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Heavy analogues of the 6π -electron anionic ring systems: Cyclopentadienide ion and cyclobutadiene dianion

Vladimir Ya. Lee ^{*}, Kazunori Takanashi, Risa Kato, Tadahiro Matsuno,
Masaaki Ichinohe, Akira Sekiguchi ^{*}

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

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Abstract

The heavy analogues of the anionic 6π -electron systems, lithium 1,2-disila-3-germacyclopentadienide $2^- \cdot [\text{Li}^+(\text{thf})]$, 1,2-disila-3,4-digerma- and 1,2,3,4-tetrasilacyclobutadiene dianions $7^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$ and $8^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$, were synthesized by the reduction of the neutral precursors **1**, **3** and **4**, respectively. $2^- \cdot [\text{Li}^+(\text{thf})]$, the heavy analogue of the cyclopentadienide ion, is an aromatic compound, whereas $7^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$ and $8^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$, the heavy analogues of the cyclobutadiene dianion, are both non-aromatic.

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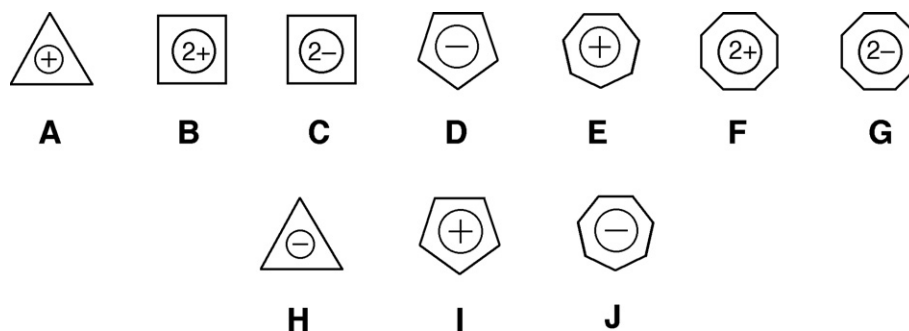
Keywords: Aromaticity; Cyclopentadienide ion; Cyclobutadiene dianion; Silicon; Germanium

1. Introduction

There is a striking relationship between the stability of the charged ring systems, both cationic and anionic, and their aromaticity (or antiaromaticity). Thus, the fundamental Hückel's rule predicts the important aromatic stabilization for $(4n + 2)$ π -electron systems, such as cyclopropenyl cation **A** (2π), cyclobutadiene dication **B** (2π), cyclobutadiene dianion **C** (6π), cyclopentadienide ion **D** (6π), cycloheptatrienyl cation **E** (6π), cyclooctatetraene dication **F** (6π) and cyclooctatetraene dianion **G** (10π), and, by contrast, great antiaromatic destabilization is a characteristic feature of $4n\pi$ -electron systems, such as cyclopropenide ion **H** (4π), cyclopentadienyl cation **I** (4π), cycloheptatrienide ion **J** (8π) (Scheme 1) [1]. And indeed, whereas the chemistry of the aromatic compounds of the types **A–G** is broadly and reliably established in organic chemistry with a variety of the stable representatives reported to date in the literature, the isolation of their

stable antiaromatic congeners **H–J** appeared to be a great problem, which is still not completely overcome. Of all aromatic charged species, the 6π -electron systems are of particular importance. However, even being significantly stabilized by the aromatic delocalization, such compounds are by far more reactive than the isoelectronic neutral benzene, which opens the unlimited possibilities for their functionalization providing the great synthetic applicability for such compounds. It is therefore not surprising, that the chemistry of charged 6π -electron aromatic systems, first of all, that of cyclobutadiene dianion, cyclopentadienide ion and cycloheptatrienyl cation (tropylium) ion, was one of the most intriguing topics in the second half of the last century and was greatly developed during this period. However, the area of the heavy congeners of the above-mentioned classes of aromatic compounds, in which the skeletal C atoms were partially (or fully) replaced by their heavier congeners of group 14 (Si, Ge, Sn, Pb), was almost unexplored until the early beginning of 1990s [2]. Of all these aromatic systems (heavy versions of cyclobutadiene dianion, cyclopentadienide ion, tropylium ion), the stable representatives of only second class of compounds, i.e. the heavy analogues of cyclopentadienide ion, have been

^{*} Corresponding authors. Tel.: +81 29 853 4523; fax: +81 29 853 4314.
E-mail addresses: vyalee@staff.chem.tsukuba.ac.jp (V.Ya. Lee),
sekiguch@staff.chem.tsukuba.ac.jp (A. Sekiguchi).



Scheme 1.

more or less studied prior to our investigations [3]. Such pioneering work on the chemistry of the stable anions and dianions of sila- and germacyclopentadienes was conducted in the research groups of Joo [4a], Boudjouk [4b,4g–j], West [4c,4d] and Tilley [4e,4f], who investigated their structures and aromaticity in details. The corresponding Sn-analogues, stannacyclopentadiene anions and dianions, have been recently synthesized by Saito and co-workers [5]. The deep theoretical insight to the problem of aromaticity of the heavy analogues of cyclopentadienide ion was provided by Schleyer in the series of papers published in the mid-1990s [6]. The lone example of the metastable silatropylium ion, reported by Komatsu group in 2000, was generated and characterized below $-50\text{ }^{\circ}\text{C}$ being irreversibly decomposed at the higher temperatures [7]. To the best of our knowledge, nothing was known about synthetic and structural aspects of the heavy analogues of cyclobutadiene dianion up to date. It is therefore evident, that even now the field of the heavy analogues of such fundamentally important species as cyclopentadienide ion and cyclobutadiene dianion is still rather “uncultivated” leaving many synthetic and mechanistic problems to be resolved. In this paper we present a full account of our recent contributions to the field, particularly emphasizing the structural peculiarities and aromaticity problems of newly synthesized heavy analogous of cyclopentadienide ion (which will be named below for simplicity as the “heavy cyclopentadienide”) [8a] and cyclobutadiene dianion (which will be named as the “heavy cyclobutadiene dianion”) [8b].

2. Results and discussion

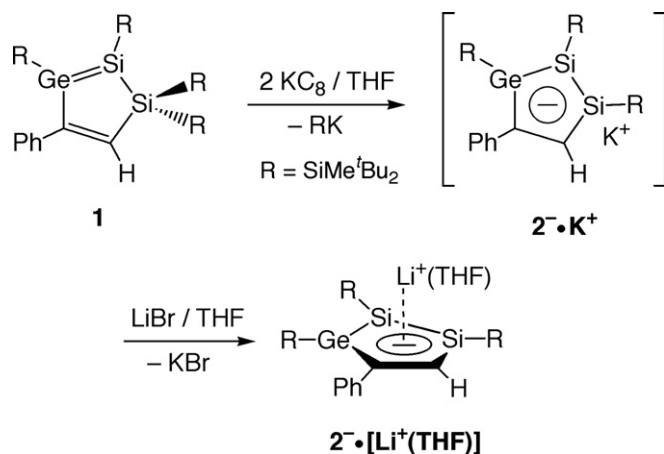
2.1. Heavy lithium cyclopentadienide

Typically, group 14 elements (E_{14}) based metalloles (siloles ($E_{14} = \text{Si}$), germales ($E_{14} = \text{Ge}$) and stannoles ($E_{14} = \text{Sn}$)) anions and dianions could be generated by the alkali metal reduction of the exocyclic E_{14} –halogen or E_{14} –Si bonds [2]. This resulted in the isolation of a variety of compounds, which were discussed as possessing a significant amount of aromaticity. However, all these derivatives included only one element E_{14} , being produced from the cyclopentadiene derivatives, in which E_{14} uniformly occupied sp^3 -position of the cyclopentadiene ring. In such view-

point the reduction of the recently prepared by us 1,2-disila-3-germacyclopenta-2,4-diene **1** [9], which incorporated the Si=Ge double bond into the Si=Ge–C=C diene system being the most electronically perturbed metallacyclopentadiene known to date, was of particular interest.

