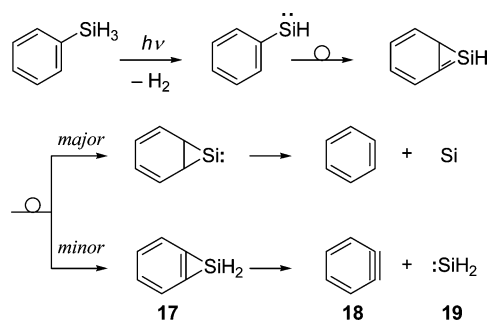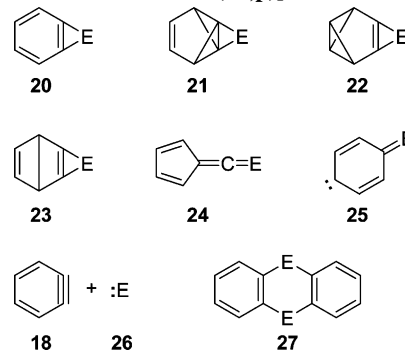
(Table 1): sila-, phospha-, aza-, and thiacyclopropabenzene derivatives.[19] In all cases, the calculation indicated that the dimerization of isomer **20** should be a highly exothermic reaction. It should be noted that the cyclopropabenzene analogues **20a** and **20b** are surprisingly more stable than the other valence isomers (**21−26**) in the cases of E = SiPh₂ and PPh, while the corresponding 2,4-cyclopentadien-1-ylidene isomers **24c** and **24d** are the most stable among the isomers for E = NPh and S. The results of these theoretical calculations led us to believe that the sila- and phosphacyclopropabenzene derivatives should be accessible and isolable when they are synthesized under mild conditions and kinetically well protected in order to prevent their self-dimerization.
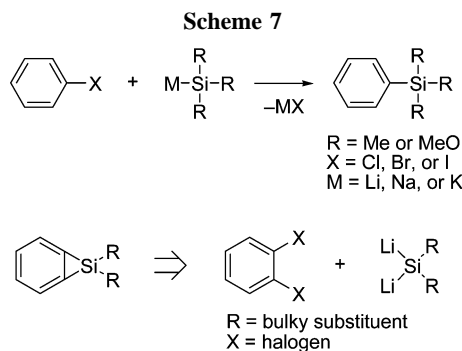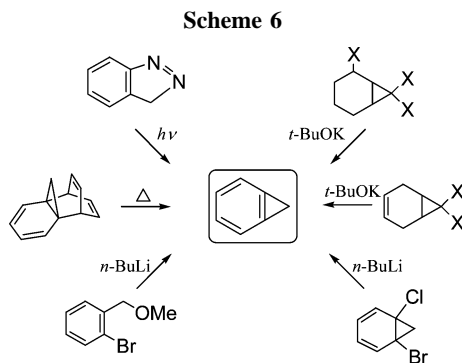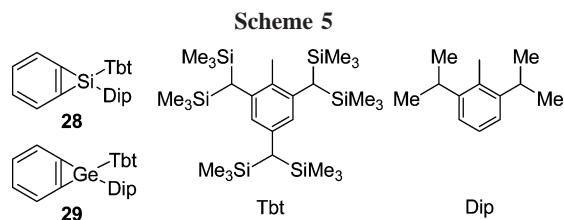
We have spent much effort to synthesize the heteracyclopropabenzenes (containing the heavier group 14 elements, silicon and germanium, as bridge atoms) and have succeeded in the synthesis of the first stable silacyclopropabenzene (**28**), germa-

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Scheme 5

Scheme 6

Scheme 7

R = Me or MeO
X = Cl, Br, or I
M = Li, Na, or K

R = bulky substituent
X = halogen

Scheme 8

32:M = Si
33:M = Ge

30:M = Si
31:M = Ge

Dis = CH(SiMe$_3$)$_2$

34:M = Si
**35**:M = Ge

Scheme 9

30:M = Si
31:M = Ge

cyclopropabenzene (**29**), and unique related compounds. This article is intended to review the recent advances in the chemistry of stable sila- and germacyclopropabenzenes.

2. Generation of Dilithiosilane and Dilithiogermane, Suitable Precursors for the Sila- and Germacyclopropabenzenes

Many synthetic routes have been established for the cyclopropabenzenes, as shown in Scheme 6.[1] However, all of them could not be applicable to the preparation of sila- and germacyclopropabenzenes, since the corresponding precursors, which should be hindered by bulky substituents for the kinetic stabilization of the resulting sila- and germacyclopropabenzenes, may not be easily available. We developed a novel synthetic strategy for the sila- and germacyclopropabenzenes, i.e., a reaction of a dilithiosilane or dilithiogermane with a 1,2-dihalobenzene, based on a previous report[20] of the reaction of a silyllithium[21] with a halobenzene giving the corresponding arylsilane (Scheme 7).

During the course of our investigation on the kinetic stabilization of the low-coordinated compounds of heavier group 14 elements, it was found that diaryldilithiosilane **30**[22] and diaryldilithiogermane **31**[23] could be generated by the exhaustive
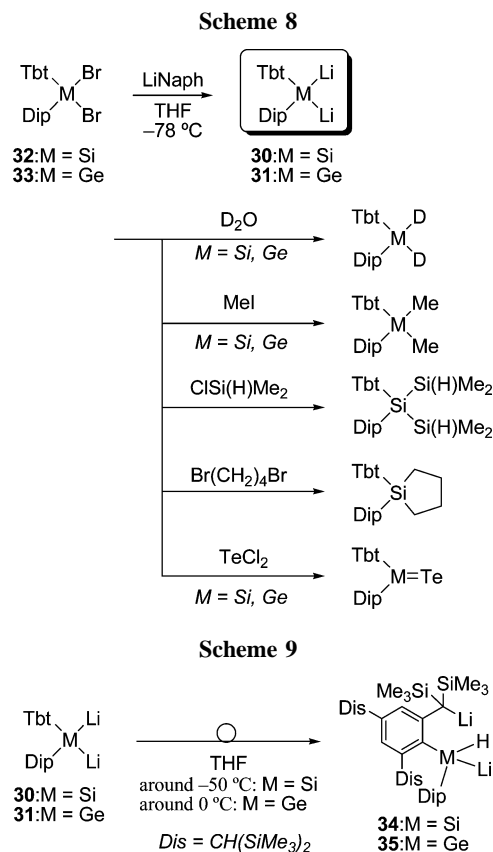
reduction of the corresponding dibromosilane **32** and dibromogermane **33** bearing bulky substituents, Tbt and Dip groups (Scheme 8). The reduction of **32** and **33** with an excess of lithium naphthalenide at −78 °C in THF afforded the corresponding dilithio derivatives **30** and **31**, respectively, the almost quantitative generation of which was confirmed by trapping reactions including those with MeI and D$_2$O (Scheme 8).

Recently, much attention has been devoted to dilithio derivatives of silicon and germanium as unique functional reagents. We have applied the dilithio compounds **30** and **31** to the synthesis of novel doubly bonded systems such as a silanetellone and a germanetellone via their reactions with TeCl$_2$.[23] Sekiguchi and co-workers have reported the stable dilithio derivatives (R$_2$MLi$_2$, M = Si, Ge, R = bulky silyl substituent) and their use in the synthesis of heteronuclear doubly bonded compounds of silicon and germanium.[24] With the overcrowded diaryldilithiosilane **30** and diaryldilithiogermane **31** in hand, we investigated their reactions with 1,2-dibromobenzene in the hope of preparing sila- and germacyclopropabenzenes.

