Heavy Cyclopropenes of Si, Ge, and Sn—A New Challenge in the Chemistry of Group 14 Elements

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Contents

I. Introduction

The small ring systems consisting of Group 14 elements heavier than carbon, i.e., Si, Ge, Sn, and Pb, have always been among the most attractive synthetic challenges in the chemistry of Group 14 elements, due to their very unusual structural properties and high reactivity. At first, they were considered as nonisolable reactive intermediates; only after many experimental efforts was their successful isolation achieved in the early 1980s, when Masamune reported the synthesis of the first stable cyclotrisilane,[1] followed by the preparation of cyclotrigermane[2] and cyclotristannane.[3] In the subsequent two decades, the chemistry of such three-membered ring compounds, also known as cyclotrimetallanes, has been greatly developed. These developments first concern the synthesis of new representatives of cyclotrimetallanes and studies of their reactivity. Similar to their carbon analogue, cyclopropane, cyclotrimetallanes were found to be highly reactive because of their significant ring strain and the weakness of the endocyclic metal−metal bonds. One of the most fundamental discoveries about their reactivity is the cycloelimination reaction to form two kinds of key reactive species: heavy carbene analogues and dimetallaalkenes (dimetallenes). This is now well established and is one of the major methods to generate such important reactive intermediates. Similarly, heterocyclotrimetallanes consisting of different heavier Group 14 elements can be reasonably imagined as a convenient source for the preparation of heterodimetallenes, which could possess unusual structural and chemical properties. Nevertheless, until now there have been only a few examples of such "mixed" cyclotrimetallanes,[4−8] which can be explained by the problems in their preparation relative to their "homo" analogues.

One could expect that after the synthesis of cyclotrimetallanes, the next target would be their unsaturated analogues, that is, cyclotrimetallenes, with a metal−metal double bond incorporated in the three-membered ring skeleton, uniting the properties of both cyclotrimetallanes and dimetallenes in one molecule (we can denote such compounds as "heavy cyclopropene analogues"). However, despite the evident importance and undoubted interest, such compounds have not been synthesized until recently, because of the many difficulties in their preparation. These difficulties include their high reactivity and great ring strain. From organic chemistry, it is well known that cyclopropene has a greater ring strain than cyclopropane, because of the stronger deviation of cyclopropene angles (60°) from the ideal angle of 120° than those of cyclopropane (60° vs 109°).[9] Theoretical calculations predicted a significant decrease in the ring strain of small ring systems of heavier Group 14 elements resulting from the introduction of electropositive silyl substituents.[10] Electronic stabilization can also be achieved by the interaction of the high-lying π-orbitals of the endocyclic E=E double bonds in the framework and the low-lying σ^*-orbitals of the exocyclic E−Si (E = Si, Ge, Sn, Pb) bonds (Figure 1). This is explained by the $\pi−\sigma^*$ conjugation concept.[11]

Indeed, the employment of bulky silyl substituents, which kinetically protect the molecule and simultaneously decrease the ring strain, enabled the successful preparation of the cyclotrimetallenes. Thus, the first synthesis of an unsaturated three-membered ring compound composed of all Ge atoms was reported in 1995 by Sekiguchi et al.[12] Since this first report, we have witnessed an explosive growth in the

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development of cyclotrimetallene chemistry, especially in the past three years.

The synthesis of cyclotrisilenes has required a longer time, and the first representatives were reported only recently, in 1999 by Kira et al.[13] and Sekiguchi et al.[14] There is still only one example of the tin analogue, which was reported in the same year (1999) by Wiberg et al.[15] Except for such homonuclear cyclotrimetallenes, one can also imagine the several possible combinations of heavier Group 14 elements in heteronuclear cyclotrimetallenes, con-
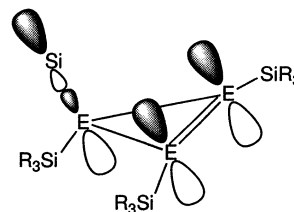

Figure 1. Schematic representation of the $\pi-\sigma^*$ conjugation concept: $\pi(\text{E}=\text{E})-\sigma^*(\text{E}-\text{Si})$ orbitals stabilizing interaction in the R_3Si-substituted cyclotrimetallenes (E = heavier Group 14 element).

sisting of different Group 14 elements. Yet such compounds were unknown until 2000, when Sekiguchi et al. reported the synthesis of the first 1- and 2-disilagermirenes, consisting of one Ge and two Si atoms.[16] Even now, there is a very limited number of methods for cyclotrimetallene synthesis, which are not general and are usually more complicated than in the case of cyclotrimetallanes. The reactivity of cyclotrimetallenes, which combine the chemical properties of both cyclotrimetallanes and dimetallenes, was found to be very rich. Numerous addition and cycloaddition reactions across the metal−metal double bond give easy and fast access to a variety of new cyclic and bicyclic compounds, whereas insertion reactions into the three-membered ring produce ring enlargement products. Oxidation of cyclotrimetallenes represents an effective and useful route for the preparation of stable aromatic silyl and germyl cations, which are free from interaction with either solvent or counteranion molecules.

In the latest review devoted to the chemistry of stable disilenes, Weidenbruch mentioned, "Molecules with endocyclic Si=Si double bonds...have also only recently become accessible and their chemistry has not yet been reviewed."[17] This article attempts to summarize the current state of affairs in this very new and quickly developing field of cyclotrimetallenes (unsaturated three-membered ring compounds) of heavier Group 14 elements, and herein are described the most recent and important developments in this area. As was mentioned above, the cyclotrimetallenes exhibit the properties of both cyclotrimetallanes and dimetallenes. Both of the last two fundamental classes of compounds have been the subject of many excellent reviews[18,19] and therefore will not be considered in the present article.

The present review is organized into four major parts: (I) Introduction; (II) Synthesis of Cyclotrimetallenes; (III) Reactivity of Cyclotrimetallenes; and (IV) Summary and Outlook. The second part describes the available synthetic routes for the preparation of cyclotrimetallenes, starting from cyclotrigermenes, which were the first to be prepared. The third part deals with the various types of reactions of cyclotrimetallenes, emphasizing the cycloaddition and oxidation reactions, for which the most important results were obtained. This article covers the literature up to the middle of 2002. Apart from the cyclotrimetallenes, there are some other examples of cyclic unsaturated compounds composed of heavier Group 14 elements. These include three cyclotetrasilenes [hexakis(*tert*-butyldimethylsilyl)cyclotetrasilene, prepared by Kira et al. in 1996;[20] 3,4-diiodo-
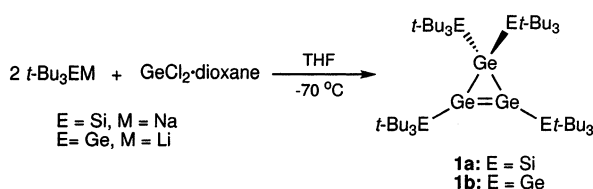
1,2,3,4-tetrakis(tri-*tert*-butylsilyl)cyclotetrasilene, reported by Wiberg et al. in 1998;[21] and 3-methyl-4,4-di-*tert*-butyl-1,2,3-tris(di-*tert*-butylmethylsilyl)cyclotetrasilene, synthesized by Sekiguchi et al. in 2001[22]] and three five-membered cyclic compounds [thia-, selena-, and telluratetrasilacyclopentenes, synthesized by Weidenbruch et al. in 1999[23]]. However, since these compounds do not represent examples of three-membered rings and they have been reviewed quite recently,[17] they will not be discussed in this article.

II. Synthesis of Cyclotrimetallenes

II.A. Cyclotrigermenes

Historically, cyclotrigermenes were the first cyclotrimetallenes composed of heavier Group 14 elements to be isolated as stable compounds. To date, 11 cyclotrigermenes have been prepared and isolated, and eight of them have been structurally characterized (Table 1). The first record of cyclotrigermenes appeared in 1995, when Sekiguchi et al. reported the unexpected formation of an unsaturated three-membered ring system consisting of Ge atoms (cyclotrigermenes) **1a,b** by the simple reaction of the dichlorogermylene–dioxane complex with tris(*tert*-butyl)silylsodium or tris(*tert*-butyl)germyllithium in THF at −70 °C (Scheme 1).[12]

Scheme 1

$2\ t\text{-Bu}_3\text{EM}\ +\ \text{GeCl}_2\cdot\text{dioxane}\ \xrightarrow[-70\ ^{\circ}\text{C}]{\text{THF}}$

E = Si, M = Na
E = Ge, M = Li

1a: E = Si
1b: E = Ge

Cyclotrigermenes **1a** and **1b**, representing a new unsaturated ring system, were isolated as dark red crystals in 20% and 13% yield, respectively. They exhibited very simple NMR spectra due to their symmetrical structures, showing only two sets of signals in ^{1}H, ^{13}C, and ^{29}Si NMR spectra. The crystal structures of both **1a** and **1b** were confirmed by X-ray crystallography, which showed a completely planar geometry around the Ge=Ge double bond, with a
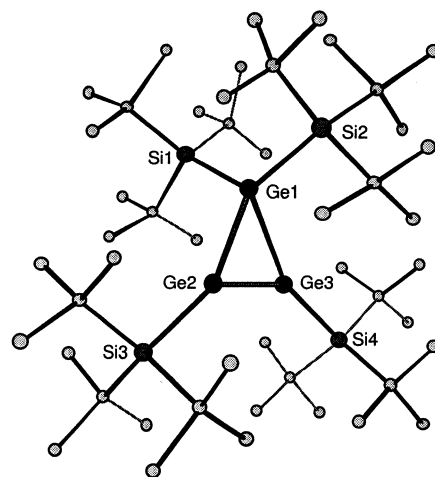
Figure 2. Crystal Designer ball-and-stick view of cyclotrigermene **1a**. Drawn from the coordinates reported in ref 12.

Ge=Ge double bond length of 2.239(4) Å (Figure 2). At that time, such planarity was somewhat unusual, since all previous digermenes were reported as having a trans-bent configuration of the Ge=Ge double bond, with folding angles ranging from 12° to 36°.[19d] Surprisingly, when the same reaction was performed at room temperature by Wiberg et al., the isolated product was completely different: tetrakis[tris(*tert*-butyl)silyl]tetragermatetrahedrane instead of cyclotrigermene.[24]

The mechanism for the formation of cyclotrigermenes was later clarified when this reaction was reexamined by the same authors.[25] They found that the reaction of equimolar amounts of the dichlorogermylene–dioxane complex and ^{t}Bu$_3$SiNa in THF at −78 °C quickly produced the *cis,trans*-1,2,3-trichloro-1,2,3-tris(tri-*tert*-butylsilyl)cyclotrigermane (**2**) in 98% yield (Scheme 2). The subsequent treatment of **2** with 2 equiv of ^{t}Bu$_3$SiNa in THF at −78 °C cleanly formed the final cyclotrigermene **1a** (Scheme 2), providing evidence that **2** is a precursor for **1a**. Finally, the reaction of GeCl$_2$·dioxane with ^{t}Bu$_3$SiNa can be explained by the following mechanism (Scheme 3). First, insertion of dichlorogermylene into the Si–Na bond occurred to form ^{t}Bu$_3$SiGeCl$_2$Na (**3**), which undergoes self-condensation to produce the digermenoid **4**, which is stable at low temperature. Above

**Table 1. Physicochemical Data of Cyclotrigermenes**

| compd	yield (%)	color	mp (°C)	^{29}Si NMR (ppm)	UV [λ (ε)]	Ge=Ge (Å), configuration, bent angle (°)	ref
1a	20	dark red	157	37.2, 50.1	217 (94000), 311 (21000), 380–620 (tailing)	2.239(4), planar	12
1b	13	dark red	178		221 (55000), 326 (13000), 380–620 (tailing)	2.239(4), planar	12
11	75	dark red	125–127	36.5, 49.9	321 (9000), 380–620 (tailing)	no data	26
12	86	dark red	148–150	−87.9, −6.5, 28.1, 50.4	314 (29500), 360 (8800), 380–600 (tailing)	2.264(2), cis, 4.4, 12.5	26
13	73	dark red	153–155	−0.5, 26.4, 49.5	310 (23700), 360 (5900), 380–600 (tailing)	no data	26
14	85	dark red	168–172	20.5, 29.7, 49.9	297 (14000), 340 (5700), 380–600 (tailing)	2.2559(12), cis, 4.0	27
15	69	red	78–82	22.2, 43.5	302 (6600), 380–560 (tailing)	no data	28
16	80	orange	142–145	20.7, 49.4	295 (14400), 335 (6700), 380–520 (tailing)	2.2680(4), trans, 4.3, 6.8	26
18	60	dark red	183	28.8, 45.1	211 (76800), 226 (sh, 64800), 247 (43600), 274 (sh, 24900), 323 (sh, 9000), 402 (tailing)	2.2723(8), trans, 19.7, 8.4	29
19	64	dark red	177	27.1, 44.7	212 (62100), 234 (42900), 278 (sh, 22000), 332 (sh, 6500), 411 (tailing)	2.2743(8), cis, 10.2, 45.1	29
20	74	dark red	173	22.3, 44.1	206 (90900), 230 (sh, 60400), 253 (sh, 41200), 289 (26900), 352 (sh, 7000), 402 (tailing)	2.2721(6), cis, 8.0, 43.3	29