The right choice of the stoichiometry, namely – 2 equivalents of the alkali metal for 1 equivalent of heavy cyclopentadiene **1**, was of crucial importance: utilization of an excess of reducing reagent resulted in unavoidable overreduction to form complicated reaction mixtures. Finally, potassium graphite KC_8 was found to be the most effective and selective reducing agent for **1**, smoothly producing the corresponding potassium salt $2^- \cdot \text{K}^+$ along with the ${}^t\text{Bu}_2\text{MeSiK}$ as the only side product of the reaction. Apparently, the two-electron reduction of the Si=Ge double bond takes place as the initial step of the reaction, which is quite reasonable since the LUMO of **1** is largely represented by the π^* -orbital of the Si=Ge bond [10]. The driving force of the next step, β -elimination of ${}^t\text{Bu}_2\text{MeSiK}$, is evidently the formation of the aromatic 6π -electron system $2^- \cdot \text{K}^+$ (its aromaticity will be discussed below). However, since the isolation of $2^- \cdot \text{K}^+$ was precluded due to its poor crystallinity, we have performed an exchange of the counter-cation from potassium to lithium by the treatment of $2^- \cdot \text{K}^+$ with an excess of dry LiBr in THF. Following this procedure, the final product, lithium 1,2,3-tris(di-*tert*-butylmethylsilyl)-4-phenyl-1,2-disila-3-germacyclopentadienide $2^- \cdot \text{Li}^+$, was isolated as bright-orange plates by recrystallization from pentane in 34% yield (Scheme 2).

The X-ray analysis revealed the composition of $2^- \cdot \text{Li}^+$ as a THF solvate, $2^- \cdot [\text{Li}^+(\text{thf})]$, featuring several particularly important structural peculiarities (Fig. 1). The Li^+ -cation is pentahapto coordinated to the anionic GeSi_2C_2 -five-membered ring, thus the overall structure represents a classical “half-sandwich” complex diagnostic of the cyclopentadienide derivatives of the type $\text{C}_5\text{R}_5\text{Li}$ [11]. The distances from the Li atom to the skeletal atoms lie within the normal range expected for Ge–Li, Si–Li and C–Li bonds. The analysis of the structural changes taking place upon the reduction of heavy cyclopentadiene **1** to form the heavy cyclopentadienide $2^- \cdot [\text{Li}^+(\text{thf})]$ is especially instructive. First of all, the planarity of the five-membered ring of the starting **1** was only very insignificantly affected by the reduction, as was demonstrated by the comparison of their



Scheme 2.

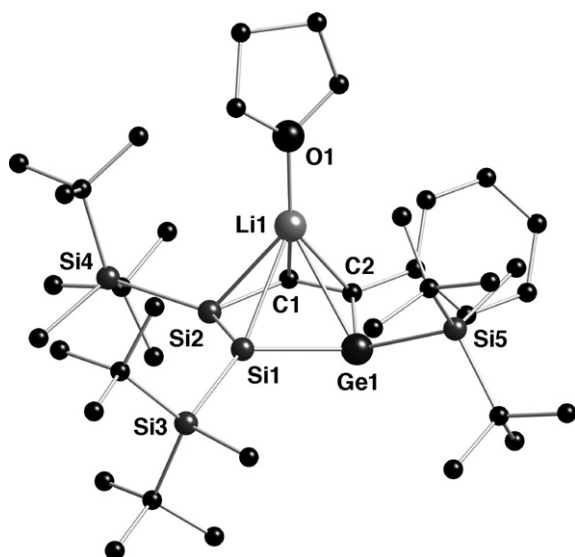


Fig. 1. Crystal Maker view of $2^- \cdot [\text{Li}^+(\text{thf})]$ (hydrogen atoms are not shown). Selected bond lengths (Å): Ge1–Si1 = 2.3220(5), Si1–Si2 = 2.2403(7), Ge1–C2 = 1.9303(17), Si2–C1 = 1.8269(18), C1–C2 = 1.402(2), Ge1–Si5 = 2.4092(5), Si1–Si3 = 2.3558(7), Si2–Si4 = 2.3550(7), Ge1–Li1 = 2.760(4), Si1–Li1 = 2.692(3), Si2–Li1 = 2.677(4), C1–Li1 = 2.259(4), C2–Li1 = 2.284(4), Li1–O1 = 1.869(4). Selected bond angles (°): Ge1–Si1–Si2 = 94.49(2), Si1–Si2–C1 = 101.48(6), Si2–C1–C2 = 122.74(13), C1–C2–Ge1 = 119.72(13), C2–Ge1–Si1 = 97.89(5).

interior bond angles: 539.9° for **1** [9] vs. 536.3° for $2^- \cdot [\text{Li}^+(\text{thf})]$. Consequently, the skeletal Ge1 and Si2 atoms are situated slightly above (0.1458 and 0.1486 Å), whereas the skeletal Si1, C1 and C2 atoms are situated slightly below (0.1507, 0.0638 and 0.0798 Å) the GeSi₂C₂-meanplane. Second, even more important, feature is the tendency in the changes of the skeletal bond lengths upon the reduction: all double bonds of the starting **1** [9] are *elongated* to form the final $2^- \cdot [\text{Li}^+(\text{thf})]$ (Ge1–Si1: 2.250(1) vs. 2.3220(5) Å, C1–C2: 1.343(5) vs. 1.402(2) Å), whereas all single bonds of **1** are *shortened* (Ge1–C2: 1.972(3) vs. 1.9303(17) Å, Si1–Si2: 2.364(1) vs. 2.2403(7) Å, Si2–C1: 1.888(3) vs. 1.8269(18) Å) (Fig. 2) [12a]. It should

be mentioned, that the lengths of all skeletal bonds in $2^- \cdot [\text{Li}^+(\text{thf})]$ are intermediate between those of the typical single and double bonds. Considering all above-mentioned structural features of $2^- \cdot [\text{Li}^+(\text{thf})]$, one should recognize that they provide a solid evidence for the delocalization of the 6 π -electron density over the entire five-membered ring, which in turn stands for its aromaticity. Evidently, the extent of aromaticity of $2^- \cdot [\text{Li}^+(\text{thf})]$ is smaller than that of the prototypical cyclopentadienide ion Cp[−]Li⁺: in contrast to CpLi, where the negative charge is equally distributed between all skeletal C atoms, one cannot assume such even distribution of electron density over all skeletal atoms in $2^- \cdot [\text{Li}^+(\text{thf})]$ because of their different electronegativities. The most essential part of the negative charge is expected to be accumulated on Ge atom, the pyramidalization of which is most important of all skeletal atoms: Ge1 (342.89°), Si1 (350.75°), Si2 (357.03°), C1 (359.94°), C2 (359.79°). The aromaticity of the model compound of $2^- \cdot \text{Li}^+$ (H₃Si-groups instead of the real ^tBu₂MeSi-substituents) was finally verified by the most effective aromaticity probe, nucleus-independent chemical shift (NICS) [13], calculated at 1 Å above the ring center: NICS(1) = −8.4 [12b]. This value is comparable (albeit smaller) to those of the classical 6 π -electron aromatic compounds: C₅H₅Li (NICS(1) = −10.3) and C₆H₆ (NICS(1) = −11.2) [12b].