Unfortunately, dilithiosilane **30** and dilithiogermane **31** were not sufficiently stable to allow their isolation at ambient temperature. Trapping experiments with **30** and **31** using D$_2$O at variable temperatures showed that **31** gradually underwent Li−H exchange at the *ortho*-position of the Tbt group at around 0 °C to afford **34**, while **30** underwent such rearrangement giving **35** at around −50 °C (Scheme 9). Since it was found that **30** and **31** certainly are generated by this method in THF

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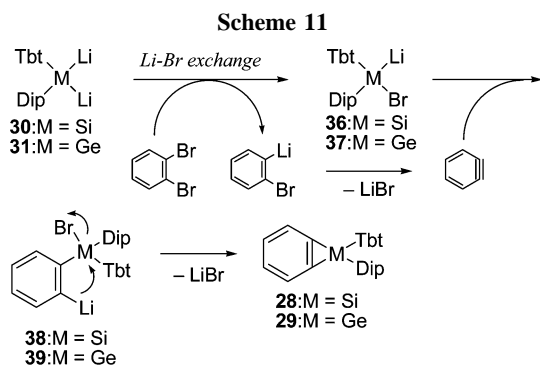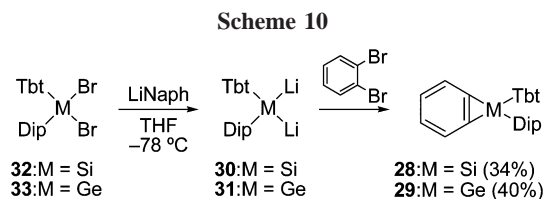
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Scheme 10

Scheme 11

Figure 1. Molecular structures of (a) **28** and (b) **29** (thermal ellipsoid plots at 50% probability).

at −78 °C, we found that they could be utilized for synthetic purposes at that temperature.

3. Synthesis of the First Stable Sila- and Germacyclopropabenzenes

Treatment of the dilithio derivatives **30** and **31** prepared as described above with 1 equiv of 1,2-dibromobenzene at −78 °C resulted in the formation of the first stable sila- and germacyclopropabenzenes, **28**[25,26] and **29**,[27] respectively, which were isolated via the purification process using HPLC (toluene) and PTLC (SiO$_2$, hexane) as colorless, prismatic crystalline compounds in 34% (for **28**) and 40% (for **29**) yields (Scheme 10). These formal double-substitution reactions of an Ar$_2$ELi$_2$ (E = Si, Ge) with 1,2-dibromobenzene represent an entirely new approach to the synthesis of heteracyclopropabenzenes.

The mechanism for the formation of **28** and **29** probably is not a simple substitution process but must be a more complicated reaction, possibly the addition of silylenoid **36** and germylenoid **37**, which might be initially formed by Li−Br exchange as shown in Scheme 11, to benzyne generated by the 1,2-elimination of LiBr from *o*-bromolithiobenzene. Intramolecular cyclization of the resulting *o*-lithiophenylsilane and germanes (**38** and **39**) then would follow (Scheme 11).

Compounds **28** and **29** have sufficient solubility in organic solvents (hexane, CHCl$_3$, benzene, and so on). In the ^{1}H and ^{13}C NMR spectra of the isolated sila- and germacyclopropabenzenes **28** and **29**, the signals attributed to the H and C atoms on the heterocyclopropabenzene rings were observed in the general aromatic region. Thus the aromatic ring current effects of the central benzene rings are retained. The ^{29}Si NMR spectrum of **28** showed a signal at high field (−104.8 ppm) characteristic of an Si-containing three-membered ring compound.[28] Heterocyclopropabenzenes **28** and **29** were found to be thermally very stable. They had not decomposed after they had been heated to their melting point (**28**, 257 °C; **29**, 235−237 °C) and remained undecomposed at 130 °C in toluene-d_8
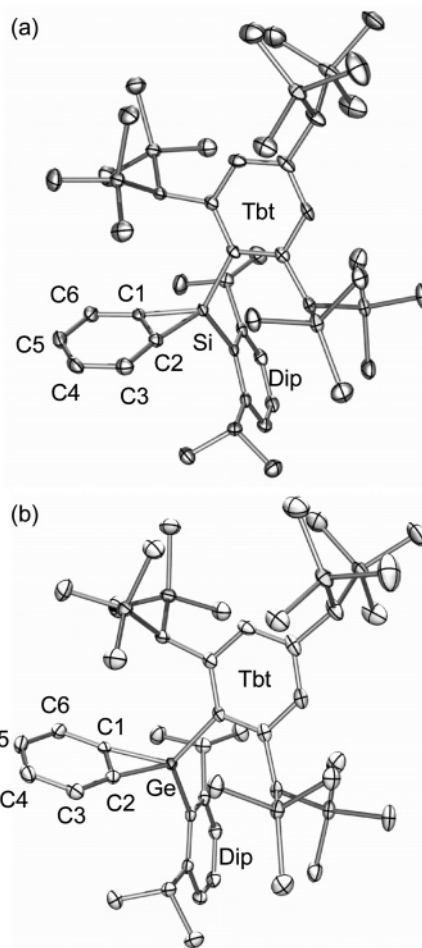
solutions. The germacyclopropabenzene **29** undergoes slow decomposition on silica gel during the purification procedure (SiO$_2$/hexane), giving the ring-opened hydrolyzed product **40**, in contrast to the silacyclopropabenzene **28**, which can be purified without any decomposition by silica gel column chromatography under the same conditions.

4. Structures of the Metallacyclopropabenzenes

The molecular structures of the heterocyclopropabenzenes **28** and **29** were determined by X-ray crystallographic analysis (Figure 1). The benzene skeletons of **28** and **29** were found to be similar to each other and have completely planar geometries. In both cases, the sums of bond angles at the juncture carbons (C1 and C2) are almost 360°, and those of interior bond angles in the benzene rings are 720°. The selected bond lengths and angles of **28** and **29** are listed in Table 2 together with those of cyclopropabenzene **2**[29] and those theoretically optimized for the model compounds of the sila- and germacyclopropabenzenes (**41a,b** and **42a,b**).

It is well known that annelation of a small ring to an aromatic system usually causes deformation of the aromatic ring. In comparison with the typical C−C distances in benzene (ca. 1.39−1.40 Å), an extreme shortening of the juncture bond **a** along with a slight shortening of its neighboring bonds **b** is observed for cyclopropabenzene **2**. The angles of δ, ε, and ζ observed for **2** deviate considerably from the ideal value (120°) for a typical bond angle of an sp^2 carbon atom. Despite such distortions, the conclusion on the structure of **2** was that the aromatic π-electron delocalization is retained in the central benzene ring.