Scheme 2
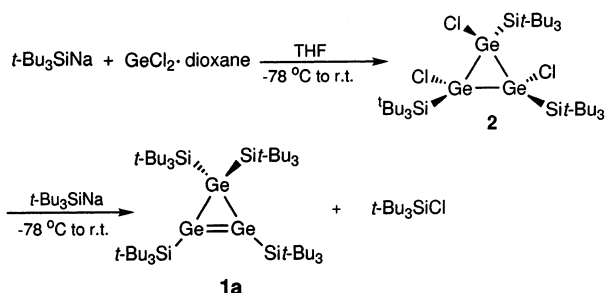
Scheme 3
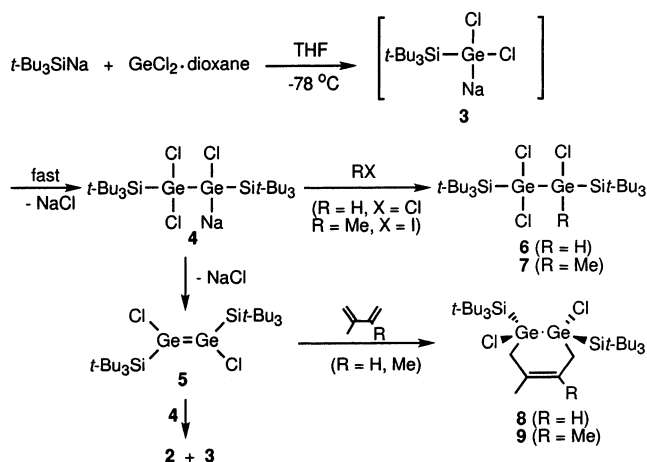
−8 °C, thermal decomposition of **4** gives the digermene **5** as a reaction intermediate. Finally, this digermene reacts with digermenoid **4**, followed by cyclization, with the formation of trichlorocyclotrigermane **2** and germylenoid **3**. The resulting **2** then undergoes reduction to form the final cyclotrigermene **1a**. Monitoring of the reaction by ^{29}Si NMR spectroscopy allowed the detection of the above-mentioned reaction intermediates, which cannot be isolated but were confirmed by trapping reactions. The intermediate digermenoid **4** was quenched with hydrochloric acid at −78 °C, with the quantitative formation of a protonated product **6**, whereas the methylated product **7** was quantitatively obtained with methyl iodide. Above −8 °C, the digermenoid **4** undergoes selective β-elimination to give another intermediate digermene, $^{t}Bu_3Si(Cl)Ge=Ge(Cl)Si^{t}Bu_3$ (**5**), which cannot be detected in the ^{29}Si NMR spectrum but can be trapped with dienes. With both isoprene and 2,3-dimethyl-1,3-butadiene, the corresponding cyclohexene derivatives **8** and **9** were obtained, whereas germacyclopentene derivatives were not found; this indicates the absence of an α-elimination pathway in the reaction.

Other cyclotrigermenes were synthesized by Sekiguchi et al., taking advantage of the previously prepared cyclotrigermenylium ion, whose synthesis will be described below (see section III.B.1). Thus, alkyl-, aryl-, silyl-, and germyl-substituted cyclotrigermenes were prepared in good yields by the reaction of tris(tri-*tert*-butylsilyl)cyclotrigermenylium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB, **10**) with the corresponding nucleophiles (Scheme 4).[26] This method appeared to be a convenient route for the preparation of new, unsymmetrically substituted cyclotrigermenes. Thus, reaction of **10** with

Scheme 4
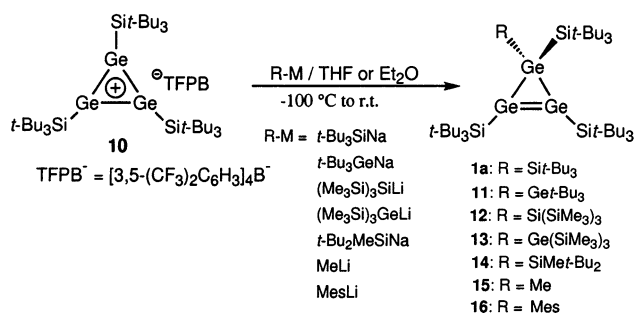
$^{t}Bu_3SiNa$,[26] $^{t}Bu_3GeNa$,[26] $(Me_3Si)_3SiLi\cdot3THF$,[26] $(Me_3Si)_3GeLi\cdot3THF$,[26] $^{t}Bu_2MeSiNa$,[27] MeLi,[28] and MesLi[26] at low temperature (−78 °C) quickly produced the corresponding cyclotrigermenes **1a**, **11**−**16** in high yields. The structures of the compounds **12**,[26] **14**,[27] and **16**[26] were determined by X-ray analysis. It was found that the geometry around the Ge=Ge double bond greatly depends on the substituents (Figure 3, Table 1). Thus, for example, as already mentioned, tri-*tert*-butylsilyl (or tri-*tert*-butylgermyl)-substituted cyclotrigermenes **1a,b** showed a planar geometry around the Ge=Ge double bond (Figure 2).[12] In contrast, mesityl-tris(tri-*tert*-butylsilyl)cyclotrigermene (**16**) revealed the usual trans-bent structure, with bending angles of 6.8° and 4.3° and a Ge=Ge double bond length of 2.2680(4) Å (Figure 3).[26] Such trans-bent geometry was characteristic for all previously isolated and characterized digermenes.[19e] Changing the substituent from mesityl to the tris(trimethylsilyl)silyl group caused a dramatic change in the geometry. Thus, cyclotrigermene **12** has a cis-bent structure with bending angles of 12.5° and 4.4° for sp² Ge atoms and a Ge=Ge bond length of 2.264(2) Å (Figure 3).[26] Such geometry was well reproduced by theoretical calculations, which gave values for the cis-bending angles of 8.8° and 5.8°, respectively.[26]
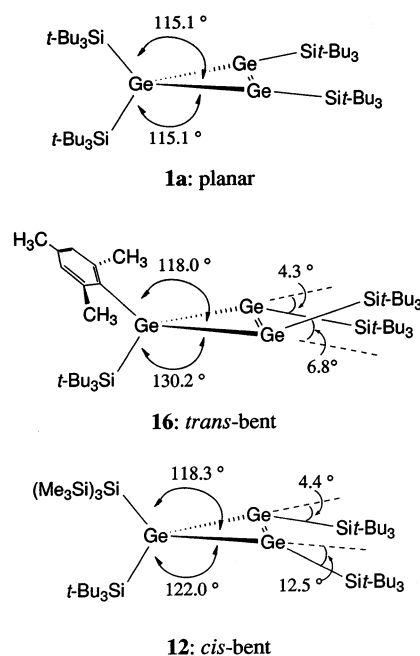

Figure 3. Geometries around the Ge=Ge double bond in cyclotrigermenes.

As was already discussed, the digermenes generally exhibit a trans-bent configuration, which becomes less pronounced upon the introduction of electropositive substituents, such as R_3Si groups. In the case of cyclotrigermene **12**, the use of such electropositive and bulky silyl substituents resulted in the formation of the Ge=Ge double bond with an unexpected cis-bent geometry. Such a configuration of the Ge=Ge double bond is not unique: the same cis-bent geometry is exhibited also by ${}^tBu_2MeSi$-substituted cyclotrigermene **14** (cis-bent angles 4.1°, Ge=Ge double bond length 2.2559(12) Å)[27] and halogen-substituted cyclotrigermenes, which will be discussed immediately below.

The reaction of cyclotrigermenylium ion **17** with potassium halides KX (X = Cl, Br, I) at room temperature in diethyl ether provides an efficient route to the very interesting new cyclotrigermenes **18**−**20**, bearing a covalently bonded halogen atom on the sp^3 Ge atom (Scheme 5, Table 1).[29] Such halogen-

Scheme 5
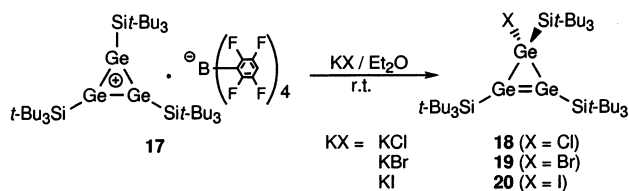
substituted cyclotrigermenes were synthesized quite recently, and their properties appeared very unusual. Thus, the crystal structures of compounds **18**−**20** (Table 1)[29] reveal some interesting structural features. The introduction of the electronegative halogen substituents on the Ge atom results in a lengthening of the Ge=Ge double bond (for example, 2.2743(8) Å for the bromine-substituted cyclotrigermene **19**[29] in Figure 4) compared with this bond in tetrakis(tri-*tert*-
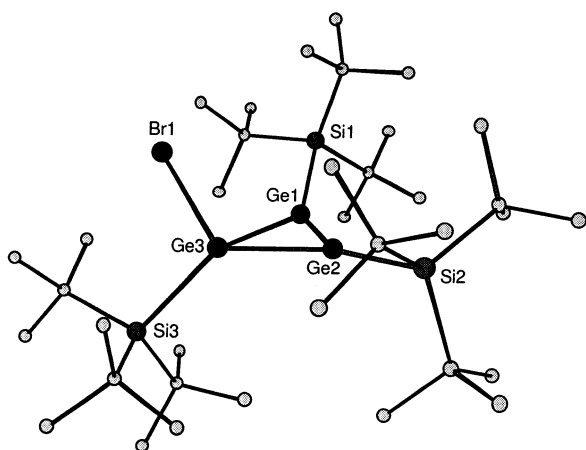

Figure 4. Crystal Designer ball-and-stick view of Br-cyclotrigermene **19**. Drawn from the coordinates reported in ref 29.

butylsilyl)cyclotrigermene (**1a**) (2.239(4) Å).[12] Such a bond lengthening was explained in terms of the π−σ^* conjugation concept;[11] that is, the donor−acceptor interaction of a π-orbital of the endocyclic Ge=Ge double bond and a σ^*-orbital of the exocyclic Ge−X
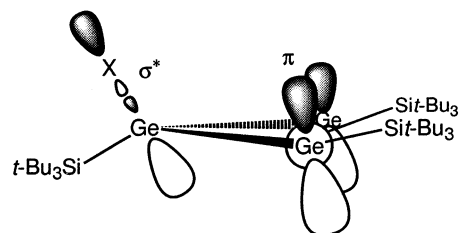

Figure 5. π(Ge=Ge)−σ^*(Ge−X) stabilizing interaction.

bond (Figure 5). This interaction also causes the remarkable cis-bent geometry around the Ge=Ge double bond in bromine- and iodine-substituted cyclotrigermenes **19** and **20** (the cis-bending angles of the Si substituents at the Ge=Ge double bond are 45.1° and 10.2°, 43.3° and 8.0°, respectively), which was supported by DFT calculations at the B3LYP/DZd level.[29] One of the most interesting features of the halogen-substituted cyclotrigermenes is the migration of the halogen atoms over the three-membered ring skeleton, which was clearly demonstrated by NMR data (Scheme 6).[29] Thus, in the ^1H NMR

Scheme 6
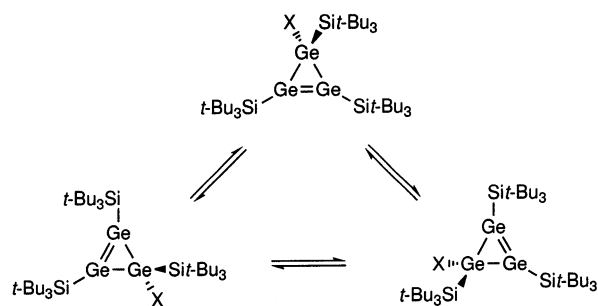
spectrum of bromine-substituted cyclotrigermene **19**, there is only one sharp singlet at 1.38 ppm due to the ${}^tBu_3Si$ groups. However, upon lowering the temperature below 250 K, this signal splits into two peaks at 1.29 and 1.45 ppm in a 2:1 ratio. These spectral changes indicate the migration of the bromine atom on the NMR time scale. The activation parameters of this Br migration (E_a = 12.8 kcal/mol, $\Delta H^{\ddagger}$ = 12.3 kcal/mol, $\Delta S^{\ddagger}$ = −0.14 cal/mol·K) are essentially independent of the concentration and solvent polarity, suggesting that the Br atom migrates intramolecularly over the three-membered ring without intermediate formation of the cyclotrigermenylium ion. Theoretical calculations on the halogen atom migration were performed for model compounds XGe_3H_3 (X = F, Cl, Br). The energy diagram of the halogen migration in halogen-substituted cyclotrigermenes is represented in Figure 6. The most important feature is the great difference in energy levels of the intermediates (local minima) for each halogen case: 12.5 kcal/mol for F migration, 7.8 kcal/mol for Cl migration, and only 4.0 kcal/mol for Br migration. This is in complete accord with the general tendencies of increasing polarizability and decreasing Ge−X bond strength on going from F to Br atoms, which provides the flexibility necessary for the 1,2-migration in highly strained three-membered ring systems.
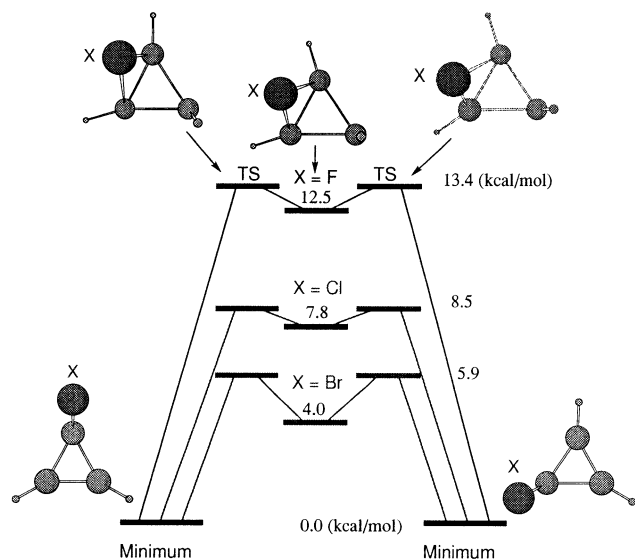
Figure 6. Energy diagram of halogen atom migration in XGe_3H_3 (X = F, Cl, Br) [B3LYP/6-31G(d)+ZPE//B3LYP/6-31G(d)].