However, in contrast to the crystal structure, the solution behavior and structure of $2^- \cdot \text{Li}^+$ is highly solvent-dependent. Thus, the heavy cyclopentadienide preserves its aromaticity in the non-polar solvents (toluene, benzene), whereas it is unable to benefit from aromatic delocalization in polar solvents (THF) anymore. The manifestation of aromaticity of $2^- \cdot \text{Li}^+$ in toluene-*d*₈ was convincingly demonstrated by NMR spectroscopy (the spectral characteristics of $2^- \cdot \text{Li}^+$ in C₆D₆ are almost identical to those in toluene-*d*₈, see Section 3). Thus, in ¹H NMR spectrum of $2^- \cdot \text{Li}^+$ all ^tBu-groups of silyl-substituents were nonequivalent because of the η^5 -coordination of Li⁺-ion to the five-membered ring breaking the symmetry of the molecule. The tendency in the changes of the ¹³C NMR resonances of the skeletal C atoms upon the reduction is in line with the theoretically predicted one [6b]: namely, CH-atom in $2^- \cdot \text{Li}^+$ is shielded comparing to that of the starting **1** [9] (143.2 vs. 150.0 ppm, $\Delta\delta$ = −6.8 ppm), whereas CPh-atom is deshielded (181.4 vs. 173.6 ppm, $\Delta\delta$ = +7.8 ppm). The skeletal Si atoms in $2^- \cdot \text{Li}^+$ resonate at 54.4 and 69.1 ppm, which values are in between those of the starting **1** [9] (−45.7 ppm for sp³-Si and 124.0 ppm for sp²-Si), that is sp³-Si atom is deshielded upon the reduction, whereas sp²-Si atom is shielded. One should also note, that both values of 54.4 and 69.1 ppm lie between those of the typical Si–Si and Si=Si bonds [14]. The most important prove for the aromaticity of $2^- \cdot \text{Li}^+$ in toluene solution was obtained from its ⁷Li NMR spectrum, which revealed a single resonance at −5.4 ppm, a very high field characteristic for the aromatic lithium cyclopentadienide derivatives [15]. However, in highly coordinating THF the behavior of heavy cyclopentadienide is totally different. The ¹H NMR

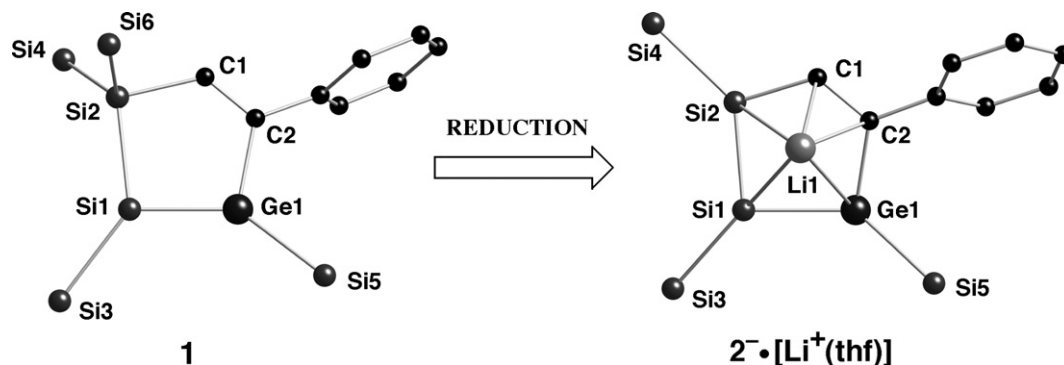
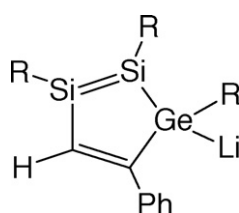


Fig. 2. Structural changes taking place upon the reduction of **1** to produce $2^- \cdot [\text{Li}^+(\text{thf})]$ (H and C atoms of the ${}^t\text{Bu}_2\text{MeSi}$ -substituents, H atoms of the Ph-group, H atom on the C1 atom, and the THF molecule coordinated to Li atom are not shown).



Scheme 3.

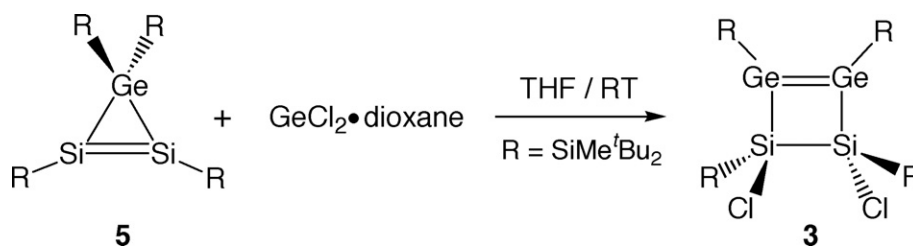
spectrum of $2^- \cdot \text{Li}^+$ in $\text{THF}-d_8$ solution displayed only three signals for ${}^t\text{Bu}$ -groups because of the breaking of pentahaptocoordination of Li^+ -ion to the heavy Cp-ring. The resonances of one of the ${}^t\text{Bu}_2\text{MeSi}$ -groups are characteristically shifted to higher fields (-0.33 ppm for Me-group and 0.80 ppm for ${}^t\text{Bu}$ -groups), indicating the accommodation of the large part of negative charge on the skeletal atom next to this ${}^t\text{Bu}_2\text{MeSi}$ -group. The resonances of both skeletal Si atoms of $2^- \cdot \text{Li}^+$ now appeared in low-field characteristic of the doubly-bonded Si atoms: 97.4 and 104.9 ppm [16]. The ${}^7\text{Li}$ NMR spectrum displayed a signal in the typical region of η^1 -germyllithiums: at -0.6 ppm [17], which is greatly shifted to lower field comparing to that measured in toluene- d_8 (-5.4 ppm) and clearly outside the range expected for the aromatic cyclopentadienide derivatives [15]. All these spectral characteristics of $2^- \cdot \text{Li}^+$ undoubtedly evidence for the change of the coordination mode from the delocalized η^5 in nonpolar toluene to a localized η^1 in polar THF (Scheme 3). Thus, one can conclude that in THF the heavy cyclopentadienide 2^- acquires the properties of the localized cyclopentadienide featuring a negative charge on Ge atom and $\text{Si}=\text{Si}$ and $\text{C}=\text{C}$ double bonds.

2.2. Heavy potassium disiladigerma- and tetrasilacyclobutadiene dianions

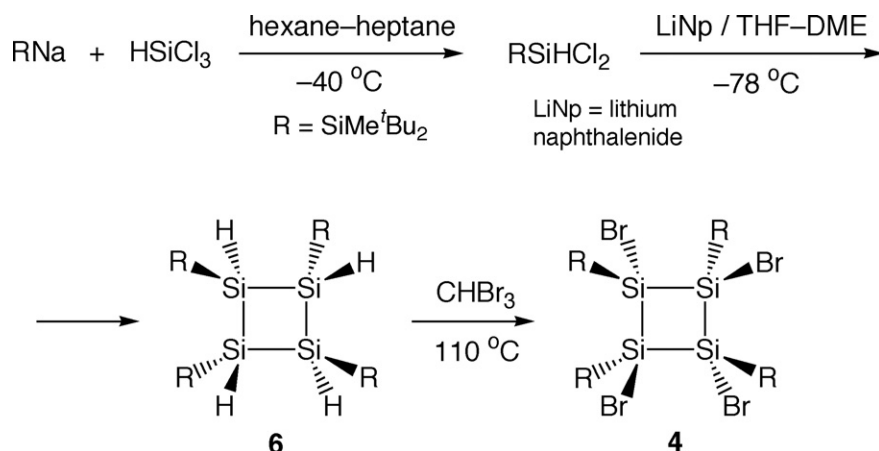
The story of the doubly-charged anionic 6π -electron systems, such as cyclobutadiene dianion, is greatly different from that of their singly-charged analogues (cyclopentadienide ion). The origin of such difference can be easily visual-

ized in terms of the interplay between the two tendencies: cyclic π -delocalization and thermodynamic stabilization. If the singly-charged species (cyclopentadienide ion) can greatly benefit from π -delocalization, which results in the overall aromatic stabilization of the molecule, the delocalization in the doubly-charged systems (cyclobutadiene dianion) has a totally opposite, destabilizing, effect due to the unavoidable mixing of the two extra electrons, which cannot be efficiently separated resulting in a strong Coulomb repulsion [18]. In general, such Coulomb repulsion can overcompensate the stability gained by delocalization, and consequently the trend for electron localization and separation may cause the significant departure of the cyclobutadiene dianion ring from planarity [18]. However, introduction of the highly positive lithium ions may greatly counteract this unfavorable tendency, significantly diminishing the degree of the extra electrons mixing, which finally results in the much greater extent of the cyclic delocalization and, in effect, in the overall aromatic stabilization of the system [19]. Recently, the first isolable dilithium salt of the cyclobutadiene dianion stabilized by the four π -accepting Me_3Si -groups was prepared, and it was shown to possess a planar four-membered ring in which the two electrons were fully delocalized as would be expected for the 6π -electron aromatic system [20]. However, the situation with the heavy analogues of the cyclobutadiene dianion, where the skeletal C atoms are replaced with the heavier group 14 elements, was still unresolved, and no information (either experimental or theoretical) concerning the synthesis and structure of such derivatives was available in the literature.

