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Aromaticity

Aromaticity of Group 14 Organometallics: Experimental Aspects

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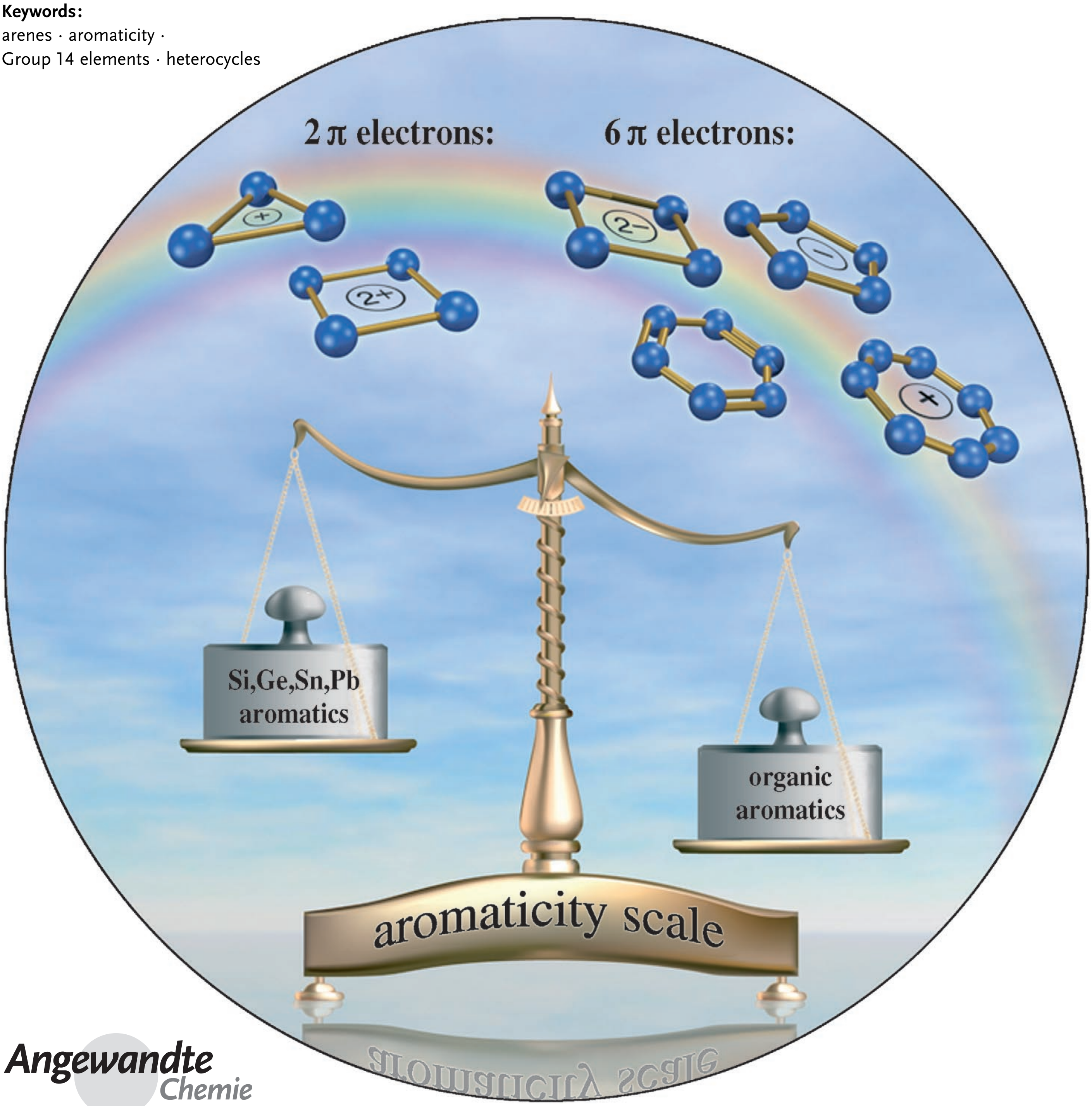