II.B. Cyclotrisilenes

The synthesis of the first cyclotrisilenes has required a longer time than that for the preparation of their germanium counterparts, due to the lack of a suitable stable silylene. Therefore, the preliminary preparation of the appropriate silylene precursors, which can generate silylenes in situ, was required for the successful synthesis of cyclotrisilenes. Only three examples of cyclotrisilenes have been reported in the literature; of those three cyclotrisilenes, two were structurally characterized (Table 2).

The first reports on the preparation of isolable cyclotrisilenes appeared in 1999, when two groups independently published consecutive papers on the synthesis of cyclotrisilenes with different substituents. Cyclotrisilene **21**, prepared by Kira's group, has three *tert*-butyldimethylsilyl substituents and a very large tris(*tert*-butyldimethylsilyl)silyl group attached to one unsaturated silicon atom.[13] Compound **21** was obtained by the reaction of $R_3SiSiBr_2Cl$ (R = $SiMe_2{}^tBu$) with potassium graphite in THF at -78 °C in 11% yield as dark red crystals (Scheme 7).

Although the crystal structure of **21** was not reported, the existence of the Si=Si double bond was proved by the ^{29}Si NMR spectrum: the two downfield signals at $+81.9$ and $+99.8$ ppm, which were significantly shifted to higher field relative to those for the acyclic tetrasilyldisilenes ($+142$ to $+154$ ppm).[30] The

Scheme 7
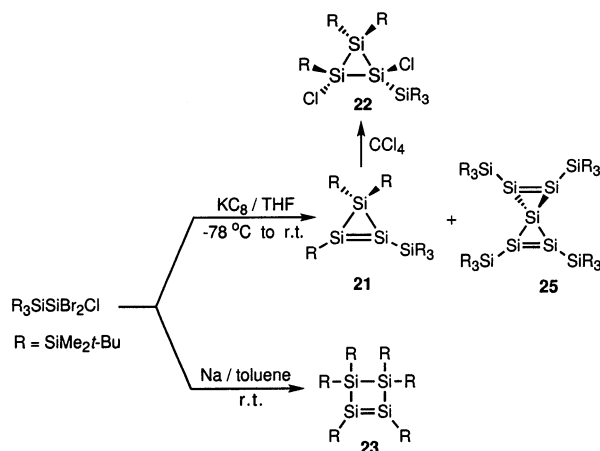
constitution of **21** was also confirmed by reaction with CCl_4; the structure of the chlorinated product **22** was established by X-ray crystallography (Scheme 7). It is interesting that the final product of the reduction of $R_3SiSiBr_2Cl$ greatly depends on the reducing reagent. Thus, treatment of $R_3SiSiBr_2Cl$ with sodium in toluene at room temperature gave the previously reported cyclotetrasilene **23**[20] in 64% yield without any formation of **21** (Scheme 7).

In the same year, Sekiguchi's group reported the second example of a stable cyclotrisilene. This compound, **24**, was prepared by the reductive coupling reaction of R_2SiBr_2 and $RSiBr_3$ (R = $SiMe^tBu_2$) with sodium in toluene at room temperature (Scheme 8,
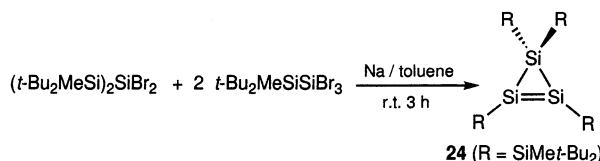
Scheme 8

Table 2).[14] Cyclotrisilene **24** was isolated as red-orange crystals in 9% yield. Its ^{29}Si NMR spectrum revealed both a downfield signal at $+97.7$ ppm, attributable to the unsaturated silicon atoms, and an upfield signal at -127.3 ppm, which is typical of an sp^3 silicon atom in a three-membered ring system. The X-ray analysis of **24** (Figure 7) showed that the geometry around the Si=Si double bond is not planar but trans-bent with a bending angle of 31.9(2)°. The Si=Si double bond length in **24** is 2.138(2) Å, which was recognized as one of the shortest distances among the Si=Si double bond lengths reported so far.[19f]

Table 2. Physicochemical Data of Cyclotrisilenes

| compd	yield (%)	color	mp (°C)	^{29}Si NMR (ppm)	UV [λ (ϵ)]	Si=Si (Å), configuration, bent angle (°)	ref
21	11	dark red	150	-117.2, -105.7, 0.4, 6.4, 14.0, 81.9 and 99.8 (Si=Si)	217 (5210), 245 (sh, 3670), 315 (sh, 7690), 401 (1340), 482 (2640)	no data	13
24	9	orange-red	207−209	-127.3, 7.9, 27.1, 97.7 (Si=Si)	223 (7490), 259 (sh, 3610), 297 (sh, 1490), 466 (440)	2.138(2), trans-bent, 31.9(2)	14
25	3.5	dark red	216−218	-100.6, 6.7, 154.2 (Si=Si)	235 (sh, 77800), 250 (sh, 86300), 265 (sh, 66100), 304 (87000), 383 (18100), 428 (11700), 500 (3640), 560 (2530)	2.186(3), trans-bent, 30.0(5)	31
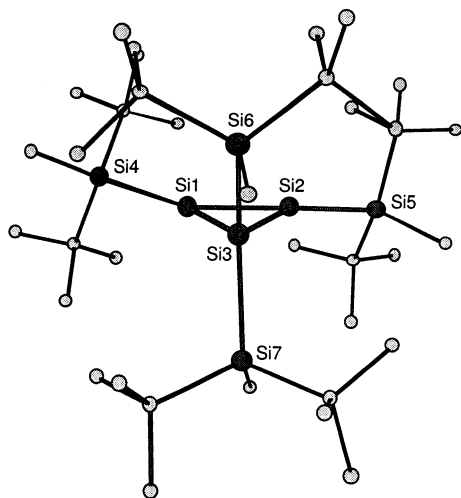
Figure 7. Crystal Designer ball-and-stick view of cyclotrisilene **24**. Drawn from the coordinates reported in ref 14.
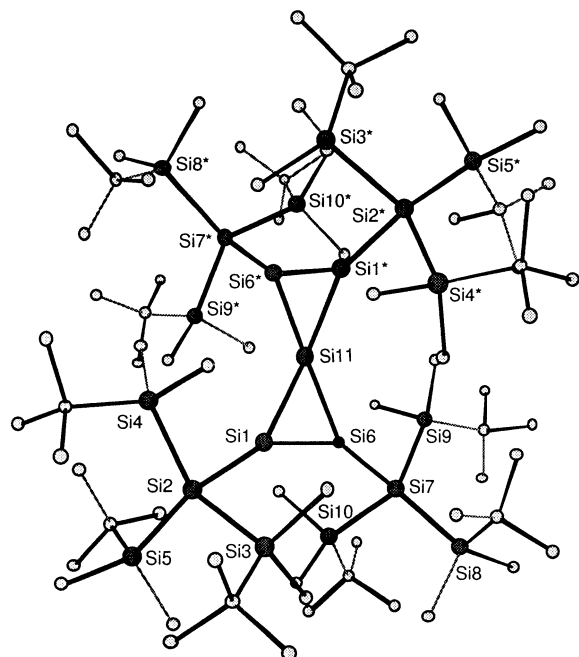

Figure 8. Crystal Designer ball-and-stick view of spiropentasiladiene **25**. Drawn from the coordinates reported in ref 31.

The last example is a cyclotrisilene with an unusual spirostructure: tetrakis[tri(*tert*-butyldimethyl-silyl)silyl]spiropentasiladiene (**25**) was reported quite recently by Kira's group as a side product of the above-mentioned reaction of $R_3SiSiBr_2Cl$ (R = $SiMe_2{}^tBu$) with potassium graphite (see Scheme 7).[31] Compound **25** was isolated as dark red crystals in 3.5% yield. The X-ray analysis (Figure 8) showed that the two three-membered rings are twisted relative to each other (twisting angle 78.3°), and the Si=Si double bond has a trans-bent configuration (bending angle 30.1°) with a Si=Si double bond length of 2.186(3) Å, which is slightly longer than that of the cyclotrisilene **24** (2.138(2) Å).[14] This elongation of the Si=Si double bond in **25** compared with that in cyclotrisilene **24** was attributed to the previously described phenomenon of $\pi-\sigma^*$ conjugation.[11] This spiropentasiladiene **25**, which has no carbon ana-

logues in organic chemistry, exhibited a significant through-space interaction between the two twisted Si=Si double bonds, which was demonstrated by the spectroscopic data and theoretical calculations. Thus, the UV spectrum of **25** showed the longest absorption maximum at 560 nm, which is significantly red-shifted compared with those of cyclotrisilenes **21**[13] and **24**[14] (482 and 466 nm, respectively). Such a bathochromic shift provides evidence for the possible through-space conjugation in **25** between the two remote Si=Si double bonds. The ²⁹Si NMR resonance of the unsaturated Si atoms appeared at +154.0 ppm, which is shifted considerably to a lower field compared with those of cyclotrisilenes **21**[13] and **24**[14] (+81.9 and +99.8 ppm for **21** and +97.7 ppm for **24**). Such a large deshielding of the sp² Si atoms in **25** may serve as an indication of the through-space interaction between the π^*-orbitals.

II.C. Cyclotristannene

Until now, only one example of a cyclotristannene, tetrakis(tri-*tert*-butylsilyl)cyclotristannene (**26**), has been reported, by Wiberg et al. in 1999.[15] Compound **26** was prepared by the reaction of ${}^tBu_3SiNa$ with stable stannylenes :Sn[N(SiMe₃)₂]₂ or :Sn(O${}^tBu$)₂ in pentane. It was isolated as dark red-brown crystals in 27% yield (Scheme 9). In accordance with the

Scheme 9
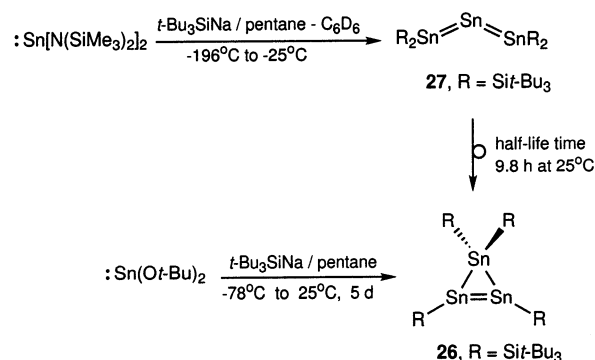
symmetrical structure of the molecule, **26** exhibits only two sets of signals in the ¹H, ¹³C, and ²⁹Si NMR spectra. The ¹¹⁹Sn NMR spectrum was the most informative, showing both upfield (−694 ppm) and downfield (+412 ppm) resonances. The latter is typical of doubly bonded tin atoms,[32,33] whereas the former was assigned to the endocyclic Sn atom in a three-membered ring system.[3,32]

The structure of **26** by X-ray analysis showed an almost planar environment around the Sn=Sn double bond, whereas all previously reported distannenes have a trans-bent configuration around the Sn=Sn double bond.[32−36] The Sn=Sn double bond length was only 2.59 Å, which is the shortest among all distannenes structurally characterized so far.[32−36]

One of the most important findings of the last reaction was the discovery of the intermediately formed tristannaallene **27**, which was not thermally stable and gradually rearranged to the isomeric cyclotristannene **26** at room temperature. Such a rearrangement apparently implies the migration of

one silyl substituent followed by cyclization. Nevertheless, it was possible to isolate compound **27** in 20% yield as dark blue crystals, which were highly air- and moisture-sensitive and slowly isomerized at room temperature to form cyclotristannene **26**. This isomerization takes place by a first-order reaction with a half-life of 9.8 h at room temperature. The structure of the tristannaallene **27** was supported by ^{119}Sn and ^{29}Si NMR spectra. In the ^{119}Sn NMR spectrum of **27**, the two downfield signals at +503 and +2233 ppm were observed with an intensity ratio of 2:1. The first one was attributed to the terminal doubly bonded Sn atoms in an allene unit. The central allenic Sn atom, which formally has sp-type hybridization, resonates at a much lower field (+2233 ppm), which is the usual shift for stannylenes.[37−39] Such behavior suggests that the central tin atom in **27** has considerable stannylene character; therefore, the bonding situation in **27** is better described by the resonance formula shown in Scheme 10. The ^{29}Si NMR spectrum of **27** showed only one signal, at +77.3 ppm.