For the synthesis of the heavy cyclobutadiene dianions, at first we designed the appropriate precursors – disiladigermetene **3** and tetrabromotetrasilene **4**. The synthesis of the first compound **3** was accomplished by the unusual ring-enlargement reaction of $3H$ -disilagermirene **5** with GeCl_2 -dioxane complex (Scheme 4) [21]. The second precursor **4** was prepared by the bromination with CHBr_3 of tetrasilene **6**, which was synthesized by the reductive cyclization of RSiHCl_2 with lithium naphthalenide (Scheme 5).



Scheme 4.



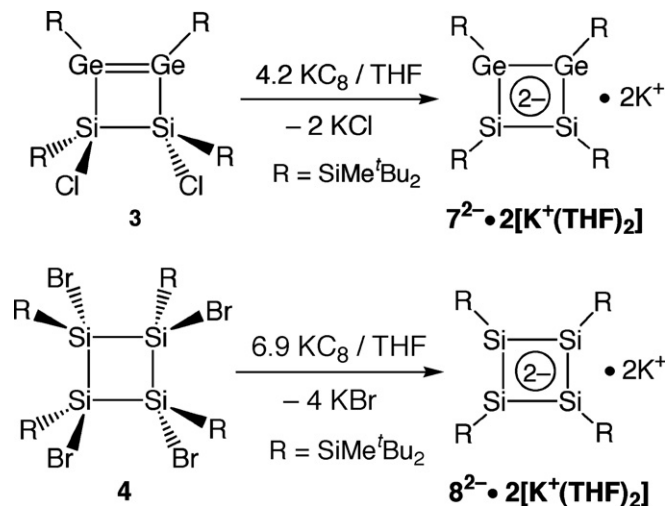
Scheme 5.

The reduction of both **3** and **4** with potassium graphite KC_8 (4.2 and 6.9 equiv., respectively) in THF smoothly and cleanly produced the corresponding dianionic derivatives, 1,2-disila-3,4-digerma- and 1,2,3,4-tetrasilacyclobutadiene dianions $\mathbf{7}^{2-} \cdot 2\mathbf{K}^+$ and $\mathbf{8}^{2-} \cdot 2\mathbf{K}^+$ (Scheme 6). Both heavy cyclobutadiene dianions were isolated by the recrystallization from hexane in the form of their THF solvates, $\mathbf{7}^{2-} \cdot 2[\mathbf{K}^+(\text{thf})_2]$ and $\mathbf{8}^{2-} \cdot 2[\mathbf{K}^+(\text{thf})_2]$, as extremely air- and moisture-sensitive emerald-green crystals in 70 and 73% yields.

Since both $\mathbf{7}^{2-} \cdot 2[\mathbf{K}^+(\text{thf})_2]$ and $\mathbf{8}^{2-} \cdot 2[\mathbf{K}^+(\text{thf})_2]$ are crystallographically isomorphous, below the structural features of only one of them, $\mathbf{8}^{2-} \cdot 2[\mathbf{K}^+(\text{thf})_2]$, will be discussed as the representative example of both compounds (Fig. 3).

The three structural peculiarities are of decisive importance: (1) the Si_4 four-membered ring is non-planar (folding angle 34°), (2) both \mathbf{K}^+ -cations are accommodated above and below the Si_4 -ring being dihaptoordinated at 1,3- and 2,4-positions, (3) the lengths of the skeletal Si–Si bonds are different: two of them, Si1–Si4 and Si2–Si3, are nearly equal (2.3301(8) and 2.3300(8) Å), whereas Si1–Si2 is shorter (2.2989(8) Å) and Si3–Si4 is longer (2.3576(8) Å), therefore the overall shape of the ring is a folded trapeze. Such geometry of the ring dictates the orientation of the bulky silyl-substituents, which are bent away from the coordinated \mathbf{K}^+ -cations, thus occupying the alternating up and down positions. Consequently, all skeletal Si atoms are appreciably pyramidalized: the sum of the three Si–Si–Si bond angles around Si1(Si2) and

Si3(Si4) atoms are 341° and 326° , respectively. The Si–K bond distances of 3.3011(8)–3.4044(7) Å are normal for silyl potassium derivatives. These structural features of $\mathbf{8}^{2-} \cdot 2[\mathbf{K}^+(\text{thf})_2]$ (as well as those of $\mathbf{7}^{2-} \cdot 2[\mathbf{K}^+(\text{thf})_2]$, which are quite similar) definitely do not fit the geometrical criteria of aromaticity in its classical sense (ring planarity, cyclic bonds equalization, tetrahaptocoordination expected for the aromatic cyclobutadiene dianion in its D_{4h} conformation) [19,20]. On the contrary, these structural characteristics are consistent with the non-aromaticity of the



Scheme 6.

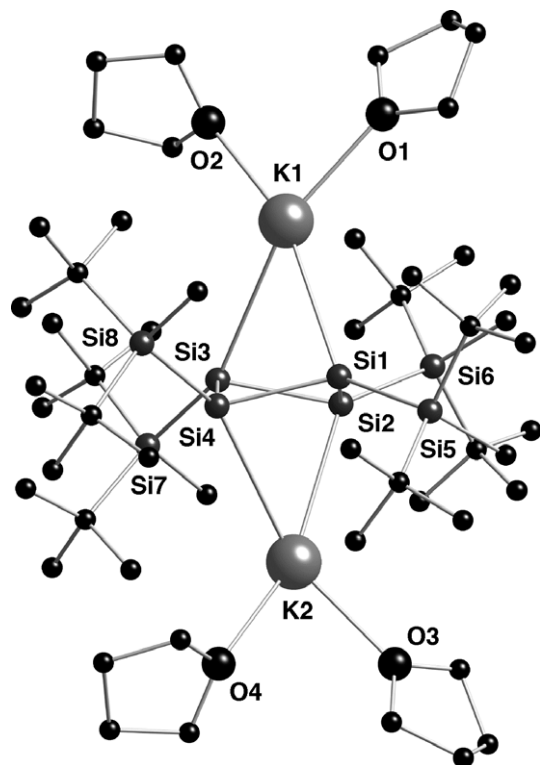
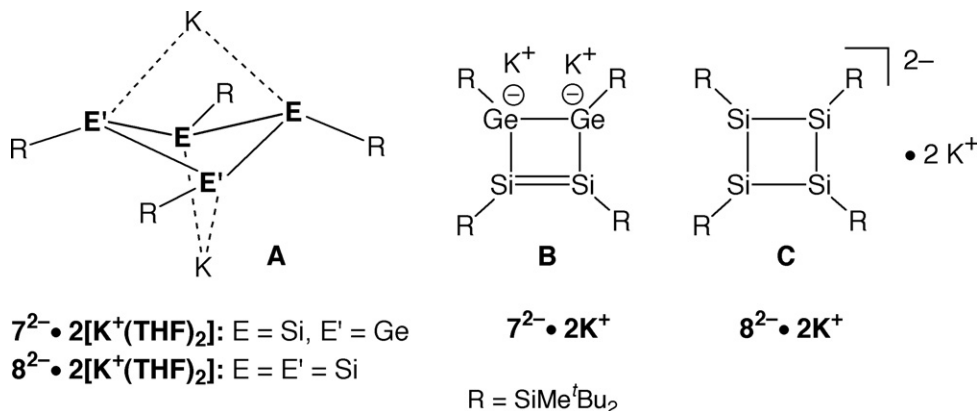