The long story of aromatic compounds has extended over almost two centuries, since the discovery by Faraday of "bicarburet of hydrogen", or C_6H_6, now called benzene. Since then, the chemistry of aromatic compounds has been developed extensively; this is reflected in the synthesis of novel classes of aromatic derivatives including charged species, nonclassical (Möbius, three-dimensional, homo-, metalla-) aromatics, and fullerenes. The theory of aromaticity has also undergone a spectacular evolution since the first definition of aromaticity by Hückel; the classification of aromaticity now requires the consideration of versatile criteria: energetic, structural, magnetic, among others. In this Review, we discuss the current state of affairs in the chemistry of aromatic compounds of the heavier Group 14 elements, the latest experimental achievements, as well as future prospects in the field.

From the Contents

1. Introduction

Aromatic compounds have been known for more than 180 years, ever since the discovery by Faraday in 1825 of the first aromatic hydrocarbon, benzene,[1] whose remarkable cyclic structure with alternating single and double bonds was suggested by Kekulé in 1866.[2] A vast number of aromatic compounds have been synthesized and reported in the scientific literature, growing exponentially since then from year to year: A literature search generated an enormous number of references directly related to the topic of aromaticity and aromatic compounds, totaling more than 300000 entries. However, the theory of aromaticity lagged behind the rapidly progressing experimental achievements, and not much was known about the structure and bonding of aromatic compounds until the development of molecular orbital (MO) theory. Even now, the seemingly simple question, "How can one define aromaticity, and to what extent is such a definition of aromaticity valid?" is, in fact, not easy to answer. A general simple textbook definition of aromatic compounds, derived from the fundamental Hückel MO theory, states: "Planar monocyclic completely conjugated hydrocarbons will be aromatic when the ring contains $(4n+2)$ π electrons."[3] Such a statement, better known as Hückel's rule (1931),[4] served for a long time as the principal criterion for the classification of organic/inorganic derivatives as aromatic compounds.

However, the groundbreaking advances in experimental chemistry associated with the synthesis of new classes of compounds that did not satisfy all requirements of Hückel's rule (for example, fullerenes, *trans* annulenes, Möbius aromatics, which are not planar), but nonetheless featured aromatic properties (nonclassical aromatics), certainly required the development of a more unified and common approach to the definition of aromaticity in its most general sense. Certainly, simple electron counting is too simplified an approach for the recognition of true aromaticity, a phenomenon that is by far more complicated and versatile. Consequently, the theory of aromaticity underwent a significant evolution (particularly in the last two decades), primarily regarding the basic criteria on which the compounds could be assigned to the class of aromatics (or non-aromatics). Although various criteria were discussed as useful tools for aromaticity evaluation, only three were recognized to be of fundamental importance: energetic, structural, and magnetic.[5]

The energetic criterion of aromaticity, based on the quantum chemical calculation of stabilization that is gained by the cyclic electron delocalization, the so-called resonance energy (RE), plays a major role in estimating the degree of aromaticity. The most commonly used estimate of RE is the aromatic stabilization energy (ASE) calculated by employing either isodesmic or homodesmotic reactions.

The structural criterion of aromaticity deals with the geometry of the molecule: Planarity and carbon–carbon bond equalization are considered as the default prerequisites necessary for the optimum overlap of the p_π orbitals. Except for the computational estimates, such a geometric manifestation of aromaticity could be visualized by means of physicochemical methods, principally by X-ray crystallography.