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Table 2. Observed and Calculated Structural Parameters for the Metallacyclopropabenzenes and Cyclopropabenzenes

2: ERR' = CH_2
28: ERR' = Si(Tbt)Dip
29: ERR' = Ge(Tbt)Dip
41a: ERR = SiH_2
41b: ERR = $SiPh_2$
42a: ERR = GeH_2
42b: ERR = $GePh_2$

	2[a]	28[b]	29[c]	2[d]	41a[d]	41b[d]	42a[d]	42b[d]
a/Å	1.334(4)	1.390(4)	1.391(3)	1.344	1.392	1.399	1.381	1.389
b/Å	1.363(3)	1.388(4)	1.385(3)	1.375	1.392	1.393	1.390	1.391
		1.394(4)	1.388(3)					
c/Å	1.387(4)	1.381(4)	1.392(3)	1.407	1.389	1.389	1.393	1.392
		1.383(4)	1.391(3)					
d/Å	1.390(5)	1.403(5)	1.397(3)	1.398	1.405	1.405	1.403	1.402
e/Å	1.498(3)	1.826(2)	1.932(2)	1.503	1.817	1.819	1.924	1.929
		1.828(3)	1.940(2)					
α/deg	52.8(2)	44.7(1)	42.11(8)	53.1	45.3	45.2	42.1	42.2
β/deg	63.6(1)	67.6(2)	68.6(1)	63.4	67.5	67.4	69.0	68.9
		67.7(1)	69.3(1)					
γ/deg	171.7(2)	170.9(2)	169.5(2)	172.1	170.7	171.1	168.7	169.2
		171.0(2)	168.7(2)					
δ/deg	124.5(2)	121.3(3)	121.9(2)	124.4	121.9	121.5	122.3	121.9
		121.5(2)	122.0(2)					
ε/deg	113.2(2)	117.3(3)	116.5(2)	113.4	116.5	117.0	116.0	116.5
		117.3(3)	116.3(2)					
ζ/deg	122.4(2)	121.2(3)	121.6(2)	122.2	121.6	121.5	121.7	121.6
		121.4(3)	121.7(2)					

[a] X-ray at −150 °C, see ref 29. [b] X-ray at −170 °C, see ref 25. [c] X-ray at −170 °C, see ref 27. [d] Optimized structure at B3LYP/ 6-311G(2d,p).
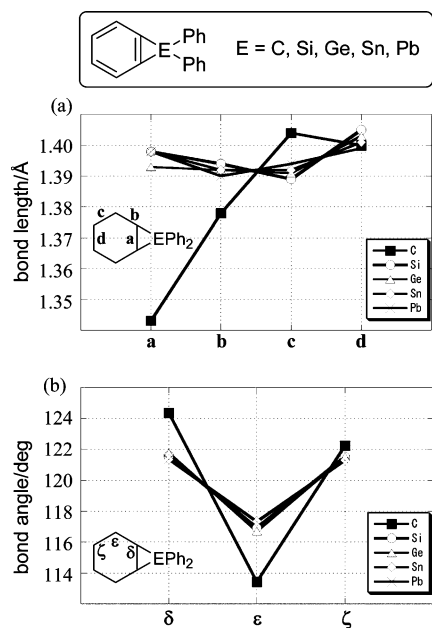

Figure 2. Calculated structural parameters for diphenylcyclopropabenzene and its heavier congeners at the B3LYP/6-311G(2d,p) (TZ(2d) for Si, Ge, Sn, Pb) level.

Sila- and germacyclopropabenzenes **28** and **29** have slightly squashed benzene moieties, in which all bond angles deviate from the ideal sp^2 bond angles (120°), although the degree of the distortion of the bond angles in the cases of **28** and **29** is smaller than that of cyclopropabenzene **2**. Such a tendency of the bond angles in the central benzene ring (α, γ > 120° > β) can be interpreted in terms of the influence of the three-membered-ring annelation. Interestingly, no obvious bond shortening (and elongation) was observed for both **28** and **29**, in contrast to the case of cyclopropabenzene **2**. In particular, the most extreme structural difference between the hydrocarbon system **2** and the sila- and germacyclopropabenzenes (**28** and **29**) is the lengths between the juncture carbon atoms (**a**, C1−
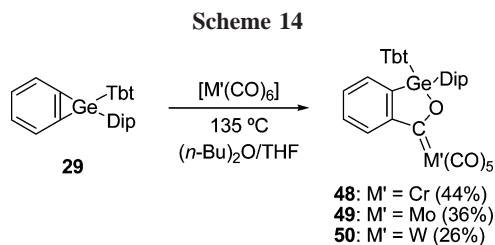
Scheme 12
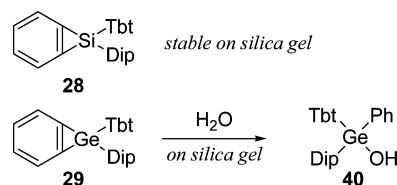
Scheme 13
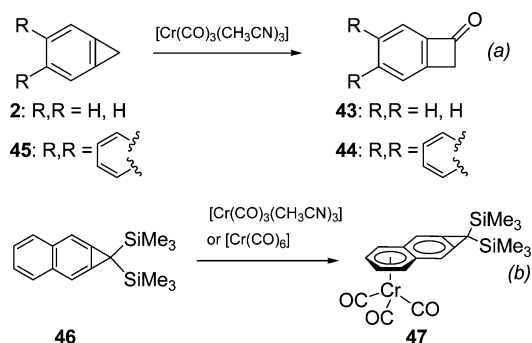
C2), indicating that the strain energies at the juncture carbon atoms are released in the cases of **28** and **29** due to the longer C−M (M = Si, Ge) bond lengths than that of C−C. The X-ray crystallographic analysis of **28** and **29** strongly suggests that the distinct molecular distortion and bond localization observed for cyclopropabenzene **2** are characteristic of only the carbon system due to the tight annelation, but are not observed for the heavier element (Si, Ge) systems. One can also see the singularity of the structure of the carbon system, cyclopropabenzene, in the systematic calculations of the structural parameters of diphenylcyclopropabenzene and its heavier congeners (sila-, germa-, stanna-, and plumbacyclopropabenzene), as shown in Figure 2.[27] These theoretical studies suggest that the central benzene ring of the cyclopropabenzene derivative is strangely deformed (especially, the juncture bond **a** and the bond angle ε) as compared with those of the heavier analogues. In addition, the central metallacyclopropabenzene moieties of **28** and **29** should be less perturbed by the bulky substituents, Tbt and Dip, since the structural parameters theoretically optimized for the model compounds **41a,b** and **42a,b**, having less bulky substituents, are in good agreement with those observed for **28** and **29**, indicating these structural features of **28** and **29** should be the inherent characters of the corresponding sila- and gremacyclopropabenzenes.