Fig. 3. Crystal Maker view of $8^{2-} \cdot 2[K^+(thf)_2]$ (hydrogen atoms are not shown). Selected bond lengths (Å): Si1–Si2 = 2.2989(8), Si2–Si3 = 2.3300(8), Si3–Si4 = 2.3576(8), Si1–Si4 = 2.3301(8), Si1–Si5 = 2.3602(8), Si2–Si6 = 2.3597(8), Si3–Si7 = 2.3728(7), Si4–Si8 = 2.3719(7). Selected bond angles (°): Si2–Si1–Si4 = 88.09(3), Si1–Si2–Si3 = 88.12(3), Si2–Si3–Si4 = 86.72(3), Si1–Si4–Si3 = 86.74(3). Dihedral angle (°): Si1–Si3–Si4 = 34.16(2).

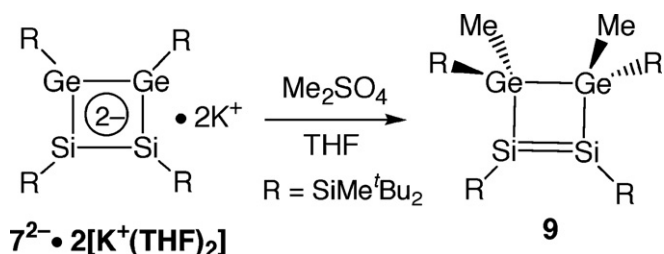
compounds, at least in the solid state. The requirement for the commonly accepted magnetic criterion of aromaticity [13] is also not fulfilled: the calculation of NICS(1) for both $7^{2-} \cdot 2[K^+(thf)_2]$ and $8^{2-} \cdot 2[K^+(thf)_2]$ (using Me_3Si -substituted model compounds) provided the positive values of +4.3 and +6.1, indicating the absence of a diatropic ring current [12b]. It should be noted, that the extent of the delocalization and aromaticity greatly depends on the nat-

ure of the counter-ions: smaller cations could approach the cyclobutadiene dianion ring more closely and therefore more effectively counteract the Coulomb repulsion of the two negative charges giving the overall stabilization of the system. Indeed, according to our preliminary results, the disodium derivative of the heavy cyclobutadiene dianion $8^{2-} \cdot 2[Na^+(thf)_2]$ has an η^4 -coordination of both Na atoms (inverted sandwich structure) and more planar, than that of $8^{2-} \cdot 2[K^+(thf)_2]$, Si_4 -ring [22].

In contrast to the evident similarity of the solid state structures **A**, the solution behavior of $7^{2-} \cdot 2[K^+(thf)_2]$ and $8^{2-} \cdot 2[K^+(thf)_2]$ is markedly different, which was clearly manifested by their ^{29}Si NMR spectra (Scheme 7). Thus, the resonances of the skeletal Si atoms in $7^{2-} \cdot 2K^+$ were observed in low-field at 113.7 ppm, characteristic of the doubly-bonded Si atoms [14]. This points out to the most important contribution of the resonance structure **B** with the preferential accommodation of both negative charges on the more electronegative Ge atoms, leaving the two skeletal Si atoms doubly-bonded (Scheme 7). That is, quite similar to the case of the heavy cyclopentadienide $2^- \cdot Li^+$, the difference in electronegativities between the Si and Ge atoms in $7^{2-} \cdot 2K^+$ favors electron localization. However, in contrast to $2^- \cdot Li^+$, in which such unfavorable electronegativity difference does not overcome the general tendency of aromatization of the singly-charged species, the electronegativity difference totally governs the situation in highly destabilized doubly-charged $7^{2-} \cdot 2K^+$ breaking the trend of cyclic delocalization and, consequently, making the molecule non-aromatic. In contrast to $7^{2-} \cdot 2K^+$, the resonances of the skeletal Si atoms of $8^{2-} \cdot 2K^+$ were measured at 17.0 ppm, which is definitely outside the range of the doubly-bonded Si atoms. This fact is to be realized as an indication of more important degree of delocalization of negative charges in $8^{2-} \cdot 2K^+$ (structure **C**), than that in $7^{2-} \cdot 2K^+$ (Scheme 7). This is not surprising, taking into account that the four-membered ring of the former compound is constituted of all identical Si atoms. The planarization of the Si_4 -ring, which is a necessary prerequisite for the cyclic delocalization, might be facilitated in solution through the fast ring flipping taking



Scheme 7.



Scheme 8.

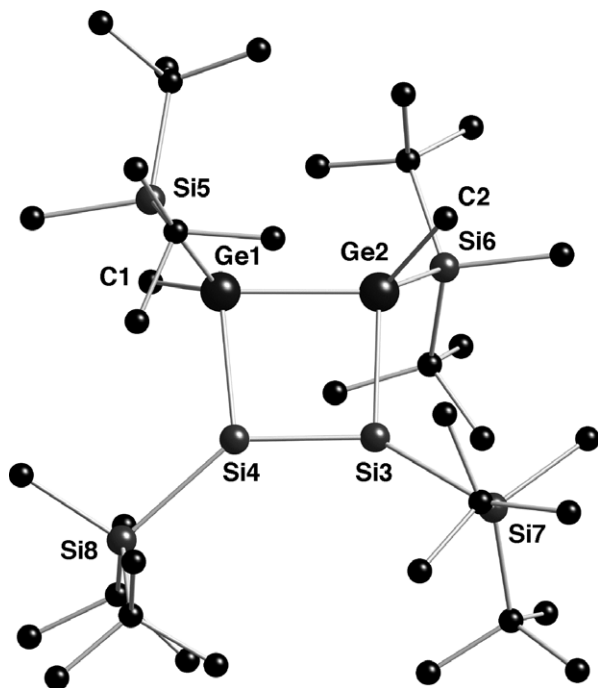


Fig. 4. Crystal Maker view of **9** (hydrogen atoms are not shown). Selected bond lengths (Å): Si3–Si4 = 2.1874(12), Si3–Ge2 = 2.3982(9), Si4–Ge1 = 2.3967(9), Ge1–Ge2 = 2.4828(5), Si3–Si7 = 2.3653(12), Si4–Si8 = 2.3629(12), Ge1–Si5 = 2.4295(10), Ge2–Si6 = 2.4288(10), Ge1–C1 = 1.984(3), Ge2–C2 = 1.989(3). Selected bond angles (°): Si4–Si3–Ge2 = 93.39(4), Si3–Ge2–Ge1 = 86.49(2), Ge2–Ge1–Si4 = 86.37(2), Ge1–Si4–Si3 = 93.59(4). Torsional angle (°): Si7–Si3–Si4–Si8 = 47.69(8).

place at room temperature. It should be noted, that the solution structures of both $7^{2-} \cdot 2K^+$ and $8^{2-} \cdot 2K^+$ do not depend on the polarity of solvents, which was clearly manifested in the striking similarity of their NMR spectra measured in both polar THF- d_8 and non-polar toluene- d_8 (see Section 3).

As expected for the cyclobutadiene dianion derivatives, both $7^{2-} \cdot 2[K^+(thf)_2]$ and $8^{2-} \cdot 2[K^+(thf)_2]$ are excellent substrates for the reaction with a variety of electrophiles to produce novel inorganic ring systems. For example, $7^{2-} \cdot 2[K^+(thf)_2]$ smoothly reacts with Me_2SO_4 to produce a single product, Δ -disiladigermetene **9**, in which both Me-groups are bound to Ge atoms, isolated as orange crystals in 95% yield (Scheme 8). The X-ray analysis of **9**, representing a novel hybrid cyclobutadiene [23], confirmed its constitution as a cyclic disilene (Fig. 4) [24].