Scheme 10
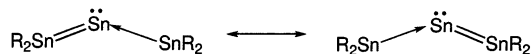
The crystal structure of **27**, confirmed by X-ray crystallography, showed an unexpectedly short Sn=Sn double bond length of 2.68 Å. This bond length is the shortest among all distannenes reported thus far (2.77−2.91 Å),[32−36] although it is longer than that of **26** (2.59 Å). Another important feature of allene **27** is a bent, rather than linear, Sn3 chain. Such a phenomenon was explained by the large contribution of the resonance formula [R₂Sn=Sn: ← SnR₂, R = Si^{t}Bu₃] in the structure of **27**, rather than the real allenic structure. The (^{t}Bu₃Si)₂Sn groups in **27** adopt a gauche configuration, similar to the R₂C groups in allenes; thus, the four ^{t}Bu₃Si groups cover the Sn3 chain almost completely to prevent intermolecular reactions between the Sn3 units.

II.D. Disilagermirenes

It was reasonably expected that "mixed" cyclotrimetallenes, that is, the unsaturated three-membered ring compounds composed of different Group 14 elements, would possess specific and unusual properties, which may significantly distinguish them from their homonuclear analogues. The synthesis of the title compounds was not evident, and so far only two examples of such molecules have been prepared. In 2000, Sekiguchi et al. reported the first representatives of such unsaturated molecules: 1- and 2-disilagermirenes **28** and **29**.[16] 1-Disilagermirene **28** was synthesized by a Würtz-type reductive coupling reac-

tion of R₂GeCl₂ and RSiBr₃ (R = SiMe^{t}Bu₂) with sodium in toluene at room temperature (Scheme 11,
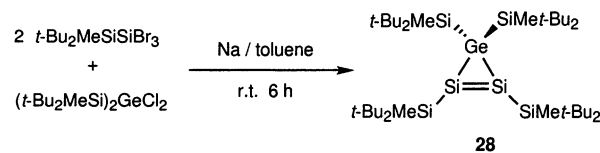
Scheme 11

Table 3). Compound **28** was isolated as hexagonal ruby crystals in 40% yield and appeared to be highly air- and moisture-sensitive. The ^{1}H and ^{13}C NMR spectra correspond well to a symmetrical structure for **28**, showing only two sets of signals for the methyl and *tert*-butyl groups. The ^{29}Si NMR spectrum displayed three resonances: +18.7, +25.6, and +107.8 ppm, of which the first two belong to the silyl substituents and the last one is characteristic of doubly bonded Si atoms.

The crystal structure of 1-disilagermirene **28** was determined by X-ray crystallography, which showed an almost isosceles triangle with internal angles of 52.71(3)°, 63.76(3)°, and 63.53(3)° (Figure 9). The
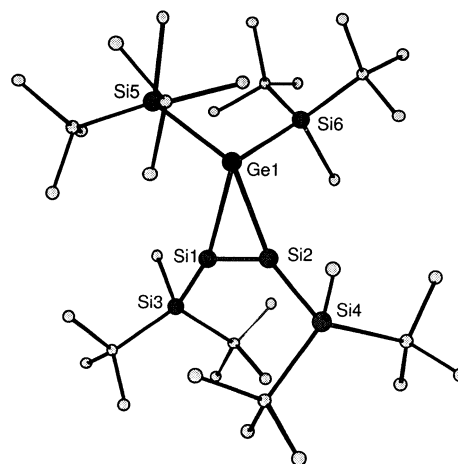

Figure 9. Crystal Designer ball-and-stick view of 1-disilagermirene **28**. Drawn from the coordinates reported in ref 16a.

Si=Si double bond length of **28** was 2.146(1) Å, which is rather short compared with other Si=Si double bond lengths reported thus far (2.138−2.289 Å).[19f] The geometry around the Si=Si bond is trans-bent, with a bending angle of 37.0(2)°. This bending of the Si=Si double bond may be due to the eclipsed conformation of the two bulky ^{t}Bu₂MeSi substituents attached to the sp² silicon atoms.

The most important chemical feature of 1-disilagermirene **28** is its easy and fast isomerization to 2-disilagermirene **29**.[16] Thus, photolysis of a benzene solution of **28** with a high-pressure Hg lamp ($\lambda > 300$

Table 3. Physicochemical Data of Disilagermirenes

compd	yield (%)	color	mp (°C)	^{29}Si NMR (ppm)	UV [λ (ϵ)]	Si=Si (Å), configuration, bent angle (°)	ref
28	40	dark red	205−207	18.7, 25.6, 107.8 (Si=Si)	230 (33440), 259 (18220), 308 (6300), 469 (1890)	2.146(1), trans-bent, 37.0(2)	16
29	quant	bright red	194−196	−120.1, 6.9, 27.8, 39.5, 100.7 (Si=Ge)	235 (58100), 263 (27000), 301 (11600), 395 (1600), 467 (4200)	trans-bent, 40.3(5)	16

nm) for 4 h at room temperature leads to migration of one of the silyl substituents from a Ge atom to a Si atom, with quantitative formation of 2-disilagermirene **29** with an endocyclic Si=Ge double bond (Scheme 12).[40] The isomerization of **28** to **29** can be

Scheme 12
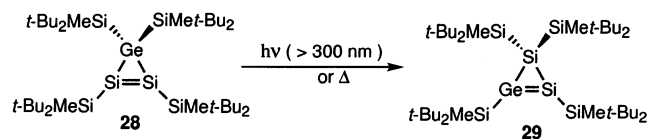
effectively monitored by either NMR or UV spectroscopy; the latter method showed the disappearance of the long-wavelength band at 469 nm corresponding to **28** and the appearance of two new bands at 395 and 467 nm, which belong to **29**. Compound **29** represents the first stable germasilene reported to date, since the only tetramesitylgermasilene, previously synthesized by Baines et al., was unstable and can survive only at low temperatures.[41]

The 2-disilagermirene **29** was isolated as scarlet plate crystals and was extremely thermally stable, with a melting point of 194−196 °C without any sign of decomposition. Such enhanced stability of 2-disilagermirene can be definitely attributed to the effect of the above-mentioned $\pi-\sigma^*$ conjugation,[11] which is also known to be responsible for the stability of 3-silirenes.[11a] The ^{1}H and ^{13}C NMR spectra of **29** are more complicated than those of **28**, because the 2-disilagermirene **29** has lost the C_{2v} symmetry of the 1-disilagermirene **28**. Thus, the ^{1}H NMR spectrum of **29** showed three resonances for three different types of methyl groups and four resonances for nonequivalent *tert*-butyl groups, whereas the ^{13}C NMR spectrum showed three sets of signals for both methyl and *tert*-butyl groups. The ^{29}Si NMR spectrum showed five signals: three belong to the silyl substituents, +6.9, +27.8, and +39.5 ppm; the endocyclic doubly bonded Si atom exhibits a downfield resonance at +100.7 ppm; and the endocyclic sp^3 Si atom has an upfield resonance at −120.1 ppm.

The molecular structure of 2-disilagermirene **29** was also established by X-ray crystallography, which revealed a triangle composed of one sp^3 silicon atom, one sp^2 silicon atom, and one sp^2 germanium atom.[16] The accurate determination of bond lengths and angles in the three-membered ring was impossible due to the significant disorder in the positions of the doubly bonded Si and Ge atoms. However, it was possible to determine the geometry around the Si=Ge double bond, which also has a trans-bent configuration with a bending angle of 40.3(5)° and eclipsed conformation of Si substituents connected to the sp^2 Si and Ge atoms.

The isomerization of **28** to **29** can also be performed under thermal conditions.[16] Thus, thermolysis of the solution of **28** in mesitylene at 120 °C in a sealed tube cleanly produced 2-disilagermirene **29** in 1 day (Scheme 12). Thermolysis in a benzene solution at temperatures from 80 to 100 °C requires a longer time, about 4 days. All thermolysis reactions of **28** produced an equilibrium mixture of starting **28** (∼2%) and resulting **29** (∼98%), from which it was

estimated that **29** is more stable than **28** by ca. 3 kcal/mol. The most effective and quickest way to prepare 2-disilagermirene **29** is the thermolysis of **28** without solvent at 215 °C; compound **29** was quantitatively produced in 20 min without any side products.

Theoretical calculations on the model H$_3$Si-substituted 1-disilagermirene **30** and 2-disilagermirene **31** at the MP2/DZd and B3LYP/DZd levels predicted the Si=Ge double bond length in **31** to be 2.180 (MP2) and 2.178 Å (B3LYP) (Scheme 13).[16] Such values are

Scheme 13
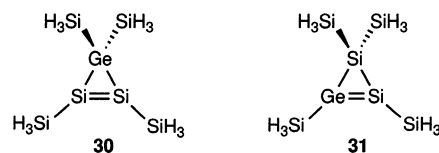
in good agreement with the previously calculated values of 2.184 Å for the parent germasilene H$_2$Ge= SiH$_2$.[42] It was also found that **31** is more stable than **30** by 3.9 (MP2) and 2.3 (B3LYP) kcal/mol; these values agree well with the experimentally estimated value of 3 kcal/mol.

## III. Reactivity of Cyclotrimetallenes

Until 2000, the reactivity of the three-membered unsaturated rings of heavier Group 14 elements was almost unexplored, although one could expect very interesting properties to arise from their unusual structures. However, this situation has greatly changed during the past two years, and our knowledge of the chemical properties of heavy cyclopropenes has significantly improved. Of all of the cyclotrimetallenes described above, the reactivity has been most intensively studied for cyclotrisilenes, cyclotrigermenes, and "mixed" cyclotrimetallenes. The chemistry of the only reported cyclotristannene is still open for investigation. Among the most important and well-studied examples of reactivity of cyclotrimetallenes, we will emphasize the addition, cycloaddition ([2 + 2] and [4 + 2]), and oxidation reactions.

III.A. Addition Reactions

III.A.1. Reaction with Haloalkanes

The reactions of cyclotrimetallenes with CCl$_4$ were studied in the case of cyclotrisilenes and "mixed" cyclotrimetallenes. Thus, cyclotrisilene **24**, 1-disilagermirene **28**, and 2-disilagermirene **29** were reacted with an excess of CCl$_4$ to form the corresponding *trans*-1,2-dichloro derivatives **32−34**, even at low temperature, in nearly quantitative yield (Scheme 14).[43] As was mentioned above, cyclotrisilene **21** also reacts with CCl$_4$ to produce the *trans*-1,2-dichloro

Scheme 14
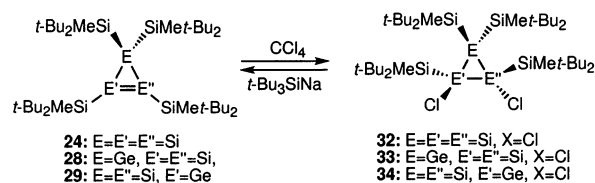
derivative **22** (Scheme 7).[13] The reaction proceeds selectively to produce only the trans-isomer, which can be explained by steric requirements, as well as by the proposed single-electron-transfer (SET) mechanism of the reaction. It is interesting that these dichloro derivatives **32**−**34** can be quantitatively converted back to the corresponding starting cyclotrimetallenes **24**, **28**, and **29** under treatment with 'Bu₃SiNa (Scheme 14).[43] The reaction of cyclotrisilene **24** with 1,2-dibromoethane quantitatively gives the corresponding *trans*-1,2-dibromocyclotrisilane,[43] whereas the 1-disilagermirene **28** reacts with MeI with quantitative formation of *trans*-1-iodo-2-methyldisilagermirane.[44]

III.A.2. Reaction with Alcohols

The reactions of disilenes toward alcohols were reported to undergo a stereoselective syn-addition of alcohols to a Si=Si double bond.[45] In contrast, in the case of 1-disilagermirene **28**, the reaction with benzyl alcohol also proceeds selectively, but as trans-addition to form only one stereoisomer **35**, in which the two bulky silyl substituents at the endocyclic silicon atoms are arranged trans to each other, presumably to decrease steric hindrance (Scheme 15).[46]

Scheme 15
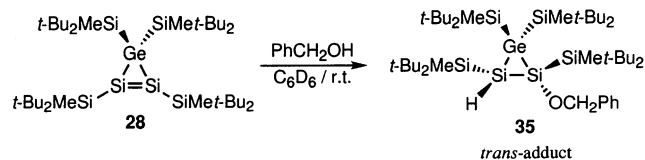
III.A.3. Cycloaddition Reactions

[2 + 2] Reactions. (i) Reaction with Phenylacetylene. The behavior of cyclotrimetallenes toward phenylacetylene was surprisingly different, showing the different nature of the three-membered-ring compounds composed of Si or Ge, or both Si and Ge atoms. Thus, reaction of phenylacetylene with the mesityl-substituted cyclotrigermene **16** proceeds as the anticipated [2 + 2] cycloaddition reaction, with the formation of the bicyclic fused three- and four-membered-ring compound **36** as orange crystals in the form of two stereoisomers, **36a** and **36b** (Scheme 16).[47]

The reaction of the "mixed" cyclotrimetallenes **28** and **29** with phenylacetylene also proceeds through