5. Reactions of the Metallacyclopropabenzenes

While a great number of papers on the reactivity of cyclopropabenzene have appeared so far,[1] most of them are the addition reactions leading to ring opening and ring expansion of its three-membered ring to release the strain energy. In most cases, the reagents were found to attack the electron-rich π-bond or the strained σ-bond of the three-membered rings of the cyclopropabenzenes. In contrast, **28** and **29** do not react with MeOH, MesCNO, and *m*CPBA at all. The insensitivity of **28** and **29** toward such reactive reagents most likely is due to the smaller strain energies and/or the steric hindrance caused by the two bulky substituents, the Tbt and Dip groups. However, germacyclopropabenzene **29** appears to be more reactive than **28**, as shown by its gradual hydrolysis on silica gel (SiO_2), as noted above.[27]

It has been reported that cycloproparenes react with carbonyl complexes of group 6 metals to give the corresponding cyclobutanone derivatives via the insertion of a :C=O unit

Scheme 14

48: M' = Cr (44%)
49: M' = Mo (36%)
50: M' = W (26%)

Scheme 15

Scheme 16

toward the cyclopropene ring. For example, benzocyclobutanone **43** and naphthocyclobutanone **44** were obtained by the reactions of [Cr(CO)$_3$(CH$_3$CN)$_3$] with cyclopropabenzene **2** and 1*H*-cyclopropa[*b*]naphthalene **45**, respectively (Scheme 13a).[30] In contrast, bis-silylated derivative **46** was found to react with the carbonyl complexes of chromium to give the corresponding π-bonded tricarbonylchromium complex **47**.[31]

In the case of germacyclopropabenzene **29**, unique reaction modes were found in the reactions with metal carbonyl complexes, but silacyclopropabenzene **28** was found to be completely inert toward such transition metal complexes. Thermal reactions of **29** with [M'(CO)$_6$] (M' = Cr, Mo, and W) resulted in the formation of the corresponding 1,2-oxagermolan-5-ylidene pentacarbonyl metal complexes **48**−**50**, which were obtained as stable deep red crystals (Scheme 14).[32,33] The products **48**−**50** should be considered as a unique type of Fischer carbene complex, even though they are fairly stable toward air and moisture. In the ^{13}C NMR spectra of **48**−**50**, the signals were observed at 336.7, 327.7, and 311.0 ppm, respectively, which are consistent with those of typical Fischer-type carbene complexes.[34] In addition, the molecular structures of the complexes **48**−**50** were determined by X-ray crystallographic analysis (Figure 3). In all cases, their 1,2-oxager-
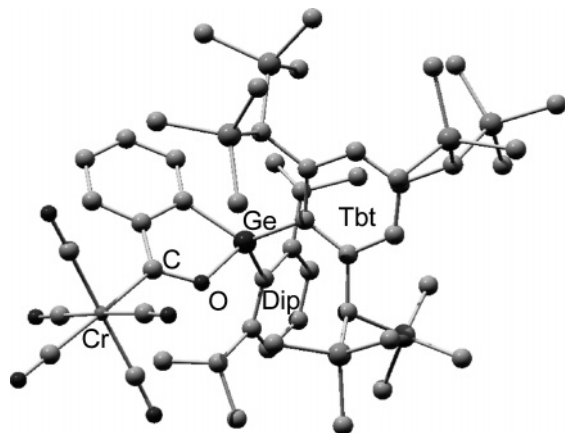

Figure 3. Molecular structure of **48**.

molene rings and the metal moieties are nearly coplanar. The C(carbene)−M' bond lengths [2.050(3) Å (**48**), 2.194(5) Å (**49**), and 2.194(4) Å (**50**)] are comparable with those of the corresponding alkoxycarbene complexes of group 6 metals. Although the formation mechanism for the complexes **48**−**50**

(29) Neidlein, R.; Christen, D.; Poigneé, V.; Boese, R.; Bläser, D.; Gieren, A.; Ruizpérez, C.; Hübner, T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 294−295.

(30) Müller, P.; Bernardinelli, G.; Jacquier, Y. *Helv. Chim. Acta* **1992**, *75*, 1995−2008.

(31) (a) Müller, P.; Bernardinelli, G.; Jacquier, Y. *Helv. Chim. Acta* **1988**, *71*, 1328−1330. (b) Müller, P.; Bernardinelli, G.; Jacquier, Y.; Ricca, A. *Helv. Chim. Acta* **1989**, *72*, 1618−1626.

(32) Tajima, T.; Sasaki, T.; Sasamori, T.; Takeda, N.; Tokitoh, N. *Chem. Commun.* **2004**, 402−403.

(33) Tajima, T.; Sasaki, T.; Sasamori, T.; Takeda, N.; Tokitoh, N. *Appl. Organomet. Chem.* **2005**, *19*, 570−577.
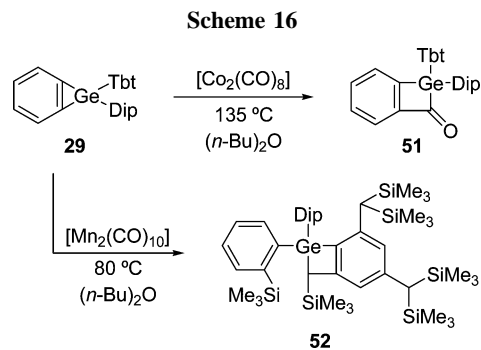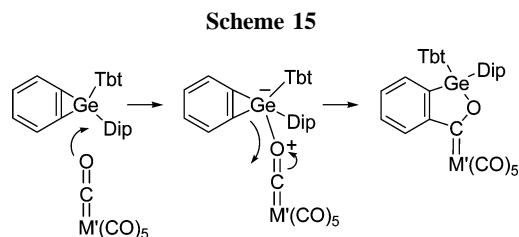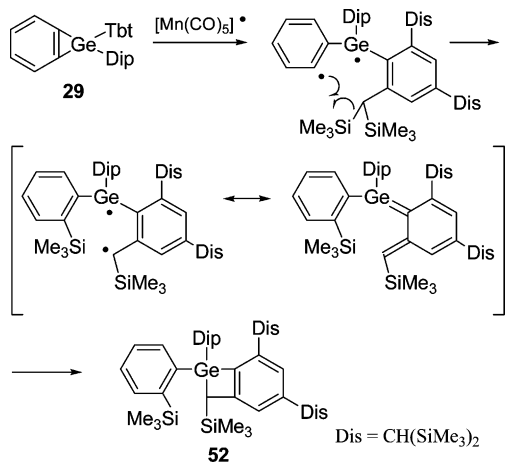
is unclear at present, it can be most likely interpreted in terms of an initial nucleophilic attack by the oxygen atom of [M'(CO)$_6$] to the oxophilic germanium atom of the germacyclopropabenzene ring in **29** followed by ring expansion, as shown in Scheme 15.

The reactions of germacyclopropabenzene **29** with other carbonyl complexes, [Co$_2$(CO)$_8$] and [Mn$_2$(CO)$_{10}$], also have been reported.[33] Heating a solution of **29** and [Co$_2$(CO)$_8$] in *n*-Bu$_2$O led to the formation of the corresponding benzogermacyclobutanone **51**, which is probably obtained via the insertion of a carbon monoxide into the C−Ge bond of the germacyclopropene ring. Here, the unique reaction mode of **29** with [Co$_2$(CO)$_8$] was found to be the same as that observed in the reaction of cyclopropabenzene **2** with [Cr(CH$_3$CN)$_3$(CO)$_3$], which gave benzocyclobutenone **43**[30] (Scheme 13a). Compound **51** was stable toward air and moisture, and the molecular structure of this novel cyclic compound was confirmed by spectroscopic and X-ray crystallographic analyses. The ^{13}C NMR spectrum of **51** in C$_6$D$_6$ showed a singlet at 225.0 ppm, which is assignable to that of the carbonyl carbon adjacent to the Ge atom. In addition, the reaction of **29** with carbon monoxide instead of [Co$_2$(CO)$_8$] was attempted in the expectation of simple CO insertion into the Ge−C bond of **29** to give **51**. Although the toluene solution of **29** was heated at 150 °C for 3 days under carbon monoxide atmosphere in an autoclave, **51** was not formed; **29** was recovered unchanged. Therefore, [Co$_2$(CO)$_8$] can be considered to be a necessary reactant in this reaction leading to the formation of **51**.