The magnetic criterion of aromaticity is based on the phenomenon of the diamagnetic ring current caused by the circulation of the π electrons and exaltation of the diamagnetic susceptibility (Λ). This property can also be theoretically estimated by quantum chemical calculations, whereas the experimental assessment of aromaticity can be achieved by NMR spectroscopic measurements. Namely, deshielding of the nuclei lying in the plane of the aromatic ring and shielding of the nuclei lying inside the anisotropy cone above or below the aromatic ring are considered as a direct evidence for

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induced ring current effects and, consequently, aromaticity of the compound. Such tendencies in the chemical shift changes can be quantified on the basis of quantum chemical calculations of the chemical shift at the center of the aromatic ring, the so-called nucleus independent chemical shift (NICS),[6] which can be calculated directly at the center of the ring mean plane [NICS(0)], or at any other distance from this center [for example, at 1 Å above this center, NICS(1)]. Typically, the classical aromatic compounds show negative NICS values (benzene: NICS(1) = −10.6), whereas antiaromatic species exhibit positive values (cyclobutadiene: NICS(1) = +12.7), and non-aromatic compounds have values near zero.[7]

Usually, the principal energetic criterion of aromaticity correlates well with the structural and magnetic criteria; however, in a number of cases compounds that would be classified as aromatic according to two of the fundamental aspects (energetic and magnetic) do not fulfill the structural requirements (bond equalization, planarity) of aromaticity. Such a conflicting situation clearly reflects the necessity for a more sophisticated classification of aromatic compounds.

The striking progress in the development of the theory of aromaticity in recent years has been well-documented in a number of excellent reviews and monographs published in the past two decades,[8] of which the monograph by Minkin et al.[8b] and the two thematic issues of *Chemical Reviews*, devoted to the problems of aromaticity (2001)[8c] and π and σ delocalization (2005),[8d] are of particular importance. All-metal aromatics have recently been reviewed.[8e–g] Many aspects of the modern chemistry of aromatic compounds (homoaromaticity, metalloaromaticity, spherical and three-dimensional aromaticity, Möbius aromaticity, structural and magnetic aspects of aromaticity, antiaromaticity, etc.) have been comprehensively covered.

Thus, the aim of this review is not to reiterate the essentials of the theory of aromaticity; instead, we present a critical viewpoint of synthetic chemists to this problem: how the novel aromatic compounds based on the heavier elements of Group 14 can be synthesized, how the degree of their aromaticity (or non-aromaticity) can be estimated, and how such novel members of the aromatic compounds family can be utilized in organometallic chemistry. It should be noted that the field of aromatic compounds of heavier Group 14 elements (Si, Ge, Sn, Pb) is still rather "uncultivated", leaving most of the synthetic and mechanistic problems still to be solved.

The synthesis of the sila-, germa-, and stanna-aromatic compounds is a nontrivial task because the classical methods widely utilized in organic chemistry for the preparation of aromatic compounds appear to not be applicable for the synthesis of the heavy congeners of organic aromatics, thus requiring the development of novel synthetic approaches. One can understand such striking synthetic difficulties in the chemistry of heavier Group 14 element aromatic compounds when taking into account the fundamental differences between carbon and its heavier neighbors (Si, Ge, Sn, Pb): electronegativity, size, and polarizability. Such a sharp distinction, together with the well-known tendency for the heavier main-group elements to be more and more reluctant to undergo s,p-hybridization owing to the progressively increasing difference between the size and energy of the s and p orbitals, is the reason for the important problems of thermodynamic stabilization of the heavy aromatics. Moreover, even once synthesized, such species manifest a greatly enhanced (compared with organic aromatics) reactivity; therefore, kinetic stabilization by bulky protective substituents is a necessary attribute of their successful synthesis.

The most comprehensive theoretical insight into the problem of the aromaticity of Group 14 elements was discussed in detail in a series of reviews by Apeloig,[9] whereas the experimental achievements in the chemistry of stable heavy aromatics were recently reviewed by Sekiguchi, Lee, et al.[10] and by Tokitoh.[11] In this Review, which by no means is intended to be comprehensive, we focus on the latest developments in the field of stable aromatics of Group 14 elements with particular emphasis on charged species with two and six π electrons, whose chemistry was recently developed in our research group. The neutral derivatives with six π electrons (heavy benzene and its homologues) are also briefly discussed in the framework of the review.