Scheme 16
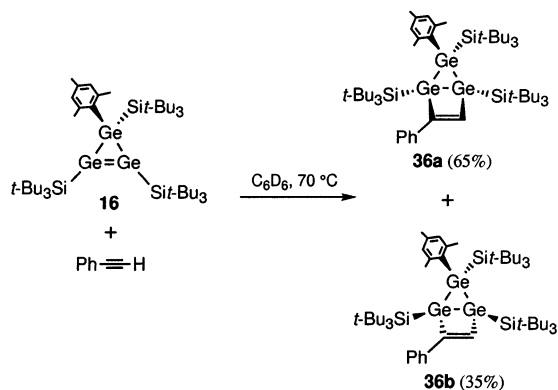
the initial [2 + 2] cycloaddition of the first molecule of phenylacetylene across the E=Si (E = Si, Ge) double bond, with the formation of the bicyclic fused three- and four-membered-ring compounds **37** and **38**.[48] However, in contrast to the reaction with cyclotrigermene **16**,[47] the reaction does not stop at this stage. Valence isomerization of the bicyclic compound takes place to form the silole-type structures **39** and **40** with one Si=C and one E'=C double bond, which in turn quickly isomerizes to give the thermodynamically more stable siloles **41** and **42** with Si=Ge and C=C double bonds (Scheme 17). The last silole-type compounds **41** and **42** react with a second molecule of phenylacetylene in a [2 + 2] cycloaddition manner to give the final bicyclic fused four- and five-membered-ring compounds **43** and **44**. In the case of 2-disilagermirene **29**, it was possible to isolate the intermediate silole **42**, representing the first metalladiene of the type E=E'−C=C (E and E' represent heavier Group 14 elements). Only two examples of isolable metalladienes of Group 14 elements have been previously reported, by Weidenbruch's group: hexakis(2,4,6-triisopropylphenyl)tetrasila-1,3-butadiene[49] and hexakis(2,4,6-triisopropylphenyl)tetragerma-1,3-butadiene.[50] The ²⁹Si NMR spectrum of **42** showed five resonances: three belong to the silyl substituents (19.4, 26.6, and 30.1 ppm), the downfield signal at +124.2 ppm was attributable to the doubly bonded silicon atom, and the upfield signal at −45.6 ppm corresponds to the endocyclic sp³ Si atom. X-ray analysis of **42** revealed an almost planar five-membered ring, although the Si=Ge double bond has a trans-bent configuration with a bending angle of 38.6(1)° (Figure 10).

The Si=Ge double bond length, determined experimentally for the first time, is 2.250(1) Å, which is intermediate between the typical values for Si=Si[19f] and Ge=Ge[19d] double bond lengths. This value is close to the theoretically predicted 2.180 Å (MP2) for H₃Si-substituted 2-disilagermirene **31**[16] (Scheme 13) and perfectly coincides with the results of the recently reported DFT calculations on the parent trans-bent germasilene H₂Ge=SiH₂, with a Si=Ge double bond length of 2.24 Å.[51] The X-ray analysis data of **42** did not show any noticeable elongation of the Si=Ge and C=C double bonds or any shortening of the Ge−C single bond, and the UV spectrum of silole **42** showed no bathochromic shift compared with the starting 2-disilagermirene **29** (472 vs 467 nm, respectively). From all of these experimental data, as well as the reactivity of silole **42**, it was found that there is actually no real conjugation between the two formally conjugated double bonds in the cyclopentadiene ring of **42**. This seems to be rather unusual, since all previously reported cyclopentadiene compounds were described as fully conjugated systems, for which Diels−Alder cycloaddition reactions are typical.[9] Apparently, such unusual behavior is caused by both a great energy difference and the difference in the size of the atoms of the Si=Ge and C=C double bonds, which prevent the effective π-overlapping of molecular orbitals of the two double bonds necessary for real conjugation. Such a conclusion was supported by NBO analysis calculations at the B3LYP/6-31G*

Scheme 17

28 (E = Ge, E' = Si)
29 (E = Si, E' = Ge)

37,38

valence
isomerization
fast

39,40

silyl group migration
fast

41,42

Ph—≡—H
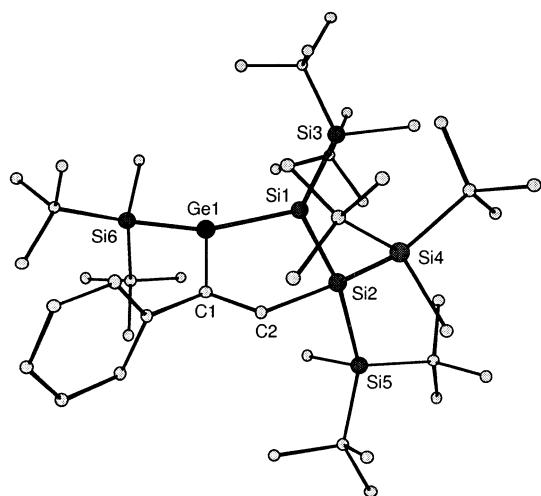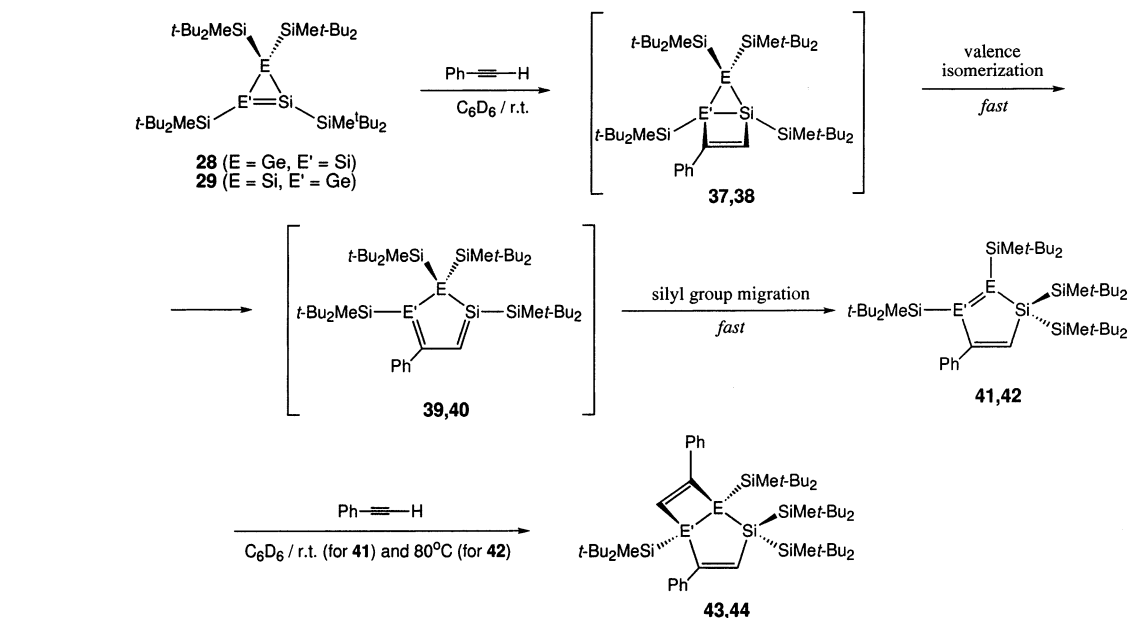C₆D₆ / r.t. (for **41**) and 80°C (for **42**)

43,44

Figure 10. Crystal Designer ball-and-stick view of silole **42**. Drawn from the coordinates reported in ref 48a.

level for the parent H-substituted silole molecule **45**, which showed the bond order for the Si=Ge and C=C double bonds to be 1.59 and 1.89, respectively, whereas the bond order for the Ge—C single bond was calculated to be 0.90 (Scheme 18).[52] The same level

Scheme 18

45

46
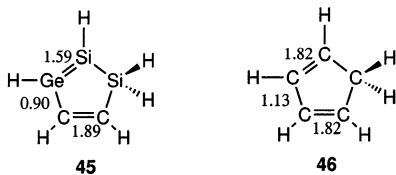
calculations for the parent cyclopenta-1,3-diene **46** gave the values expected for the conjugated system C=C—C=C, with C=C double bond orders of 1.82 and a C—C single bond order of 1.13 (Scheme 18).[52] For the acyclic 1,3-dienes with two equal double bonds containing heavier Group 14 elements, such as 2,3-digerma-1,3-butadiene (H₂C=GeH—GeH= CH₂), the theoretical calculations have predicted

about half the degree of conjugation of the parent 1,3-butadiene.[53] Indeed, both symmetrical tetrasila- and tetragerma-1,3-butadienes were reported by Weidenbruch as conjugated systems.[49,50]

Cyclotrisilene **24** also easily reacts with phenylacetylene to finally form the four- and five-membered bicyclic compound **47** (Scheme 19), whose structure

Scheme 19

24

Ph—≡—H
C₆D₆ / r.t.

47
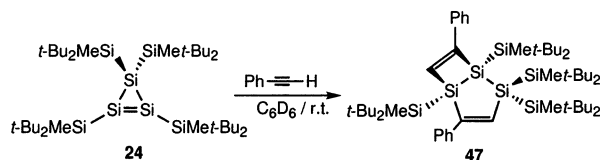
is similar to those of **43** and **44**.[54] In this case, the isolation of the intermediate silole-type compound was impossible because of its very high reactivity and short lifetime.

Silole **42** exhibited very interesting reactivity. In light of the nonconjugated nature of this cyclopentadiene compound discussed above, it is not surprising that this silole undergoes [2 + 2] rather than [4 + 2] cycloaddition reactions. One example of such reactivity is the above-mentioned reaction of silole **42** with phenylacetylene to form the final bicyclic compound **44** (Scheme 17).[48] Another example is the oxidation of silole **42** in solution (Scheme 20).[55] Oxidation of the Si=Ge double bond produced the

Scheme 20

42

O₂

48

49

H₂O

50
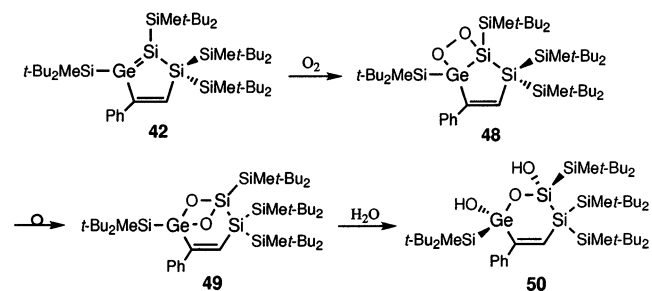
expected 1,2-dioxetane **48** in the first step, which rearranges to the thermodynamically more favorable 1,3-dioxetane **49**.[56] The last compound undergoes hydrolytic ring opening to give the final cis-1,3-diol **50**.

The most exciting example of the reactivity of silole **42** is its thermolysis reaction, which quantitatively leads to the isomeric tricyclo[2.1.0.0$^{2.5}$]pentane derivative **51**, representing a new type of cage compound of Group 14 elements (Scheme 21, Figure 11).[57]

Scheme 21
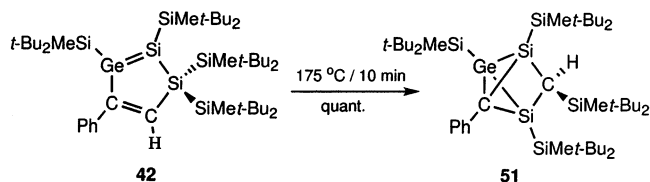
Such a highly strained molecule has several very important structural features. It has an extremely long Ge−C bridging σ bond (2.242 Å), which is much longer than the average value of a Ge−C bond (1.95 Å) by 15%, and an extremely short Si−Si nonbonding distance (2.558 Å), which is longer than the normal Si−Si bond (2.34 Å) by only 9% (Figure 11). In organic chemistry, the analogous tricyclopentane compounds exhibit the completely opposite tendency for the bridging bonds, which are unusually short.[58] Evidently, cage compound **51** is much closer to [1.1.1]propellane compounds,[59] rather than to the real tricyclo[2.1.0.0$^{2.5}$]pentane derivatives. The second unusual structural feature is an inverted tetrahedral geometry at the Ge atom, the so-called "umbrella"-type configuration.[60] Despite the usual explanation of such phenomena in organic chemistry as the result of large steric hindrance, the inversion of the geometry at the Ge atom is not caused by steric problems in this case. The calculated geometries (B3LYP/6-31G* level) of the parent H- and model H$_3$Si-
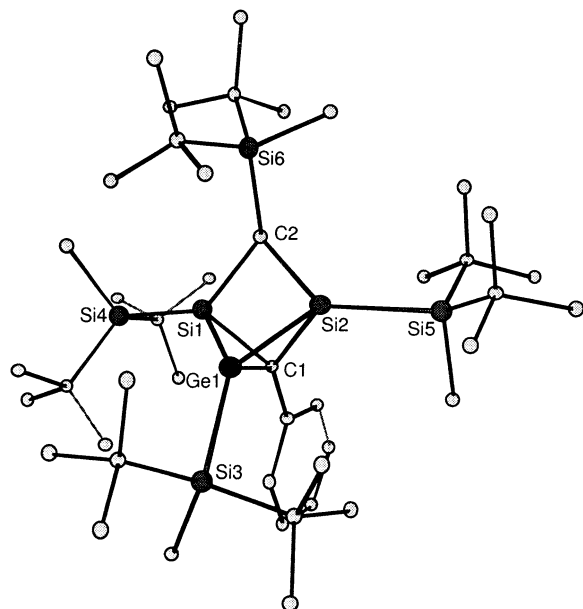

Figure 11. Crystal Designer ball-and-stick view of cage compound **51**. Drawn from the coordinates reported in ref 57.

substituted cage compounds perfectly reproduced the real molecule. Moreover, there were no changes on going from H- to H$_3$Si-substituted model compounds, which clearly showed the minimum influence of steric factors.[57] These unusual structural peculiarities, as well as the strongly downfield-shifted resonance of the bridgehead C atom in the ^{13}C NMR spectrum (+61 ppm), were explained in terms of the singlet biradical character of the Ge−C bridging bond, which is quite similar to the case of [1.1.1]propellanes. Indeed, the NBO analysis (B3LYP/6-31G(d)) of the model H$_3$Si-substituted cage compound showed a Ge−C bridging bond order of only 0.63 (Wiberg bond index), with Ge and C atoms both having sp$^{2.2}$ hybridization.[57] On the other hand, NBO analysis clearly demonstrated that the Ge−C bridging σ bond is formed by almost pure p-orbitals (92% p character and 8% s character for the Ge atom; 98% p character and 2% s character for the C atom), which is fully consistent with our understanding of the singlet biradical character of the Ge−C bond.