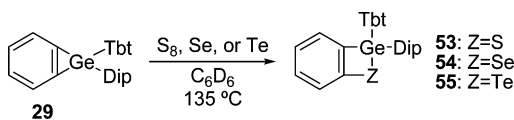When **29** was treated with an excess of [Mn$_2$(CO)$_{10}$] in *n*-Bu$_2$O at 80 °C, an unexpected cyclic compound, germacyclobutabenzene **52**, was obtained as stable colorless crystals (Scheme 16). The structure of **52** was confirmed by spectral data and X-ray crystallographic analysis. In this case, a carbonyl group of [Mn$_2$(CO)$_{10}$] is not contained in the product. Compound **52** may have been generated just by self-isomerization via ring rearrangement. Although the formation mechanism for **52** is not clear at present, the intermediacy of the [Mn(CO)$_5$] radical,

(34) (a) Bodner, G. M.; Kahl, S. B.; Bork, K.; Storhoff, B. N.; Wuller, J. E.; Todd, L. J. *Inorg. Chem.* **1973**, *12*, 1071−1074. (b) Lattuada, L.; Licandro, E.; Maiorana, S.; Molinari, H.; Papagni, A. *Organometallics* **1991**, *10*, 807−812. (c) Segundo, A.; Moretó, J. M.; Viñas, J. M.; Ricart, S.; Molins, E. *Organometallics* **1994**, *13*, 2467−2471.

Scheme 17

Dis = CH(SiMe₃)₂

Dis = CH(SiMe$_3$)$_2$

Scheme 18

53: Z=S
54: Z=Se
55: Z=Te

Scheme 19

Z = S, Se, Te

Scheme 20

(X = Cl or Br)

Scheme 21

Tip=2,4,6-triisopropylphenyl

thermally generated from $[Mn_2(CO)_{10}]$,[35] may give rise to the initial homolytic cleavage of the Ge–C bond of the germacyclopropabenzene ring of **29** (Scheme 17) in consideration of the stability of **29** itself under these reaction conditions.

Thus, germacyclopropabenzene **29** was found to undergo unique reactions with transition metal carbonyl complexes to give a variety of novel Ge-containing cyclic compounds, such as Fischer-type carbene complexes **48**−**50**, benzogermacyclobutenone **51**, and germacyclobutabenzene **52**, depending on the transition metal used.
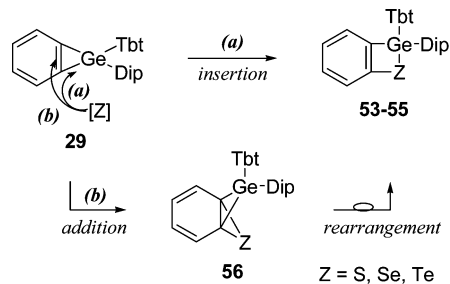
The reactions of germacyclopropabenzene **29** with elemental chalcogens such as sulfur, selenium, and tellurium also have been investigated. In these reactions, insertion of the chalcogen atom into the three-membered ring of **29** occurred to give the corresponding chalcogenagermete derivatives.[36] Heating a C_6D_6 solution of germacyclopropabenzene **29** with an excess of elemental sulfur at 135 °C afforded the corresponding 2*H*-benzo[*c*][1,2]thiagermete **53** exclusively in 63% isolated yield (Scheme 18). No other identifiable products were observed, as judged by the ¹H NMR spectrum of the crude reaction products. Thus **53** does not appear to undergo over-sulfurization reactions leading to the formation of five- or six-membered cyclic compounds under these conditions. In contrast, silacyclopropabenzene **28** was quite inert toward elemental sulfur under the same conditions.

When germacyclopropabenzene **29** was treated with an excess of elemental selenium and elemental tellurium under the same conditions as those used for the sulfurization reaction of **29**, the corresponding 2*H*-benzo[*c*][1,2]chalcogenagermete derivatives **54** and **55**, respectively, were obtained as the sole products. The chalcogen-containing products **53**−**55** were stable enough to be purified by HPLC and column chromatography on silica gel. The structures of **53**−**55** were characterized by spectroscopic and X-ray crystallographic analyses.

Considering the reactivity of cyclopropabenzenes,[1,37,38] it can be considered that germacyclopropabenzene **29** has two reactive sites, the strained Ge–C bond and the C=C bond in the three-membered ring system. The formation of chalcogenagermetes **53**−**55** can be explained by the simple insertion of a chalcogen atom into the reactive Ge–C bond of **29**. Indeed, the assumption is supported by the previously reported reactivity of cyclopropabenzene **2** toward transition metal complexes such as those of Ni, Pd, and others.[38] However, other pathways can be considered, such as the addition of the elemental chalcogen to the reactive C=C bond of the fused three-membered ring of **29** leading to the formation of compound **56** followed by its isomerization to the final products **53**−**55** (Scheme 19). This hypothesis might find support in the interesting reactions of cyclopropabenzene **2** with dichloro- or dibromocarbene (generated from CHX_3 (X = Cl, Br) with NaOH and a catalytic amount of benzyltriethylammonium chloride), in which the corresponding ring-expanded cyclobutabenzenes **57** were formed in quantitative yield. These reactions possibly proceed via an initial [1+2]-cycloaddition to give **58** followed by isomerization with re-aromatization of the fused ring (Scheme 20).[39] In any case, it is interesting that chalcogenagermetes **53**−**55**, model compounds of which are computed to be thermodynamically
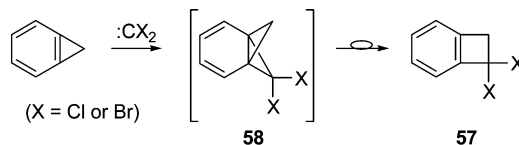
(35) (a) McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 3528−3533. (b) Mach, K.; Nováková, J.; Raynor, J. B. *J. Organomet. Chem.* **1992**, *439*, 341−345.

(36) Sasamori, T.; Sasaki, T.; Takeda, N.; Tokitoh, N. *Organometallics* **2005**, *24*, 612−618.
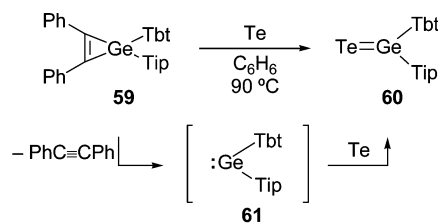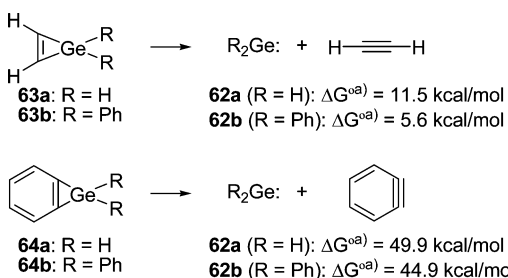
(37) (a) Neidlein, R.; Kohl, M.; Kramer, W. *Helv. Chim. Acta* **1989**, *72*, 1311−1318. (b) Saracoglu, N.; Durucasu, I.; Balci, M. *Tetrahedron* **1995**, *51*, 10979−10986. (c) Brinker, U. H.; Wuster, H. *Tetrahedron Lett.* **1991**, *32*, 593−596. (d) Halton, B.; Russell, S. G. G. *Aust. J. Chem.* **1990**, *43*, 2099−2105. (e) Saito, K.; Ishihara, H.; Kagabu, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4141−4142.