2. Species with Two π Electrons

Among the most fundamental aromatic species with two π electrons, the derivatives of singly charged cyclopropenylium ion $[R_3C_3]^+$ and doubly charged cyclobutadiene dication $[R_4C_4]^{2+}$ types should first be noted. The structures and

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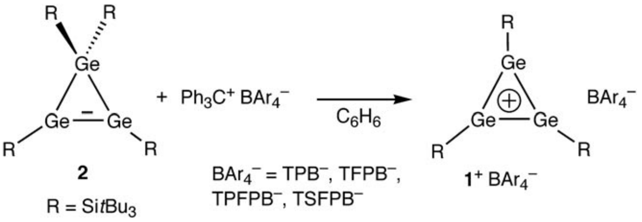
stabilities of these two classes of delocalized cyclic systems are strikingly different: A number of stable $[R_3C_3]^+$-type compounds have been synthesized since the pioneering work of Breslow,[12] whereas no isolable $[R_4C_4]^{2+}$ derivatives have been reported to date. Below, we briefly review the current state of affairs in the field of heavy analogues of the cationic species with two π electrons of the type $[R_3E_3]^+$ and $[R_4E_4]^{2+}$ (E = Si, Ge, Sn, Pb).

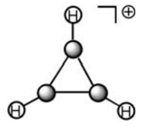
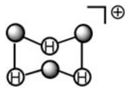
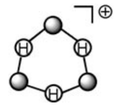
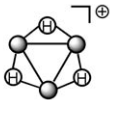


Scheme 1. Synthesis of the cyclotrigermenylium derivatives $1^+BAr_4^-$.

2.1. Heavy Analogues of the Cyclopropenylium Ion

The synthesis of the Si and Ge versions of the cyclopropenylium ion was preceded by calculations by Schleyer and co-workers, who predicted that the classical planar D_{3h} cyclopropenylium ion is favored over the nonplanar triply H-bridged C_{3v} isomeric structure only for $[Si_3H_3]^+$ ion by 23.7 kcal mol⁻¹ at the B3LYP/6-311++G(2d,2p) level, whereas for all $[Ge_3H_3]^+$, $[Sn_3H_3]^+$, and $[Pb_3H_3]^+$ derivatives the planar D_{3h} conformation was highly destabilized in favor of the bridged C_{3v} conformer by 17.4, 32.4, and 63.3 kcal mol⁻¹, respectively, at the B3LYP/TZ2P+ level (Table 1).[13]

Table 1: Stability of the $[E_3H_3]^+$ isomeric structures (relative energies are given in kcal mol⁻¹, number of imaginary frequences in parentheses).

	 D_{3h}	 C_{3v}	 D_{3h}	 D_{3h}
C	0.0 (0)	–	–	194.8 (3)
Si	0.0 (0)	23.7 (0)	55.6 (3)	53.5 (3)
Ge	0.0 (0)	−17.4 (0)	5.5 (3)	–
Sn	0.0 (1)	−32.4 (0)	−15.7 (3)	–
Pb	0.0 (3)	−63.3 (0)	−8.1 (3)	–

A subsequent ab initio MP2/6-31G* study by the same authors elaborated that the planar D_{3h} form of $[Si_3H_3]^+$ represents, indeed, a global minimum on the potential energy surface (PES), favored by 42.1 kcal mol⁻¹ over the triply H-bridged C_{3v} conformer.[14] However, the degree of RE and ASE values of the aromatic D_{3h} form of $[Si_3H_3]^+$ with two π electrons was estimated to be only half that of the parent cyclopropenylium ion, $[C_3H_3]^+$.[14]