(ii) Reaction with Aldehydes and Ketones. Reaction with carbonyl compounds is also very sensitive to steric requirements. Thus, the highly sterically protected tetrakis(tri-*tert*-butylsilyl)cyclotrigermene (**1a**) does not react with benzaldehyde,[61] whereas the reaction of 1-disilagermirene **28** with benzaldehyde proceeds almost immediately, even at low temperature, to give a set of products depending on the reaction conditions and the ratio of the reagents (Scheme 22).[62] Thus, at room temperature, 1-disila-

Scheme 22
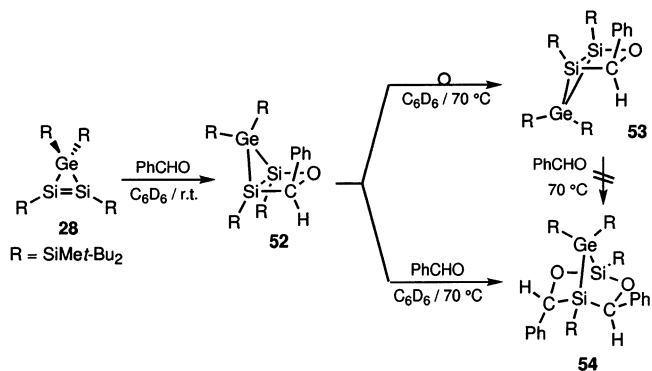
germirene **28** reacts with one molecule of benzaldehyde to give the bicyclic fused three- and four-membered-ring compound **52**. Compound **52** can be considered as a kinetically controlled product, which presumably is stabilized by the attractive through-space interaction of the electron-rich phenyl group and the empty σ*-orbital of the exocyclic Si−Ge bond. Nevertheless, such an arrangement of the phenyl group is not favorable, due to its steric repulsion with silyl substituents on the Ge atom. Therefore, upon heating at mild conditions (70 °C, 1 h), compound **52** was quantitatively isomerized to the thermodynamically more stable compound **53**. The initially formed bicyclic compound **52** has a highly strained bridging Si−Si bond. It can easily react with a second molecule of benzaldehyde by the insertion pathway to form a new bicyclic compound, **54**, with a norbornane-type skeleton (Scheme 22).

Although this last reaction greatly resembles the previous case of phenylacetylene,[48] the mechanism is evidently different. In the case of phenylacetylene, the final product **43** (Scheme 17) is a result of [2 + 2] cycloaddition of the second molecule of phenylacetylene across the Si=Ge double bond of silole **41**. However, in the case of benzaldehyde, the final norbornane **54** is a result of the insertion of the second molecule of benzaldehyde into the strained Si–Si bridging bond. Apparently, the reactions of 1-disilagermirene with phenylacetylene and benzaldehyde have the same initial steps to form bicyclic compounds by a [2 + 2] cycloaddition, but then the reaction pathways become different due to the different nature of these intermediate bicyclic compounds.

The reaction of 1-disilagermirene **28** with enolizable carbonyl compounds having an α-hydrogen atom proceeds in a manner completely different from the benzaldehyde case. Thus, **28** reacts with acetophenone to form the cis-adduct **55** in the first step, which gradually isomerizes to the thermodynamically more stable trans-isomer **56** (Scheme 23).[63] The

Scheme 23
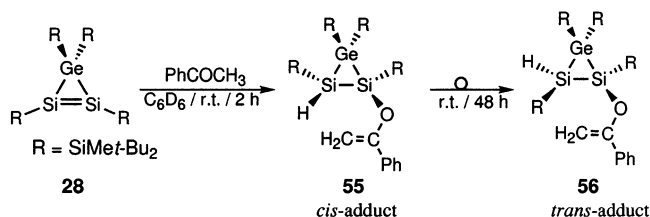
driving force for such an isomerization is most likely the decrease of steric hindrance on going from the cis- to the trans-isomer. The reaction of **28** with dicarbonyl compounds proceeds in a similar, although more complicated, way. Disilagermirene **28** reacts with butane-2,3-dione to finally give product **57**, which has a norbornane-type skeleton.[63] It is most likely that cis-adduct **58** is formed in the first step and quickly isomerizes to the more stable trans-isomer **59** (Scheme 24). In the last step, the second
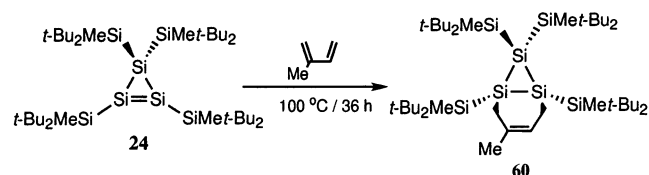
Scheme 24
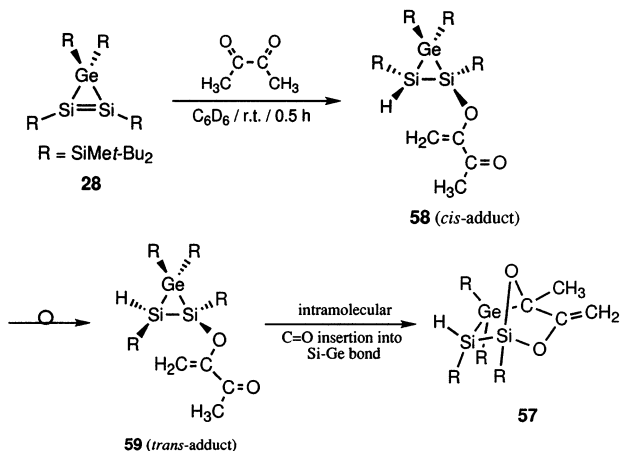
carbonyl group undergoes an intramolecular insertion into the endocyclic Si–Ge bond to form norbornane **57**. Such "ene"-type reactions of **28** with

enolizable ketones represent a new pathway in the reaction of disilenes with carbonyl compounds.[64]

[4 + 2] Reactions. Reaction with 1,3-Dienes. Conjugated dienes, such as 2,3-dimethyl-1,3-butadiene and isoprene, are traditionally widely used as trapping reagents for both transient and stable dimetallenes of Group 14 elements, forming the corresponding Diels–Alder adducts. While reacting with the cyclotrimetallenes of Group 14 elements, conjugated dienes have produced the corresponding [4 + 2] adducts in the form of bicyclic fused three- and six-membered-ring compounds.

Thus, the [4 + 2] cycloaddition reaction of cyclotrisilene **24** with isoprene proceeds under rather severe conditions (toluene, 100 °C, 36 h) to complete the formation of bicyclic product **60** in 82% yield (Scheme 25).[65] A similar reaction of mesityl-substi-

Scheme 25

tuted cyclotrigermene **16** with both isoprene and 2,3-dimethyl-1,3-butadiene proceeds under much milder conditions (hexane, room temperature, 6 h) to form bicyclic adducts **61** and **62** in good yields (Scheme 26).[47] Only one of the two possible stereoisomers is
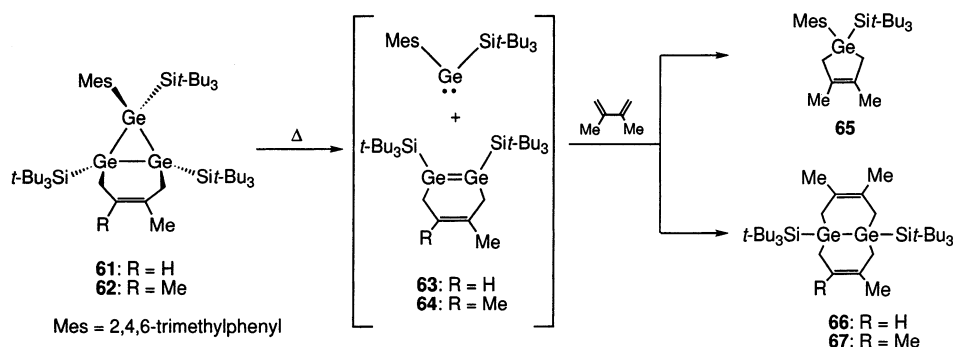
Scheme 26
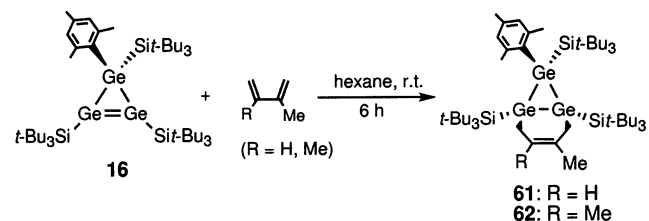
formed, which corresponds to an attack of the isoprene on the Ge=Ge double bond from the mesityl side; this is probably due to the lower steric bulkiness of the mesityl group compared with the $^tBu_3Si$ group.

It is noteworthy that the previous bicyclic three- and six-membered ring compounds **61** and **62** can serve, under mild conditions (C₆D₆, 70 °C), as precursors for both germylene $^tBu_3Si(Mes)Ge$: and digermenes **63** and **64**, which can be effectively trapped by 2,3-dimethyl-1,3-butadiene to form germacyclopentene **65** and bicyclic compounds **66** and **67** (Scheme 27).[47] The most interesting point in these reactions is the ring contraction that takes place in the intermediate digermacyclohexadienes **63** and **64** during reaction with diphenylacetylene (Scheme 28).[66] Thus, upon thermolysis of the bicyclic compounds **61** and **62**, ring contraction in the intermediate digermenes **63** and **64** takes place, resulting in the formation of germylgermylene species **68** and **69**. These last germylenes were trapped by diphenylacetylene to produce the corresponding germacyclopentenyl-substituted germirenes **70** and **71** (Scheme 28). The similar digermene–germylgermylene rearrangement of tetramesityldigermene[67] and germa-

Scheme 27

Mes = 2,4,6-trimethylphenyl

Scheme 28
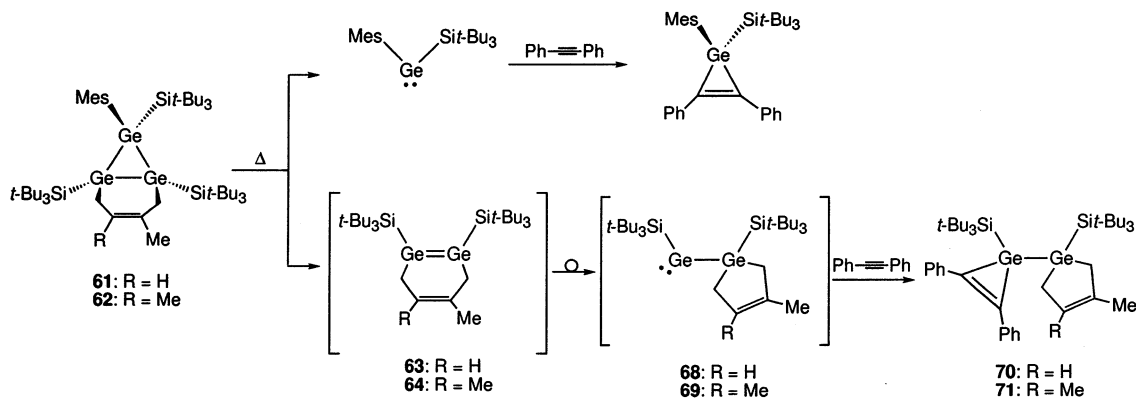
silene−silylgermylene rearrangement of tetra-mesitylgermasilene[41] were previously reported by Baines and co-workers.

The halogen-substituted cyclotrigermenes **18**−**20** also react easily with 2,3-dimethyl-1,3-butadiene at room temperature to form stereoselectively only one stereoisomer of the bicyclic compounds **72** and **73** (Scheme 29).[29] Thus, the butadiene attacks the

Scheme 29
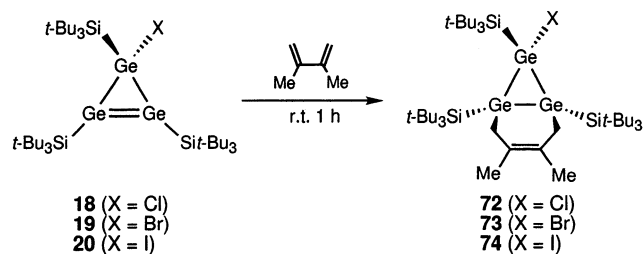
Ge=Ge double bond from the side of the bulkier ^{t}Bu$_3$Si group, in contrast to the above-mentioned case of mesityl-substituted cyclotrigermene **16**. Evidently, the cis-bent geometry of the Ge=Ge double bond of the halogen-substituted cyclotrigermenes also influences the face selectivity of the Diels−Alder reaction with butadiene.