Remarkably, the four-membered ring Si_2Ge_2 -core was planar in contrast to the starting cyclic disiladigermetene **3** [21], which features a folded Ge_2Si_2 -skeleton. The Si=Si double bond length in **9** of 2.1874(12) Å is typical for the cyclic disilenes [25], and it is expectedly *trans*-bent ($47.69(8)^\circ$). The methylation of the heavy cyclobutadiene dianion $7^{2-} \cdot 2[K^+(thf)_2]$ exclusively proceeded at Ge atoms, which gives a solid support for the above-discussed thesis on the predominant localization of the negative charges on Ge atoms. The Ge-bound Me-groups are regularly arranged in a *trans*-fashion to minimize the steric hindrances around Ge atoms. Typically for the four-membered cyclic disilenes [23a,23b,23c], the doubly-bonded skeletal Si atoms of **9** exhibited a low-field signal at 167.6 ppm.

The search for other synthetic applications of the heavy cyclopentadienide $2^- \cdot [Li^+(thf)]$ and heavy cyclobutadiene dianions $7^{2-} \cdot 2[K^+(thf)_2]$ and $8^{2-} \cdot 2[K^+(thf)_2]$, particularly their utilization as the novel ligands for transition metal complexes of the new generation, is currently under investigation in our research group.

3. Experimental

3.1. General procedures

All experiments were carried out using high-vacuum line techniques or in an argon atmosphere of MBRAUN MB 150B-G glove box. The solvents were predried over sodium benzophenone ketyl and finally dried and degassed over potassium mirror in vacuum immediately prior to use. NMR spectra were recorded on Bruker AC-300FT NMR (1H NMR at 300.13 MHz; ^{13}C NMR at 75.47 MHz; ^{29}Si NMR at 59.63 MHz; 7Li NMR at 116.64 MHz) and Bruker ARX-400FT NMR (1H NMR at 400.23 MHz; ^{13}C NMR at 100.64 MHz; ^{29}Si NMR at 79.52 MHz) spectrometers. GC–MS spectra were measured on Shimadzu GCMS-QP5000 instrument and direct mass spectra were obtained on JEOL JMS SX-102 instrument. UV-spectra were recorded on Shimadzu UV-3150 UV–Vis spectrophotometer in hexane. Elemental analyses were performed at the Analytical Center of the University of Tsukuba (Tsukuba, Japan).

The starting compounds were prepared according to the described procedures: 1,2-disila-3-germacyclopentadiene **1** [9], 3*H*-disilagermirene [26], dichlorogermylene dioxane complex [27].

3.2. Synthesis of lithium 1,2,3-tris(di-*tert*-butylmethylsilyl)-4-phenyl-1,2-disila-3-germacyclopentadienide ($2^- \cdot [Li^+(thf)]$)

Dry oxygen-free THF (4 ml) was added by vacuum transfer to a mixture of 1,2-disila-3-germacyclopenta-2,4-diene **1** (298 mg, 0.35 mmol) and potassium graphite KC_8 (102 mg, 0.76 mmol). The color of the reaction mixture immediately turned to a very dark red. After 30 min

stirring at room temperature, THF was replaced with dry oxygen-free hexane (4 ml) and graphite was removed by centrifugation. After evaporation of hexane, dry LiBr (464 mg, 5.35 mmol) was added to the residue followed by the vacuum transfer of dry THF (4 ml). After one day stirring at room temperature in a sealed tube, THF was again replaced with dry hexane (4 ml) and inorganic salts were removed by centrifugation. The dark red residue was recrystallized from dry pentane to give $2^- \cdot [\text{Li}^+(\text{thf})]$ as bright orange plates (92 mg, 34%). M.p. $>135^\circ\text{C}$ (dec.); ^1H NMR (toluene- d_8): δ 0.19 (s, 3H, Me), 0.55 (s, 3H, Me), 0.69 (s, 3H, Me), 1.09 (s, 9H, CMe_3), 1.19 (s, 9H, CMe_3), 1.24 (s, 9H, CMe_3), 1.26 (s, 9H, CMe_3), 1.33 (s, 9H, CMe_3), 1.34 (s, 9H, CMe_3), 7.08 (t, $J = 7.4$ Hz, 1H_{para}), 7.20 (t, $J = 7.4$ Hz, 2H_{meta}), 7.56 (d, $J = 7.4$ Hz, 2H_{ortho}), 8.21 (s, 1H, $\text{C}(\text{Ph})=\text{CH}$); ^{13}C NMR (toluene- d_8): δ -4.8 (Me), -2.9 (Me), -2.1 (Me), 21.1 (CMe_3), 21.4 (CMe_3), 21.8 (CMe_3), 22.1 (CMe_3), 22.6 (CMe_3), 23.2 (CMe_3), 30.0 (CMe_3), 30.2 (CMe_3), 30.3 (CMe_3), 30.39 (CMe_3), 30.44 (2CMe_3), 125.0 (C_{arom}), 127.8 (C_{arom}), 128.9 (C_{arom}), 143.2 ($\text{C}(\text{Ph})=\text{CH}$), 153.5 (C_{ipso}), 181.4 ($\text{C}(\text{Ph})=\text{CH}$); ^{29}Si NMR (toluene- d_8): δ 15.5, 23.2, 31.3, 54.4 and 69.1 (skeletal Si atoms); ^7Li NMR (toluene- d_8): δ -5.4; ^1H NMR (C_6D_6): δ 0.24 (s, 3H, Me), 0.58 (s, 3H, Me), 0.73 (s, 3H, Me), 1.13 (s, 9H, CMe_3), 1.22 (s, 9H, CMe_3), 1.26 (s, 9H, CMe_3), 1.27 (s, 9H, CMe_3), 1.37 (s, 18H, 2CMe_3), 7.10 (t, $J = 7.4$ Hz, 1H_{para}), 7.23 (t, $J = 7.4$ Hz, 2H_{meta}), 7.63 (d, $J = 7.4$ Hz, 2H_{ortho}), 8.30 (s, 1H, $\text{C}(\text{Ph})=\text{CH}$); ^{13}C NMR (C_6D_6): δ -4.8 (Me), -3.0 (Me), -2.1 (Me), 20.9 (4 CMe_3), 22.7 (CMe_3), 23.0 (CMe_3), 30.2 (3 CMe_3), 30.4 (3 CMe_3), 124.9 (C_{arom}), 127.7 (C_{arom}), 128.8 (C_{arom}), 143.2 ($\text{C}(\text{Ph})=\text{CH}$), 153.5 (C_{ipso}), 181.0 ($\text{C}(\text{Ph})=\text{CH}$); ^{29}Si NMR (C_6D_6): δ 15.6, 23.3, 31.2, 54.0 and 68.2 (skeletal Si atoms); ^7Li NMR (C_6D_6): δ -5.7; ^1H NMR (THF- d_8): δ -0.33 (s, 3H, Me), 0.38 (s, 3H, Me), 0.46 (s, 3H, Me), 0.80 (s, 18H, 2CMe_3), 1.16 (s, 18H, 2CMe_3), 1.19 (s, 18H, 2CMe_3), 6.83 (t, $J = 7.5$ Hz, 1H_{para}), 6.99 (t, $J = 7.5$ Hz, 2H_{meta}), 7.46 (d, $J = 7.5$ Hz, 2H_{ortho}), 8.13 (s, 1H, $\text{C}(\text{Ph})=\text{CH}$); ^{13}C NMR (THF- d_8): δ -4.4 (Me), -2.2 (Me), -0.6 (Me), 21.6 (2 CMe_3), 22.0 (2 CMe_3), 24.1 (2 CMe_3), 30.9 (2 CMe_3), 31.0 (2 CMe_3), 31.3 (2 CMe_3), 122.9 (C_{arom}), 127.0 (C_{arom}), 129.1 (C_{arom}), 150.6 ($\text{C}(\text{Ph})=\text{CH}$), 155.6 (C_{ipso}), 198.8 ($\text{C}(\text{Ph})=\text{CH}$); ^{29}Si NMR (THF- d_8): δ 8.0, 20.4, 28.1, 97.4 and 104.9 (skeletal Si atoms); ^7Li NMR (THF- d_8): δ -0.6; UV-Vis (hexane) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 375 (4050), 474 (4020).