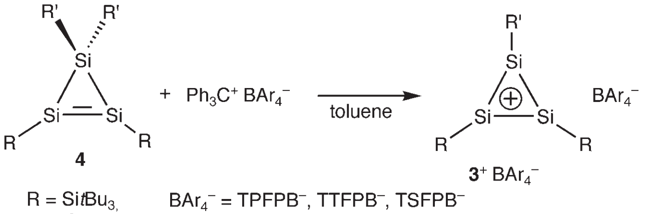
However, in marked contrast to such theoretical expectations, the very first heavy analogue of the cyclopropenylium ion with two π electrons, cyclotrigermenylium tetraphenylborate $\mathbf{1}^+TPB^-$, which was prepared by the oxidative cleavage of the exocyclic Ge–Si bond of the starting cyclotrigermene **2** by trityl tetraphenylborate in benzene, showed a perfectly planar structure, as deduced by crystallographic analysis (Scheme 1).[15] Consequently, all three Si atoms of the silyl substituents are nearly coplanar with the $\{Ge_3\}$ ring, and the geometry at all three Ge atoms is almost planar with the sum of the bond angles around them ranging from 359.7(2) to 359.9(2)°. The shape of the $\{Ge_3\}$ ring is best described as a nearly equilateral triangle with internal Ge-Ge-Ge bond angles of 60° (average value), and the skeletal Ge–Ge bond lengths are right between those of the Ge–Ge double (2.239(4) Å) and single bonds (2.522(4) Å) of precursor **2**: 2.321(4)–2.326(4) Å. This fact was interpreted as direct evidence for the even delocalization of the positive charge over the three skeletal Ge atoms, producing a planar two-π-electron aromatic structure similar to that of the cyclopropenylium ion.[15a] The separations from the cationic Ge centers and the nearest atoms of the BPh_4^- counterion were large enough to rule out the possibility of any cation–anion interactions, implying that $\mathbf{1}^+$ is a truly "free" cation in the crystalline form.

The striking discrepancy between the calculation (nonplanar H-bridged C_{3v} structure)[13] and experiment (planar aromatic D_{3h} structure)[15a] is evidently due to the different substitution pattern: small and easily mobile H atoms on the calculated models versus very bulky tBu_3Si groups in the real compound, which are reluctant to move and whose migratory and bridging aptitudes are almost negligible.

Except for the important kinetic protection of the reactive molecule, the electropositive tBu_3Si groups play another key role as the "extinguisher" of the positive charge on the highly electrophilic Ge atoms, thus greatly contributing to the overall thermodynamic stabilization of the compound. This situation was manifested in the appreciable low-field shift of the ^{29}Si NMR resonances of the Si substituents ($\delta = 64.0$ ppm in CD_2Cl_2) and supported by the HF/6-31G* calculations: The Mulliken charge of the skeletal Ge atoms was −0.07, whereas that of the substituent Si atoms was +0.64.[16b,c]

With the same reaction procedure, cyclotrigermenylium ion $\mathbf{1}^+$ was prepared with a variety of other counterions (see Scheme 1).[16] Such derivatives appeared to be significantly more stable in solution than the original cyclotrigermenylium ion $\mathbf{1}^+$ with the BPh_4^- counterion, which opened the possibility of studying the solution structure of $\mathbf{1}^+$. Interestingly, the cyclotrigermenylium ion $\mathbf{1}^+$ remained a free ion in the liquid phase as well, as clearly demonstrated by its NMR spectra, which were essentially independent of both counterion (TFPB, TPFPB, TSFPB) and solvent. The specta were almost the same in CD_2Cl_2, $CDCl_3$, [D$_8$]toluene, and Et_2O: $\delta = 64.0$, 64.2, 64.4, and 64.5 ppm (^{29}Si NMR resonances), respectively.[16]

In accord with theoretical predictions,[14] the full Si version of the cyclopropenylium ion, cyclotrisilenylium ion $\mathbf{3}^+$ with voluminous tBu_2MeSi and tBu_3Si groups, is remarkably planar, quite similar to the above case of the cyclotrigermenylium ion $\mathbf{1}^+$. The $\{Si_3\}^+$ ion was prepared by the same synthetic route as the $\{Ge_3\}^+$ ion,[15a] namely, by the one-electron oxidation of cyclotrisilene **4** with $Ph_3C^+BAr_4^-$ (Scheme 2).[17]



Scheme 2. Synthesis of the cyclotrisilenylium derivatives $\mathbf{3}^+BAr_4^-$.