(38) (a) Stang, P. J.; Song, L.; Halton, B. *J. Organomet. Chem.* **1990**, *388*, 215−220. (b) Krüger, C.; Laakmann, K.; Schroth, G.; Schwager, H.; Wilke, G. *Chem. Ber.* **1987**, *120*, 471−475. (c) Schwager, H.; Krüger, C.; Neidlein, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 65−67. (d) Schwager, H.; Benn, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 67−68. (e) Benn, R.; Schwager, H.; Wilke, G. *J. Organomet. Chem.* **1986**, *316*, 229−231. (f) Neidlein, R.; Rufinska, A.; Schwager, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 640−642.
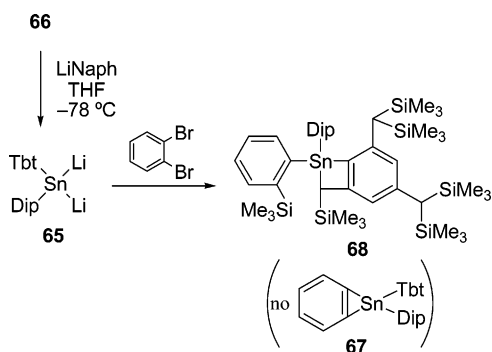
Scheme 22 [a]

63a: R = H
63b: R = Ph

62a (R = H): $\Delta G^{oa)}$ = 11.5 kcal/mol
62b (R = Ph): $\Delta G^{oa)}$ = 5.6 kcal/mol

64a: R = H
64b: R = Ph

62a (R = H): $\Delta G^{oa)}$ = 49.9 kcal/mol
62b (R = Ph): $\Delta G^{oa)}$ = 44.9 kcal/mol

[a] Calculated free energies (298 K, 1.0 atm) at the B3LYP/6-311G(2d,p) level.

Scheme 23
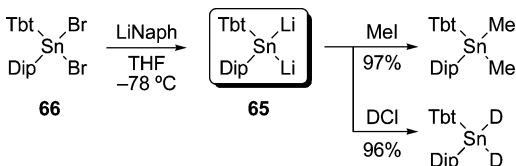
Scheme 24

more stable by ca. 70 kcal/mol than the postulated intermediacy **56**, can be formed via the chalcogenation reactions of germacyclopropabenzene **29** as stable products.

The reactivity of germacyclopropabenzene **29** differs from that of germacyclopropenes (germirenes). Thermal reaction of the overcrowded germirene **59** (which was prepared as a stable crystalline compound by the reaction of germylene Tbt(Tip)-Ge: (Tip = 2,4,6-triisopropylphenyl) with diphenylacetylene) with elemental tellurium was reported to afford the stable germanetellone **60**, Tbt(Tip)Ge=Te (Scheme 21).[40] The formation of **60** most likely occurs by way of the germylene **61**, which then reacts with elemental tellurium to give **60**. No telluragermete derivative was obtained, since germirene **59** more easily

undergoes a thermal retro-cycloaddition reaction to afford germylene **61** as compared with the case of germacyclopropabenzene **29**. Indeed, theoretical calculations [B3LYP/6-311G-(2d,p)] indicated that the generation of germylenes **62a,b** (R₂Ge:, R = H, Ph) from germacyclopropenes **63a,b** is much less endothermic than that from germacyclopropabenzenes **64a,b** (Scheme 22).

The molecular structures of 2*H*-benzo[*c*][1,2]chalcogenagermetes **53−55** were determined by X-ray crystallographic analysis. Their benzochalcogenagermete rings are almost planar, and the observed bond lengths and bond angles in the benzene rings are 1.367−1.412 Å and 117.0−122.7°, respectively, which are close to those of an unperturbed benzene; that is, almost no bond alternation was observed.[41]

Considering the reactions described above, it is clear that the germacyclopropabenzene could be a good precursor for the synthesis of novel small-ring compounds of germanium.
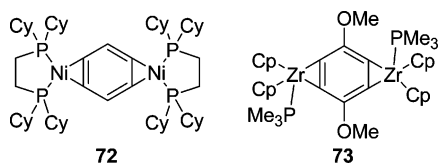
6. Attempted Synthesis of a Much Heavier Analogue, Stannacyclopropabenzene

As an extension of the chemistry of sila- and germacyclopropabenzenes, a stannacyclopropabenzene would be an interesting synthetic target from the viewpoints of systematic studies on group 14 heterocyclopropabenzenes. To start with, it was not known if the synthetic procedure used for **28** and **29** would be applicable to the preparation of a stannacyclopropabenzene. There have been a few reports of the generation of metastable dilithiostannanes.[42,43] We found that dilithiostannane **65** could be generated by the reaction of dibromostannane **66** with an excess of lithium naphthalenide, a procedure successful in the case of dilithiosilane **30** and dilithiogermane **31**.[44] The resulting dilithiostannane **65** was stable enough to be trapped by MeI or DCl in THF at −78 °C. With the required dilithostannane species in hand, the reaction of **65** with 1,2-dibromobenzene was attempted in the expectation of obtaining stannacyclopropabenzene **67**.[44] However, only the unexpected stannabutabenzene **68** was isolated as a stable compound. There was no evidence for the generation of **67**. The two reaction paths, in which the same intermediate **69** generated by the reaction of bromolithiostannane **70** with benzyne could reasonably be involved, might explain the formation of **68** as shown in Scheme 25. It is unclear whether the intermediacy of the highly strained stannacyclopropabenzene **67** should be necessarily postulated in this reaction.
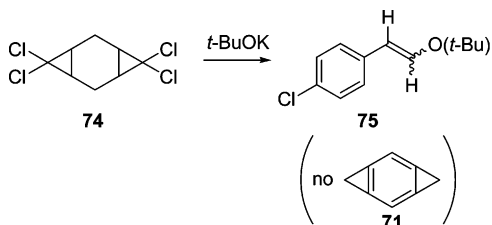
Scheme 25 [a]
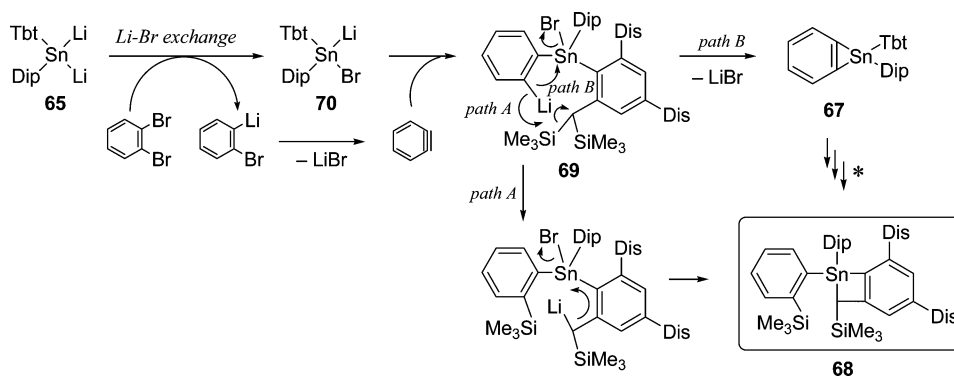
[a] The formation mechanism of **68** from **67** can be reasonably explained by the initial cleavage of the Sn−C bond followed by radical reactions similar to those of the formation of **52** from **29**, as shown in Scheme 17.
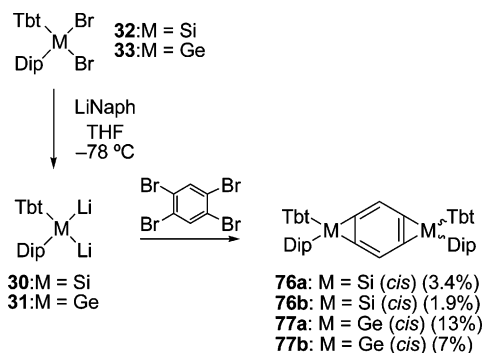
Scheme 26