3.3. Synthesis of 1,1-di-tert-butyl-2,2-dichloro-1-methyldisilane $^t\text{Bu}_2\text{MeSiSiHCl}_2$

A solution of $^t\text{Bu}_2\text{MeSiNa}$ (prepared from $^t\text{Bu}_2\text{MeSiBr}$ (11.2 g, 47 mmol) and Na (9.0 g, 391 mmol)) in heptane (150 ml) [28] was added at -40°C to a solution of HSiCl_3 (51.0 g, 377 mmol) in hexane (100 ml). The mixture was stirred at room temperature for 2 h, then inorganic salt

was filtered off and solvent was evaporated in vacuum. The product $^t\text{Bu}_2\text{MeSiSiHCl}_2$ was isolated by Kugelrohr distillation as a colorless solid (7.0 g, 57%). B.p. $90\text{--}100^\circ\text{C}/10\text{ mmHg}$; ^1H NMR (C_6D_6): δ 0.04 (s, 3H, Me), 0.97 (s, 18H, 2CMe_3), 5.86 (s, 1H, Si-H); ^{13}C NMR (C_6D_6): δ -9.2 (Me), 20.9 (CMe_3), 28.9 (CMe_3); ^{29}Si NMR (C_6D_6): δ 3.8 ($^t\text{Bu}_2\text{MeSi}$), 12.6 (SiHCl_2).

3.4. Synthesis of trans,trans,trans-1,2,3,4-tetrakis(di-tert-butylmethylsilyl)tetrakisiletane (6)

A solution of lithium naphthalenide (prepared from naphthalene (6.2 g, 48 mmol) and lithium (1.4 g, 202 mmol) in 1,2-dimethoxyethane (60 ml)) was added to a solution of $^t\text{Bu}_2\text{MeSiSiHCl}_2$ (5.7 g, 22 mmol) in THF (30 ml) at -78°C . Then the reaction mixture was stirred at room temperature for 15 h. After evaporation of solvent, dry hexane was introduced to the residue and inorganic salt was filtered off. After evaporation of hexane, naphthalene was separated by Kugelrohr distillation under vacuum ($50^\circ\text{C}/0.1\text{ mmHg}$), and the residue was recrystallized from hexane to give **6** as colorless crystals (1.6 g, 42%). M.p. $213\text{--}215^\circ\text{C}$; ^1H NMR (C_6D_6): δ 0.33 (s, 12H, 4 Me), 1.19 (s, 72H, 4CMe_3), 4.03 (s, 4H, 4 Si-H); ^{13}C NMR (C_6D_6): δ -5.5 (Me), 21.7 (CMe_3), 29.9 (CMe_3); ^{29}Si NMR (C_6D_6): δ -86.4 (d, $J_{^{29}\text{Si}-^1\text{H}} = 162.6$ Hz, Si-H), 13.8 ($^t\text{Bu}_2\text{MeSi}$). Anal. Calc. for $\text{C}_{36}\text{H}_{88}\text{Si}_8$: C, 57.98; H, 11.89. Found: C, 57.68; H, 11.84%.

3.5. Synthesis of trans,trans,trans-1,2,3,4-tetrabromo-1,2,3,4-tetrakis(di-tert-butylmethylsilyl)tetrakisiletane (4)

A solution of **6** (200 mg, 0.29 mmol) in bromoform (30 ml) was stirred at 110°C for 2 h. After the solvent was evaporated in vacuum, the residue was recrystallized from hexane to give **4** as colorless crystals (262 mg, 86%). M.p. $233\text{--}234^\circ\text{C}$; ^1H NMR (C_6D_6): δ 0.62 (s, 12H, 4 Me), 1.29 (s, 72H, 4CMe_3); ^{13}C NMR (C_6D_6): δ -3.1 (Me), 23.3 (CMe_3), 31.0 (CMe_3); ^{29}Si NMR (C_6D_6): δ 0.1 (Si-Br), 21.3 ($^t\text{Bu}_2\text{MeSi}$).

3.6. Synthesis of 1,2-dichloro-1,2,3,4-tetrakis(di-tert-butylmethylsilyl)- $^3\Delta$ -1,2,3,4-disiladigermetene (3)

A mixture of 3H-disilagermirene (60 mg, 0.08 mmol) and dichlorogermylene dioxane complex (20 mg, 0.09 mmol) was placed in a glass tube, and dry oxygen-free THF (0.5 ml) was vacuum transferred into this tube. Reaction immediately took place even at low temperature, and the color of the reaction mixture changed from dark red to bright orange. After evaporation of solvent, the residue was recrystallized from hexane to give **3** quantitatively as bright orange crystals. M.p. $158\text{--}160^\circ\text{C}$; ^1H NMR (C_6D_6): δ 0.36 (s, 6H, 2 Me), 0.54 (s, 6H, 2 Me), 1.15 (s, 18H, 2CMe_3), 1.19 (s, 18H, 2CMe_3), 1.30 (s, 18H, 2CMe_3), 1.37 (s, 18H, 2CMe_3); ^{13}C NMR (C_6D_6):

δ –5.3 (Me), –3.3 (Me), 22.3 (CMe₃), 22.4 (CMe₃), 22.46 (CMe₃), 22.50 (CMe₃), 29.8 (CMe₃), 30.0 (CMe₃), 30.5 (CMe₃), 30.7 (CMe₃); ²⁹Si NMR (C₆D₆): δ 12.5 (skeletal Si), 17.1 and 38.3 (SiMe^tBu₂); UV–Vis (hexane) λ_{max} /nm (ϵ) 327 (11500), 432 (11600). Anal. Calc. for C₃₆H₈₄Cl₂Ge₂Si₆: C, 47.96; H, 9.39. Found: C, 47.76; H, 9.12%.

3.7. Synthesis of tetrakis(di-tert-butylmethylsilyl)-1,2-disila-3,4-digermacyclobutadiene dianion dipotassium salt ($7^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$)

Δ -1,2,3,4-Disiladigermetene **3** (190 mg, 0.21 mmol) and KC₈ (120 mg, 0.89 mmol) were placed in a reaction tube with a magnetic stirring bar. The dry oxygen-free THF (2 ml) was introduced by vacuum transfer, and the reaction mixture was stirred at room temperature to give a dark green solution in 30 min. Then solvent was removed in vacuum and dry oxygen-free hexane (7 ml) was introduced by vacuum transfer. After the graphite was removed by centrifugation, the solution was cooled to –30 °C to afford $7^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$ as emerald-green crystals (176 mg, 70%). ¹H NMR (THF-*d*₈): δ 0.28 (s, 6H, 2 Me), 0.31 (s, 6H, 2 Me), 1.13 (s, 36H, 4CMe₃), 1.15 (s, 36H, 4CMe₃); ¹³C NMR (THF-*d*₈): δ –1.7 (Me), 0.7 (Me), 22.3 (CMe₃), 23.3 (CMe₃), 31.6 (CMe₃), 31.7 (CMe₃); ²⁹Si NMR (THF-*d*₈): δ 5.3, 20.8, 113.7 (skeletal Si atoms). ¹H NMR (toluene-*d*₈): δ 0.54 (s, 6H, 2 Me), 0.56 (s, 6H, 2 Me), 1.35 (s, 36H, 4CMe₃), 1.42 (s, 36H, 4CMe₃); ¹³C NMR (toluene-*d*₈): δ –1.7 (Me), 0.6 (Me), 22.0 (CMe₃), 23.1 (CMe₃), 31.4 (CMe₃), 31.5 (CMe₃); ²⁹Si NMR (toluene-*d*₈): δ 8.3, 22.6, 111.9 (skeletal Si atoms).