The absence of any notable coordination of external nucleophiles (either counterion or solvent) to $\mathbf{3}^+$ in both crystalline form and in solution was demonstrated by X-ray crystallographic analysis and NMR spectroscopy, with the latter revealing the independence of the chemical shifts of $\mathbf{3}^+$ from both counterion (TPFPB, TSFPB, TTFPB) and solvent (benzene, toluene, chlorobenzene). The manifestation of the positive charges developed on the skeletal Si atoms was clearly seen in their low-field shifted resonances: $\delta = 284.6$ and 288.1 ppm, that is, in the highly deshielded region typical for noncoordinated silyl cations (calculated value for the model $[(H_3Si)_3Si]^+$ was $\delta = 300.9$ ppm). The cyclopropenylium-type delocalization of the two π electrons over the entire three-membered $\{Si_3\}$ ring was also confirmed by the particular geometrical features of $\mathbf{3}^+$, namely, its equilateral triangle shape with internal Si-Si-Si bond angles of nearly 60° (average) and endocyclic Si–Si bond lengths of 2.217(3) Å (average), which are intermediate between those of the Si–Si double (2.1612(8) Å) and Si–Si single bonds (av 2.3728(8) Å) of the precursor **4** (Figure 1).[17]

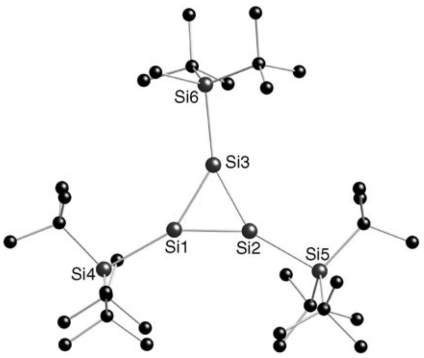
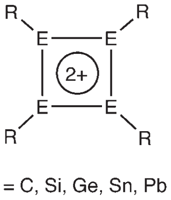


Figure 1. Crystal structure of $\mathbf{3}^+$ (Crystal Maker view; $TSFPB^-$, crystallization molecules, and hydrogen atoms are not shown).

2.2. Heavy Analogues of the Cyclobutadiene Dication

The first organic cyclobutadiene dication was observed spectroscopically by ionization of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene in SbF_5/SO_2 solution at −75 °C by Olah et al. (Scheme 3; E = C, R = Me).[18] The same research group subsequently reported the generation of tetraphenyl-,[19] 1,2-difluoro-3,4-diphenyl-,[20] and 1,2-diphenylcyclobutadiene[20] dications under conditions for stable ions. However, the synthesis of compounds of this type that were stable at room temperature was not achieved; therefore, real structural information is not available for the discussion of the bonding nature of such intriguing species.



Scheme 3. Derivatives of the cyclobutadiene dication.