72   73

Scheme 27

74   75

$$\left(\text{no} \quad \text{71} \right)$$

Scheme 28

32:M = Si
33:M = Ge

LiNaph
THF
−78 °C

30:M = Si
31:M = Ge

76a: M = Si (*cis*) (3.4%)
76b: M = Si (*cis*) (1.9%)
77a: M = Ge (*cis*) (13%)
77b: M = Ge (*cis*) (7%)

7. Synthesis of the First Stable Bis(silacyclopropa)-benzene and Bis(germacyclopropa)benzene

The remarkable developments of the chemistry of cyclopropabenzenes have attracted the interest of many chemists to bis(cyclopropa)benzenes, in which two cyclopropene rings are fused to a single benzene ring. Although the synthesis of an all-carbon bis(cyclopropa)benzene (**71**) has not been achieved as yet probably due to its severe skeletal strain and the lack of a suitable synthetic method, bis-benzyne transition metal complexes **72**[45] and **73**,[46] formal bis(metallacyclopropa)benzenes, have been reported as stable compounds. The attempted sysnthesis of bis(cyclopropa)benzene **71** by the reaction of precursor **74** with *t*-BuOK resulted in the formation of an unexpected product, **75** (Scheme 27).[47]
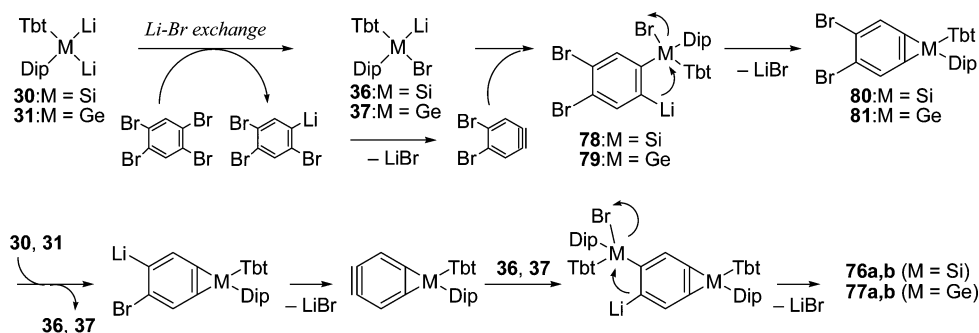
In view of the successful isolation of the first stable sila- and germacyclopropabenzenes as described above, the idea that the stable dilithio derivatives **30** and **31** may be applicable to synthesis of bis(sila- and germacyclopropa)benzenes is an obvious one. After a number of attempts, the first stable bis-
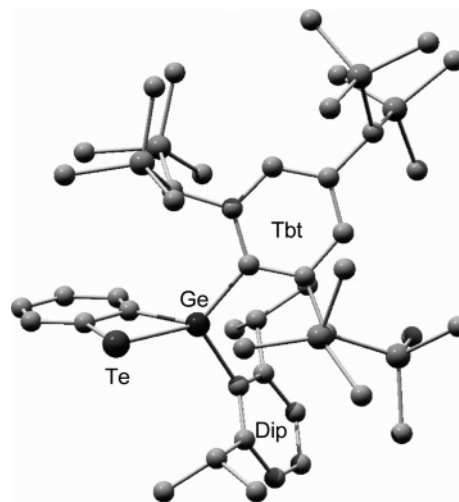
Figure 4. Molecular structure of **55**.

(silacyclopropa)benzenes **76a** (*cis*-isomer) and **76b** (*trans*-isomer) were synthesized and isolated by the reaction of dilithiosilane **30** with 1,2,4,5-tetrabromobenzene in 2003.[26,48] Furthermore, the germanium analogues **77a** (*cis*-isomer) and **77b** (*trans*-isomer) also were prepared very recently using a similar procedure.[49] Bis(heteracyclopropa)benzenes **76a,b** and **77a,b** are surprisingly stable enough to be handled in the open air and in hydrocarbon solvents such as hexane and benzene. However, the germanium analogues **77a,b** undergo decomposition in halogenated solvents such as CHCl₃ or on treatment with silica gel, as had been found in the case of germacyclopropabenzene **29**.

The formation of bis(sila- and germacyclopropa)benzenes **76a,b** and **77a,b** can be explained in terms of a reaction mechanism similar to that for the sila- and germacyclopropabenzenes **28** and **29** (Scheme 29). The silylenoid **36** and germylenoid **37**, formed initially by Li−Br exchange of dilithio derivatives **30** and **31** with 1,2,4,5-tetrabromobenzene, reacted with 4,5-dibromobenzyne by the 1,2-elimination of LiBr from 1,2,4-tribromo-5-lithiobenzene. Intramolecular cyclization of the resulting *o*-metalated phenyllithiums **78** and **79** would afford the intermediary 3,4-dibromo-1-sila- and germacyclopropabenzenes **80** and **81**, respectively. The subsequent cyclization process at the 3,4-positions of **80** and **81** would afford the final products **76a,b** and **77a,b**, respectively. This confusing reaction mechanism involving highly reactive intermediates such as benzynes and silyl- and germylenoids **36** and **37** might result in low product yields. Although no evidence for the generation of 3,4-dibromo-1-heteracyclopropabenzenes **80** and **81** was obtained, it might be conceivable that **80** and **81** would be very
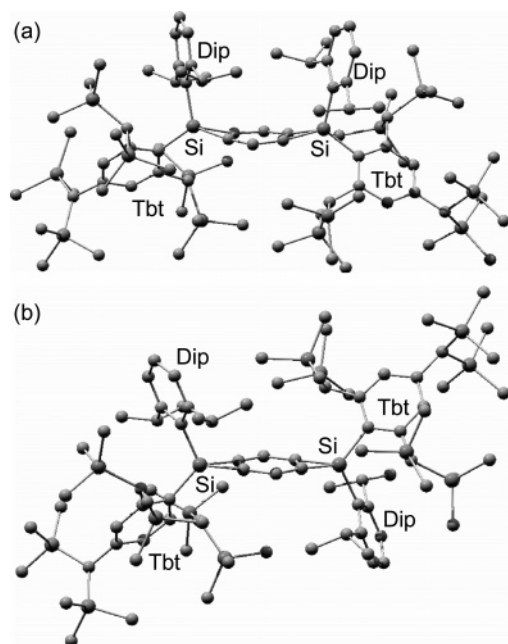
Scheme 29