III.B. Oxidation of Cyclotrimetallenes

III.B.1. Oxidation of Cyclotrigermene to Cyclotrigermenylium Ion

It is well known that the cyclopropenylium ion with a Hückel-type aromatic 2π-electron system is the simplest and smallest aromatic compound, being relatively stable due to its resonance stabilization,

despite the very large ring strain.[68] In contrast to the chemistry of the well-established cyclopropenylium ion, the analogues of this compound consisting of heavier Group 14 elements were unknown until recently. Theoretical calculations on the stability of $A_3H_3^+$ ions (A = C, Si, Ge, Sn, Pb) predicted a preference for the classical cyclopropenylium ion structures with D_{3h} symmetry for the carbon and silicon cases, whereas hydrogen-bridged forms were expected to be favored for germanium, tin, and lead (Figure 12).[69] In contrast to these calculations, the
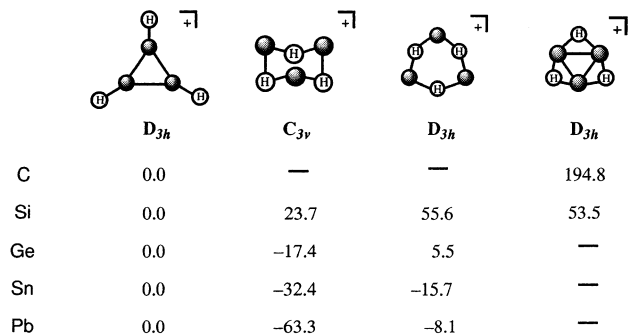

	D_{3h}	C_{3v}	D_{3h}	D_{3h}
C	0.0	—	—	194.8
Si	0.0	23.7	55.6	53.5
Ge	0.0	−17.4	5.5	—
Sn	0.0	−32.4	−15.7	—
Pb	0.0	−63.3	−8.1	—

Figure 12. Schematic representation of $A_3H_3^+$ cation structures (relative energies in kcal/mol).

first free germyl cation with a 2π-electron system was reported by Sekiguchi et al. in 1997 as a classical cyclopropenylium-type structure.[70] Thus, tris(tri-*tert*-butylsilyl)cyclotrigermenylium tetraphenylborate [(^{t}Bu$_3$SiGe)$_3^+$·TPB$^-$] (TPB$^-$ = tetraphenylborate) (**75**) was prepared by treatment of tetrakis(tri-*tert*-butyl-silyl)cyclotrigermene (**1a**) with trityl tetraphenyl-borate in dry benzene and was isolated as air- and moisture-sensitive yellow crystals (Scheme 30).[71,72]

Scheme 30
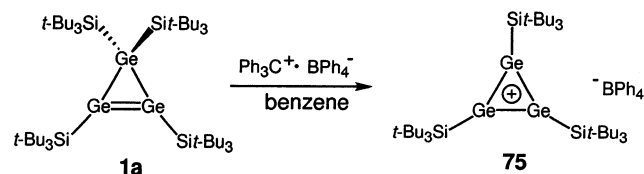
The structure of **75** was determined on the basis of NMR spectral data and finally confirmed by X-ray crystallographic analysis (Figure 13). The three
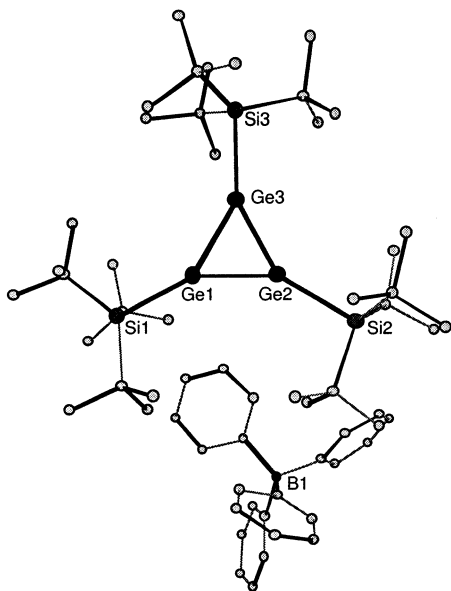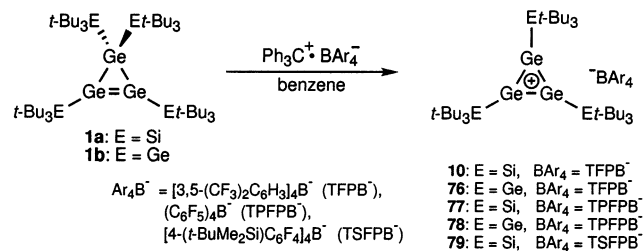

Figure 13. Crystal Designer ball-and-stick view of [(^{t}Bu$_3$SiGe)$_3$$^+$·TPB$^-$] (**75**). Drawn from the coordinates reported in ref 70.

germanium atoms form an equilateral triangle [Ge–Ge bond lengths, 2.321(4)–2.356(4) Å; Ge–Ge–Ge bond angles, 59.8(1)–60.3(1)°]. The Ge–Ge bond lengths observed in **72** are intermediate between the Ge=Ge double bond [2.239(4) Å] and the Ge–Ge single bond [2.522(4) Å] of the precursor **1a**.[12] The closest distance between germanium and the aromatic carbon atoms of TPB$^-$ is more than 4 Å, which is well beyond the range of any significant interaction. These structural features indicate that **75** has a cyclotrigermenylium skeleton and that it is a free germyl cation with a 2π-electron system.

However, the problem with TPB$^-$ is its chemical instability,[73] because **75** can survive in a solution of dichloromethane only at temperatures below −78 °C. [3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$B$^-$ (TFPB$^-$ = tetrakis-{3,5-bis(trifluoromethyl)phenyl}borate),[74] (C$_6$F$_5$)$_4$B$^-$ (TPFPB$^-$ = tetrakis(pentafluorophenyl)borate),[75] and [4-(^{t}BuMe$_2$Si)C$_6$F$_4$]$_4$B$^-$ (TSFPB$^-$ = tetrakis{4-[tert-butyl(dimethyl)silyl]-2,3,5,6-tetrafluorophenyl}-borate)[76,77] were used as the stable borate anions, which can increase the stability of the resulting cyclotrigermenylium ion.[78–80] In fact, the reaction of (^{t}Bu$_3$Si)$_4$Ge$_3$ (**1a**) and Ph$_3$C$^+$·TFPB$^-$ in benzene at room temperature produced the ionic (^{t}Bu$_3$SiGe)$_3$$^+$·TFPB$^-$ (**10**), which was isolated as a yellow powder in 81% yield (Scheme 31).[78–80] The reaction of **1b** with Ph$_3$C$^+$·TFPB$^-$ in benzene also proceeded smoothly to give (^{t}Bu$_3$GeGe)$_3$$^+$·TFPB$^-$ (**76**) in 76% yield. In a

Scheme 31

similar way, the reaction of **1a** and **1b** with Ph$_3$C$^+$· TPFPB$^-$ in benzene produced (^{t}Bu$_3$SiGe)$_3$$^+$·TPFPB$^-$ (**77**) (80%) and (^{t}Bu$_3$GeGe)$_3$$^+$·TPFPB$^-$ (**78**) (80%), respectively. The reaction of **1a** with Ph$_3$C$^+$·TSFPB$^-$ produced (^{t}Bu$_3$SiGe)$_3$$^+$·TSFPB$^-$ (**79**) as orange crystals in 88% yield. The resulting germyl cations can survive for extensive periods without decomposition, both in solution and in the solid state.

The molecular structure of **10** is shown in Figure 14. The three-membered ring consisting of ger-
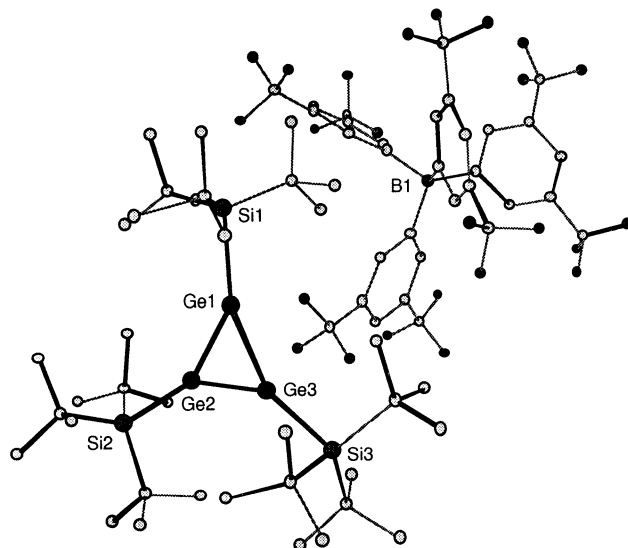

Figure 14. Crystal Designer ball-and-stick view of [(^{t}Bu$_3$SiGe)$_3$$^+$·TFPB$^-$] (**10**). Drawn from the coordinates reported in ref 78.

manium atoms is almost an equilateral triangle, with the Ge–Ge distances of the three-membered ring being almost equal, ranging from 2.3284(8) to 2.3398(8) Å (average 2.3333(8) Å). The Si–Ge bond lengths [Si1–Ge1, 2.425(1) Å; Si2–Ge2, 2.442(1) Å; Si3–Ge3, 2.444(1) Å] of **10** are shortened compared with those of **1a**[12] [2.629(7) Å for the Si–Ge bond length of the sp^3 Ge atom and 2.448(7) Å for the Si–Ge bond length of the sp^2 Ge atoms]. The perspective view appears to show a weak electrostatic interaction between the germanium and fluorine atoms. The three closest distances range from 3.823 to 5.097 Å, which are longer than the sum (3.57 Å) of the van der Waals radii for germanium and fluorine atoms.[81]

X-ray diffraction data were also obtained for **79**. Due to the steric bulkiness of the ^{t}BuMe$_2$Si group attached to the para positions of the phenyl rings of the borate anion, no interaction between the cation moiety and the counteranion can be found (Figure 15). As a consequence, the skeleton of the three-membered framework forms an equilateral triangle;
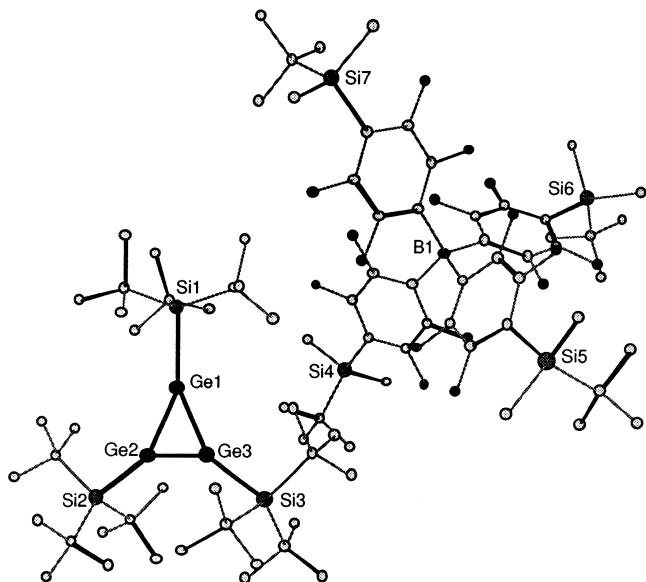
Figure 15. Crystal Designer ball-and-stick view of [(^{t}Bu$_3$SiGe)$_3$$^+$·TSFPB$^-$] (**79**). Drawn from the coordinates reported in ref 80.

the Ge—Ge bond lengths are 2.3310(8) Å for Ge1—Ge2, 2.3315(7) Å for Ge1—Ge3, and 2.3349(8) Å for Ge2—Ge3, and the Ge—Ge—Ge bond angles are 60.10(2)° for Ge2—Ge1—Ge3, 59.96(2)° for Ge1—Ge2—Ge3, and 59.94(2)° for Ge1—Ge3—Ge2. The structural features for **10** and **79** are practically the same as those of **75**.[70]
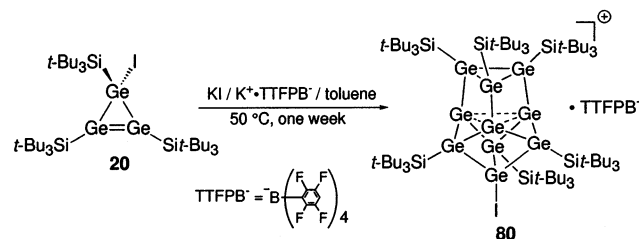
The evidence for the existence of the free cyclotrigermenylium ion in solution was supported by the NMR spectroscopic data. The ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts for the cyclotrigermenylium ion moiety of **10**, **77**, and **78** in CD$_2$Cl$_2$ are practically the same. For example, the ^{29}Si NMR chemical shifts of **10**, **77**, and **78** are independent of the counteranion. The ^{29}Si NMR chemical shift of **10** is also essentially the same in different solvents, appearing at $\delta = 64.0$ in CD$_2$Cl$_2$, $\delta = 64.2$ in CDCl$_3$, $\delta = 64.4$ in toluene-d_8, and $\delta = 64.5$ in Et$_2$O. This independence from both the counteranion and solvent clearly indicates that (^{t}Bu$_3$SiGe)$_3$$^+$ is a free germyl cation in solution. The large downfield-shifted ^{29}Si NMR resonance of (^{t}Bu$_3$SiGe)$_3$$^+$, relative to that of the precursor **1a** ($\delta = 37.2$ for the ^{t}Bu$_3$Si substituent attached to the saturated Ge atom and 50.1 ppm for the ^{t}Bu$_3$Si group attached to the Ge=Ge double bond),[12] is due to the positive charge of the cyclotrigermenylium ion, which is not localized on the germanium atoms but is significantly transferred to the silicon centers. The atomic charges on (H$_3$SiGe)$_3$$^+$, according to calculations at the HF/6-31G* level, indicate a distribution of the positive charge: -0.07 for the ring germanium atoms and $+0.64$ for the silicon atoms of the SiH$_3$ substituents.