According to ab initio calculations of the tetramethylcyclobutadiene dication (Scheme 3; E = C, R = Me), the planar D_{4h} structure represents a transition state for the inversion of the folded D_{2d} structure (folding angle 39°) with an inversion barrier of about 7.0 kcal mol^{-1}.[21a] The planar D_{4h} structure is destabilized compared with the puckered D_{2d} structure because of the unfavorable 1,3-antibonding interactions in the former.[21] Moreover, the experimental ^{13}C NMR chemical shifts of $[(MeC)_4]^+$ are in better agreement with those calculated for the D_{2d} rather than the D_{4h} structure.[20,21a,22,23] Consequently, it was concluded that in small doubly charged four-membered ring systems, such as the cyclobutadiene dication and cyclobutadiene dianion, the Coulomb repulsive interaction between the two charges becomes more important than the advantage gained by the π delocalization and therefore may overcome the effects of Hückel aromatic stabilization.[21a,24,25] The latest computations by Schleyer et al. corroborate well with the previous conclusions, confirming the preference of the folded structure for the cyclobutadiene dication and its alkyl derivatives (Scheme 3; E = C, R = H, alkyl), which were nevertheless aromatic according to NICS(0) calculations: −9.0 (unsubstituted cyclobutadiene dication, D_{2d} minimum structure), −17.2 (tetra-*tert*-butylcyclobutadiene dication, C_2 minimum structure).[26]

For the heavy analogues of the cyclobutadiene dication, no experimental information on the stable derivatives of the *cyclo*-$[E_4R_4]^{2+}$ type (E = Si, Ge, Sn, Pb) is available to date (Scheme 3; E = Si–Pb). Calculations on the parent tetrasilacyclobutadiene dication (Scheme 3; E = Si, R = H) showed that the most stable isomer on the $[Si_4H_4]^{2+}$ PES has a slightly puckered (9.0°) D_{2d} structure, similar to the case of its carbon counterpart, the cyclobutadiene dication (Scheme 3; E = C, R = H), although the latter is considerably more puckered (32.5°) than the former.[27,28] However, despite the nonplanar structure, all Si–Si bonds in the tetrasilacyclobutadiene dication are equivalent (2.268 Å), indicating electron delocalization and, consequently, two-π-electron aromaticity.[27,28] Considering the perspectives for the experimental synthesis of a tetrasilacyclobutadiene dication (and its heavier analogues), one can imagine either two-electron oxidation of a tetrasilacyclobutadiene or oxidative dehalogenation of a dihalotetrasilacyclobutene as reasonable preparation routes. However, the applicability of these synthetic strategies is limited owing to the lack of availability of the materials (especially tetrasilacyclobutadiene), which also require the implementation of the special experimental methods.

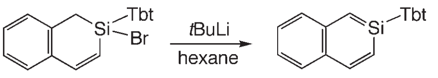
3. Species with Six π Electrons

Species with six π electrons can be divided into two main classes: neutral (benzene and its homologues) and charged [anionic (cyclopentadienide ion, cyclobutadiene dianion) and cationic (cycloheptatrienylium (tropylium) ion, cyclooctatetraene dication)]. The stability of the neutral aromatic compounds is commonly associated with their chemical inertness, whereas the charged aromatic species, even being thermodynamically stabilized by π delocalization, retain their intrinsic high reactivity. The methods for the generation of the charged aromatic derivatives are also very different from those of the classical neutral aromatics. In this review, we deal with the recent experimental achievements in the field of stable heavy analogues of benzene, the cyclopentadienide ion, cyclobutadiene dianion, and tropylium ion.[29]

3.1. Heavy Analogues of Benzene and Its Homologues

The chemistry of the neutral heavy aromatics, that is, heavy analogues of benzene, naphthalene, anthracene, and phenanthrene, was recently comprehensively reviewed by Tokitoh;[11] therefore, we will just briefly overview the most essential advances in this research area. The silabenzene, as well as its heavier analogues, has been a long-standing synthetic attraction for many research groups,[30] yet the isolation of the first stable sila-aromatics was accomplished only a decade ago. Earlier, the closest approach to the synthesis of a silabenzene derivative was demonstrated by Märkl and Schlosser, who reported the generation and NMR observation of the 1,4-di-*tert*-butyl-2,6-bis(trimethylsilyl)-1-silabenzene.[31] However, the silabenzene generated by this method was stable only at temperatures below −100 °C; moreover, it was evidently coordinated by the nucleophilic solvent (THF), as shown by its high-field ^{29}Si NMR resonance at $\delta = 26.8$ ppm.