30:M = Si
31:M = Ge

Li-Br exchange

36:M = Si
37:M = Ge

78:M = Si
79:M = Ge

80:M = Si
81:M = Ge

30, 31

36, 37

76a,b (M = Si)
77a,b (M = Ge)

Figure 5. Molecular structure of bis(silacyclopropa)benzenes (a) **76a** and (b) **76b**.
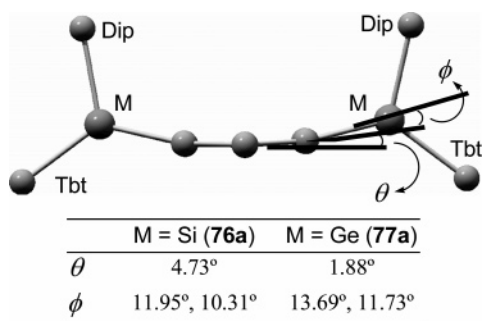

Figure 6. Folded core benzene rings of bis(silacyclopropa)benzenes **76a** and **77a**.

sensitive to the coexisting reductants such as lithium naphthalenide and/or dilithio derivatives **30** and **31** under these reaction conditions.

8. Structures of the Bis(sila- and germacyclopropa)-benzenes

The molecular structures of bis(sila- and germacyclopropa)-benzenes **76a,b** and **77a,b** were determined by X-ray crystallographic analysis at −170 °C (Figure 5).[48,49] Interestingly, the central benzene rings of the *cis*-isomers, **76a** and **77a**, are slightly folded, as shown in Figure 6, in contrast to the completely planar geometries of the *trans*-isomers, **76b** and **77b**. Theoretically optimized structures of the parent bis(sila- and germacyclopropa)benzenes **76c** and **77c** exhibit completely planar geometry for their central benzene rings (Table 3), indicating that the unusual folded structure of the central benzene ring of **76a** and **77a** is probably due to the severe steric repulsion between the two extremely bulky Tbt groups. The observed and optimized structural parameters of bis(sila- and germacyclopr-

Table 3. Observed and Calculated Structural Parameters for Bis(metallacyclopropa)benzenes and Bis(cyclopropa)benzenes

76a(cis): ERR' = Si(Tbt)Dip
76b(trans): ERR' = Si(Tbt)Dip
77a(cis): ERR' = Ge(Tbt)Dip
77b(trans): ERR' = Ge(Tbt)Dip
71: ERR = CH₂
76c: ERR' = SiH₂
77c: ERR' = GeH₂

Σ: sum of the interior angles of the central benzene ring

	76a[a]	**76b**[a,b]	**77a**[c]	**77b**[c]	**71**[d]	**76c**[d]	**77c**[d]
a/Å	1.415(6)	1.405(11) 1.398(11)	1.408(10)	1.394(6)	1.346	1.404	1.391
b/Å	1.409(5)	1.388(11) 1.389(11)	1.381(8)	1.394(6)	1.392	1.391	1.392
c/Å	1.397(6)	1.414(10) 1.376(11)	1.403(9)	1.403(6)	1.392	1.391	1.392
a'/Å	1.412(6)	1.420(10) 1.380(11)	1.364(9)	1.389(6)	1.346	1.404	1.391
b'/Å	1.414(6)	1.395(10) 1.405(11)	1.396(9)	1.397(6)	1.392	1.391	1.392
c'/Å	1.394(6)	1.389(11) 1.401(11)	1.416(9)	1.391(6)	1.392	1.391	1.392
α/deg	123.2(4)	124.7(7) 123.0(7)	123.1(6)	123.8(4)	126.1	123.3	124.0
β/deg	122.9(3)	121.2(7) 123.2(8)	123.5(6)	123.6(4)	126.1	123.3	124.0
γ/deg	114.3(4)	114.8(7) 114.6(7)	111.9(6)	112.3(4)	107.8	113.3	112.0
α'/deg	122.9(4)	122.9(4) 124.2(7)	124.2(6)	123.7(4)	126.1	123.3	124.0
β'/deg	123.1(4)	122.7(4) 121.8(7)	123.9(6)	124.2(4)	126.1	123.3	124.0
γ'/deg	113.7(7)	113.7(7) 113.0(7)	113.3(6)	112.5(4)	107.8	113.3	112.0
Σ/deg	720.1	720.0 719.8	719.9	720.1	720.0	719.8	720.0

[a] X-ray at −170 °C, see refs 26, 48. *[b]* Two independent molecules were found in the unit cell. *[c]* X-ray at −170 °C, see ref 49. *[d]* Optimized structure at B3LYP/ 6-311G(2d,p), see ref 51.

opa)benzenes **76a**−**c** and **77a**−**c** are shown in Table 3 together with those of the theoretically optimized bis(cyclopropa)benzene **71**.[50,51] One can see almost no variation in the bond lengths of the central benzene rings of **76a,b** and **77a,b**, in contrast to the case of those theoretically optimized for bis(cyclopropa)benzene **71**, which features the noticeably short juncture C−C bonds (**a**,**a'** in Table 3) in the central benzene ring (**a**,**a'** < **b**,**b'**, **c**,**c'**). Interestingly, the central benzene rings of bis(sila- and germacyclopropa)benzenes **76a,b** and **77a,b** show bond angles deviating from those of a normal benzene ring (120°). The bond angles at the nonjuncture carbon atoms (α,α' and δ,δ' in Table 3) are

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(40) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 2337−2338.

(41) The parent cyclobutabenzene, in which a four-membered ring is fused with a benzene ring, also shows almost no bond alternation, see: Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304−305.

smaller than 120°, and those at the juncture carbon atoms (β,β' and γ,γ') are larger than 120°. These deviations of the bond angles are slightly larger than those of metallacyclopropabenzenes **28** and **29**.

9. Conclusion

The successful generation of the dilithio derivatives, Tbt-(Dip)MLi$_2$ (M = Si, Ge), has made possible the synthesis and isolation of stable sila- and germacyclopropabenzenes. The first examples of sila- and germacyclopropabenzenes, **28** and **29**, extend the chemistry of cyclopropabenzenes. It can be concluded that the aromatic rings of heavier analogues of cyclopropabenzene, i.e., sila- and germacyclopropabenzenes, are much less strained compared to that of a parent all-carbon cyclopropabenzene. A three-membered ring containing a heavier group 14 element can undergo annelation to a benzene ring with much less perturbation. In addition, bis(sila- and germacyclopropa)benzenes have real existence as stable compounds when a suitable synthetic method is used, although the all-carbon analogues, bis(cyclopropa)benzenes, are still elusive. It was demonstrated by the reactivity of germacyclopropabenzene **29** that heteracyclopropabenzenes can be useful precursors for a variety of novel small-ring compounds such as 2*H*-benzo[*c*][1,2]chalcogenagermetes. Small-ring compounds containing a heavier atom fused with a benzene moiety thus are attractive targets because of their unique properties as new π-electron systems with high planarity.

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(51) Although a number of theoretical works on a bis(cyclopropa)benzene have been reported (see ref 50), the calculated structural parameters of bis-(cyclopropa)benzene **71** shown here were obtained by the calculations done by the authors for the purpose of standardization of the calculation method [B3LYP/6-311G(2d,p)].