III.B.2. Germanium Cation Cluster with Trishomoaromaticity

The successful synthesis of the cyclotrigermenylium ions suggests that the factor of aromaticity is extremely important for the stabilization of the elusive three-coordinated cations of Group 14 ele-

ments. The heavier Group 14 elements cation cluster compound, [(^{t}Bu$_3$Si)$_6$Ge$_{10}$I]$^+$·TTFPB$^-$ (TTFPB$^-$ = tetrakis(2,3,5,6-tetrafluorophenyl)borate), was unexpectedly obtained by thermolysis of in situ prepared iodocyclotrigermene, (^{t}Bu$_3$Si)$_3$Ge$_3$I (**20**), in toluene in the presence of KI and K$^+$·TTFPB$^-$.[82] The molecular structure of **80** was determined by X-ray crystallography, showing that **80** is a free germyl cation (Scheme 32). The three "naked" cationic germanium
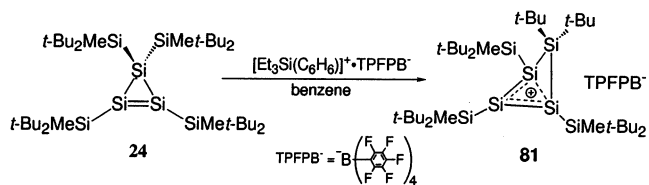
Scheme 32

atoms in the framework form three-center, two-electron (3c-2e) bonds with a trishomocyclotrigermenylium character, which is well supported by a theoretical calculation on the model compound Ge$_{10}$H$_7$$^+$.[82]

III.B.3. Oxidation of Cyclotrisilene to Cyclotetrasilenylium Ion

The problem of the stable "free" silyl cation was raised in the early 1990s, when Lambert and Reed reported the crystal structures of [Et$_3$Si(toluene)]$^+$·B(C$_6$F$_5$)$_4$$^-$ [83] and ^{i}Pr$_3$Si$^+$·CB$_{11}$H$_6$Br$_6$$^-$,[84] respectively; however, such silyl cations were not "free", being coordinated with either counteranion or solvent. Later, Lambert et al. synthesized the first example of a "free" silyl cation, Mes$_3$Si$^+$·B(C$_6$F$_5$)$_4$$^-$,[85] although without X-ray analysis data. Finally, the stable "free" silyl cation stabilized by homoaromatic character, whose structure was unequivocally confirmed by X-ray crystallography, was reported quite recently by Sekiguchi et al., resulting from the reaction of the cyclotrisilene **24** with [Et$_3$Si(benzene)]$^+$·B(C$_6$F$_5$)$_4$$^-$].[86] Oxidation of **24** with Et$_3$Si(benzene)$^+$ immediately took place to produce a dark red viscous oil, from which 1,2,3-tris[di-*tert*-butyl(methyl)silyl]-4,4-di-*tert*-butylcyclotetrasilenylium ion (**81**) was isolated as air- and moisture-sensitive yellow crystals in 91% yield (Scheme 33).[86]

Scheme 33

The mechanism of the formation of **81** was elucidated by the reaction of deuterium-labeled cyclotrisilene **24**-d_6 with Et$_3$Si(benzene)$^+$, which produced **81a**$^+$-d_3 and **81b**$^+$-d_3 in a 2:1 mole ratio (Scheme 34). Such results indicate the initial abstraction of the methyl group on the saturated silicon atom of **24** by the Et$_3$Si(benzene)$^+$ to form the intermediate silyl

Scheme 34
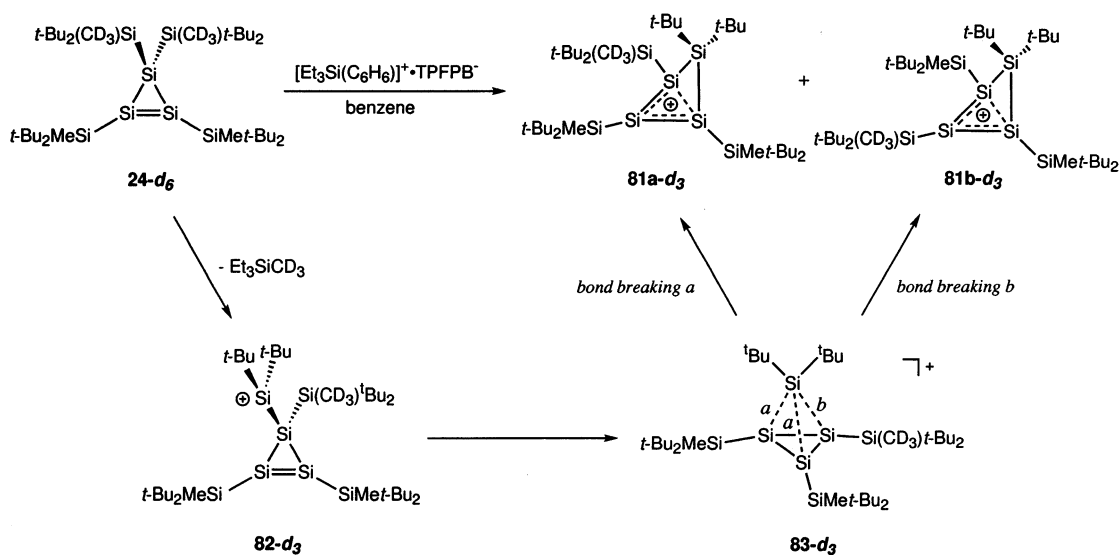
cation **82**, followed by isomerization to (**81a$^+$**-d_3 + **81b$^+$**-d_3) through an intermediate or transition state **83**.

The structure of **81** was determined by X-ray analysis to reveal the four-membered-ring cation system (Figure 16). The distances between the cat-
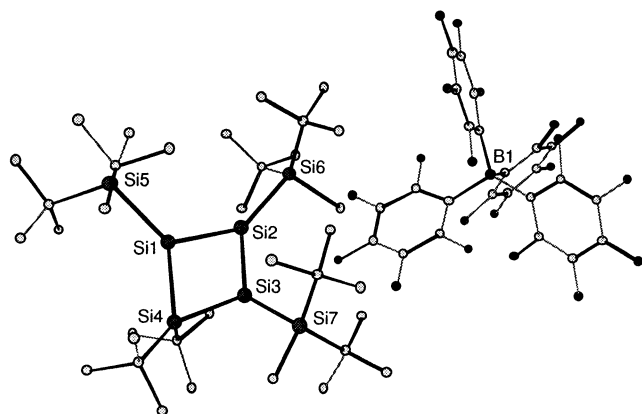

Figure 16. Crystal Designer ball-and-stick view of [(^{t}Bu$_2$(^{t}Bu$_2$MeSi)$_3$Si$_4$)$^+$·TPFPB$^-$] (**81**). Drawn from the co-ordinates reported in ref 86.

ionic silicon atoms (Si1, Si2, Si3) and the carbon atoms of the solvated benzene molecules range from 6.71(2) to 7.70(2) Å, showing no interactions between them. The closest distance between the cationic silicon atoms and fluorine atoms of B(C$_6$F$_5$)$_4^-$ is 4.861(8) Å, again showing the absence of any significant interactions. These results indicate that cyclotetrasilenylium ion **81** is a free silyl cation in the solid state. The four-membered ring is folded (folding angle is 46.6°), and the cationic part of the four-membered ring (Si1, Si2, Si3) has a planar sp^2 geometry, whereas Si4 has a distorted sp^3 geometry. The Si1–Si2 and Si2–Si3 bond lengths of the cationic part are 2.240(2) and 2.244(2) Å, respectively, which are intermediate between the Si=Si double bond [2.138(2) Å] and the Si–Si single bond [2.364(3) and 2.352(3) Å] of the precursor **24**. The interatomic distance between Si1 and Si3 is 2.692(2) Å, which is only 15% longer than the normal Si–Si single bond, indicating

the possibility of 1,3-orbital interaction to produce a homoaromatic cyclotrisilenylium ion as part of the cyclotetrasilenylium ion.[87]

The ^{29}Si NMR spectrum of **81** showed five resonances, appearing at 15.7, 34.3, 44.0, 77.3, and 315.7 ppm. These chemical shifts are independent of the solvent (dichloromethane, benzene, toluene), implying the lack of any interaction with the solvent molecules and the existence of the "free" silyl cation in solution. The positive charge is delocalized over the three silicon atoms, from which the central one (δ = 315.7 ppm for Si2) is more deshielded than the terminal ones (δ = 77.3 ppm for Si1 and Si3). Such delocalization of the positive charge over the Si1, Si2, and Si3 atoms, as well as shortening of the interatomic distance between the Si1 and Si3 atoms, may be attributed to the effect of the homoaromaticity of **81**. Thus, both the structural and spectroscopic characteristics of **81** are similar to those of the cyclobutenylium ion that is a homocyclopropenylium ion, as is well established by both experimental and theoretical studies.[87] The latest result in the field of stable silyl cations was published quite recently by Lambert's and Reed's groups, who have reported the crystal structure of the above-mentioned "free" trimesitylsilylium ion with a different counteranion: Mes$_3$Si$^+$·HCB$_{11}$Me$_5$Br$_6^-$·C$_6$H$_6$.[88]

The increasing interest in the heavy cyclopropenylium ions is reflected by the number of theoretical works on this subject that have appeared in the past few years. As well as the above-mentioned remarkable paper from Schleyer and co-workers,[69] there have been other important theoretical contributions. Thus, the same authors later reinvestigated a variety of Si$_3$H$_3^+$ isomers at the MP2/6-31G* level and found that the classical planar 2π-electron aromatic D_{3h} structure represents a global minimum, although its resonance and aromatic stabilization energies are only half those of the parent cyclopropenylium ion.[89] Moreover, the Si$_3$H$_3$ cyclopropenylium-type ion was found to form η^3-Si$_3$H$_3$ sandwich compounds with main group elements (boron, carbon) that are stabilized by charge transfer from the Si$_3$H$_3$ ligand to the

central atom [B3LYP/6-311++G(2d,2p) level]. On the other hand, when Be was used as a central atom, such sandwich structures were found to be unstable because of the much greater electropositive nature of the Be atom.[90] Such cyclopropenylium ions $E_3H_3^+$ (E = Si, Ge) may also serve as effective π-ligands for the η^3-π-complexes of $E_3H_3^+$ with the transition metal fragments $Co(CO)_3$, $Rh(CO)_3$, $Ir(CO)_3$, $Ni(CO)_3$, $Co(PH_3)_3$, and $Ni(PH_3)_3$ [B3LYP/6-31G(d) and B3P86/6-31G(d) levels]. In such complexes, charge transfer from a ligand to the transition metal center takes place, producing Si_3H_3 and Ge_3H_3 cationic ligands.[91]

IV. Summary and Outlook

In the present review, we have concentrated on a new field in the chemistry of Group 14 elements: the chemistry of cyclotrimetallenes, unsaturated three-membered rings consisting of Group 14 elements heavier than carbon. Cyclopropene, which is the smallest unsaturated ring system, and its derivatives are among the most important classes of organic compounds due to their enhanced reactivity caused by a great ring strain. One can easily imagine that the heavy cyclopropene analogues, that is, cyclotrimetallenes composed of Si, Ge, Sn, and Pb atoms, would occupy a similarly important position in the chemistry of heavier Group 14 elements, since their high reactivity is even more pronounced than that of cyclopropene, due to the extremely reactive endocyclic metal−metal double bonds and the weakness of the endocyclic metal−metal single bonds.

Thus, cyclotrimetallenes of heavier Group 14 elements constitute a new, highly promising and quickly developing class of organometallic compounds. In the most recent review on stable disilenes, Weidenbruch[17] pointed out, "...the synthesis of molecules containing endocyclic Si=Si double bonds as well as of a tetrasilabutadiene...have revealed that the formation of fundamentally new classes of compounds, the chemistry of which has mostly not yet been fully uncovered, is still possible". Certainly, the same is true for the molecules with endocyclic Ge=Ge, Sn=Sn, Si=Ge, etc. double bonds.

The chemistry of such compounds, which often exhibit great differences in the structures, physical properties, and reactivity from their carbon counterparts, is still in its earliest stages, and there are many problems to be solved. The reactivity of cyclotrimetallenes is widely open for investigation; moreover, the first preliminary studies have shown the extremely high synthetic possibilities of such compounds, since a very rich chemistry can be developed from them. Thus, we can reasonably expect great progress and important new developments in this "hot" field of Group 14 elements chemistry in the near future, which will have a significant impact on our understanding of the nature of bonding and reactivity in the systems composed of Group 14 elements heavier than carbon.[92]

V. Acknowledgments

VI. References

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