3.8. Synthesis of tetrakis(di-tert-butylmethylsilyl)tetrasilacyclobutadiene dianion dipotassium salt ($8^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$)

1,2,3,4-Tetrabromo-1,2,3,4-tetrakis(di-tert-butylmethylsilyl)tetrasiletane **4** (48 mg, 0.045 mmol) and KC₈ (42 mg, 0.31 mmol) were placed in a reaction tube with a magnetic stirring bar. The dry oxygen-free THF (1.5 ml) was introduced by vacuum transfer, and the reaction mixture was stirred at room temperature to give a dark green solution in 30 min. Then solvent was removed in vacuum and dry oxygen-free hexane (5 ml) was introduced by vacuum transfer. After the graphite was removed by centrifugation, the solution was cooled to –30 °C to afford $8^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$ as emerald-green crystals (37 mg, 73%). ¹H NMR (THF-*d*₈): δ 0.34 (s, 12H, 4 Me), 1.20 (s, 72H, 8CMe₃); ¹³C NMR (THF-*d*₈): δ –0.4 (Me), 22.6 (CMe₃), 31.7 (CMe₃); ²⁹Si NMR (THF-*d*₈): δ 10.0, 17.0 (skeletal Si atoms). ¹H NMR (toluene-*d*₈): δ 0.55 (s, 12H, 4 Me), 1.40 (s, 72H, 8CMe₃); ¹³C NMR (toluene-*d*₈): δ –0.5 (Me), 22.4 (CMe₃), 31.4 (CMe₃); ²⁹Si NMR (toluene-*d*₈): δ 11.8, 18.4 (skeletal Si atoms).

3.9. Synthesis of trans-3,4-dimethyl-1,2,3,4-tetrakis(di-tert-butylmethylsilyl)- Δ -1,2,3,4-disiladigermetene (**9**)

Excess Me₂SO₄ (1.59 mmol) was added by vacuum transfer to the solution of $7^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$ (311 mg, 0.26 mmol) in hexane (2 ml). The color of the reaction mixture quickly changed from dark green to orange. After evaporation of solvent and excess Me₂SO₄, the residue was recrystallized from hexane to afford **9** as orange crystals (213 mg, 95%). M.p. 175–177 °C; ¹H NMR (C₆D₆): δ 0.33 (s, 6H, 2 Me), 0.38 (s, 6H, 2 Me), 1.08 (s, 6H, 2 Me, GeMe), 1.20 (s, 18H, 2CMe₃), 1.21 (s, 18H, 2CMe₃), 1.22 (s, 18H, 2CMe₃), 1.23 (s, 18H, 2CMe₃); ¹³C NMR (C₆D₆): δ –5.0 (Me), –4.0 (Me), 5.5 (Me, GeMe), 21.4 (CMe₃), 21.6 (CMe₃), 22.2 (CMe₃), 22.4 (CMe₃), 29.9 (CMe₃), 30.28 (CMe₃), 30.30 (CMe₃), 30.5 (CMe₃); ²⁹Si NMR (C₆D₆): δ 19.0, 23.0, 167.6 (Si=Si); UV–Vis (hexane) λ_{max} /nm (ϵ) 337 (820), 388 (1160), 441 (2890). Anal. Calc. for C₃₈H₉₀Ge₂Si₆: C, 53.02; H, 10.54. Found: C, 53.33; H, 10.28%.

3.10. Crystal structure analyses of the compounds $2^- \cdot [\text{Li}^+(\text{thf})]$, $8^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$ and **9**

The single crystals of compounds $2^- \cdot [\text{Li}^+(\text{thf})]$, $8^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$ and **9** for X-ray diffraction study were grown from the saturated hexane solutions. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo-K α radiation ($\lambda = 0.71070$ Å). The structures were solved by the direct method, using SIR-92 program [29], and refined by the full-matrix least-squares method by SHELXL-97 program [30]. The crystal data and experimental parameters for the X-ray analysis of $2^- \cdot [\text{Li}^+(\text{thf})]$, $8^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$ and **9** are listed in Table 1. Crystallographic data of $2^- \cdot [\text{Li}^+(\text{thf})]$, $8^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$ and **9** have been deposited with the Cambridge Crystallographic Data Centre.

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Appendix A. Supplementary material

CCDC 288755, 238469 and 623571 contain the supplementary crystallographic data for $2^- \cdot [\text{Li}^+(\text{thf})]$, $8^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$ and **9**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be

Table 1

Crystallographic data and experimental parameters for the crystal structure analysis of $2^- \cdot [\text{Li}^+(\text{thf})]$, $8^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$ and **9**

Compound	$2^- \cdot [\text{Li}^+(\text{thf})]$	$8^{2-} \cdot 2[\text{K}^+(\text{thf})_2]$	9
Empirical formula	$\text{C}_{42}\text{H}_{84}\text{GeLiOSi}_5$	$\text{C}_{52}\text{H}_{116}\text{K}_2\text{O}_4\text{Si}_8$	$\text{C}_{38}\text{H}_{90}\text{Ge}_2\text{Si}_6$
Formula mass (g mol^{-1})	825.07	1108.37	860.83
Collection temperature (K)	120	120	120
λ (Mo K α) (\AA)	0.71070	0.71070	0.71070
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$
Unit cell parameters			
a (\AA)	13.8930(2)	13.0830(7)	52.7310(12)
b (\AA)	32.5110(8)	13.3180(4)	12.5420(3)
c (\AA)	11.7920(4)	22.2070(10)	36.0270(10)
α ($^\circ$)	90	89.659(3)	90
β ($^\circ$)	110.6800(10)	88.870(2)	120.659(2)
γ ($^\circ$)	90	61.283(3)	90
V (\AA^3)	4983.0(2)	3392.7(3)	20496.0(9)
Z	4	2	16
D_{calc} (g cm^{-3})	1.100	1.085	1.116
μ (mm^{-1})	0.763	0.317	1.336
$F(000)$	1796	1220	7456
Crystal dimensions (mm)	$0.50 \times 0.10 \times 0.05$	$0.30 \times 0.30 \times 0.25$	$0.25 \times 0.20 \times 0.20$
θ Range ($^\circ$)	2.05–27.95	2.53–28.01	2.09–27.89
Index ranges	$-18 \leq h \leq 17, -42 \leq k \leq 0, 0 \leq l \leq 14$	$0 \leq h \leq 17, -14 \leq k \leq 16, -29 \leq l \leq 29$	$0 \leq h \leq 69, 0 \leq k \leq 16, -47 \leq l \leq 40$
Collected reflections	53097	31087	97713
Independent reflections	11029	14318	23077
R_{int}	0.043	0.0280	0.0600
Reflections used	11029	14318	23077
Parameters	452	596	830
S^a	1.021	1.018	1.015
Weight parameters a/b^b	0.0690/1.5463	0.0960/1.4696	0.0785/0.0000
R_1^c [$I > 2\sigma(I)$]	0.0387	0.0532	0.0508
wR_2^d (all data)	0.1102	0.1535	0.1391
Maximum/minimum residual electron density (e \AA^{-3})	0.454/−0.620	0.841/−0.446	0.695/−0.757

^a $S = \left\{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \right\}^{0.5}$ where n is the number of reflections and p is number of parameters.

^b $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2) / 3$.

^c $R_1 = \sum \|F_o| - |F_c| \| / \sum |F_o|$.

^d $wR_2 = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right\}^{0.5}$.

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