The first sila-aromatics shown to be stable at room temperature, 2-silanaphthalene **5**, was prepared by Tokitoh et al. in 1997.[32] Compound **5** was synthesized by the dehydrohalogenative reduction of the bromosilane precursor with *t*BuLi in hexane, utilizing as a crucial factor the kinetic stabilization of the highly reactive molecule by a very bulky substituent Tbt (Scheme 4).



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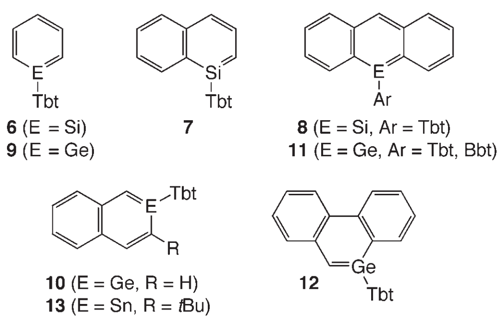
Scheme 4. Synthesis of the 2-silanaphthalene derivative **5**.

Applying the same synthetic strategy and the protective power of Tbt and Bbt groups, the same authors prepared a variety of other stable sila-aromatics, including silabenzene **6**,[33] 1-silanaphthalene **7**,[34] and 9-sila-anthracene **8**[35] (Scheme 5). Within Group 14, the problem of kinetic stabilization of aromatics becomes increasingly serious for the heavier analogues, reflecting a general tendency of reluctance of the heavier elements (particularly Sn and Pb) toward s,p hybridization and multiple-bond formation. Thus, whereas several germa-aromatic derivatives have been synthesized as stable compounds, including germabenzene **9**,[36] 2-germanaphthalene **10**,[37] 9-germa-anthracene **11**, and 9-germaphenanthrene **12**,[38] the number of corresponding stable stanna-aromatic compounds is limited to only one example of the 2-stannanaphthalene derivative **13**[39] (Scheme 5). The preparation of a stable stannabenzene derivative has not yet been accomplished, whereas the attempted synthesis of 9-stannaphenanthrene resulted in the formation of its head-to-tail dimer, although the intermediacy of 9-stannaphenanthrene at −78 °C was confirmed by trapping reactions.[40] No representatives of stable aromatic compounds incorporating Pb atoms in the ring have been reported thus far.



Scheme 5. Stable heavy analogues of benzene, 2-naphthalene, anthracene, and phenanthrene.

The most fundamental question of sila/germabenzenes and their analogues is their aromaticity compared with that of their carbon counterparts: Is this a real, observable, and measurable phenomenon? The requirements of the structural aromaticity criterion are satisfied for the sila-, germa-, and stanna-aromatic compounds discussed above. All of them possess almost planar six-membered rings, the geometry around the Si, Ge, and Sn atoms is trigonal-planar, and the cyclic C−C bond lengths are nearly identical (except for the 2-sila- and 2-germanaphthalene derivatives **5** and **10**, for which a small C−C bond alternation was observed, similar to the case of the parent naphthalene; Scheme 5). The calculated geometries for these compounds are in reasonable agreement with the experimental observations. The skeletal atoms are characteristically deshielded, indicating the sp^2 hybridization of these atoms, as was observed in their ^{29}Si NMR [$\delta =$ 93.6 ppm (**6**),[33a] $\delta = 91.7$ ppm (**7**),[34a] $\delta = 87.3$ ppm (**5**),[32a] $\delta = 87.2$ ppm (**8**)[35]] and ^{119}Sn NMR spectra [$\delta = 264$ ppm (**13**)][39] (Scheme 5). Consequently, the ^{13}C NMR resonances of the ring carbon atoms were observed in the region diagnostic of aromatic compounds. The ring protons were also characteristically deshielded, indicating the presence of a diamagnetic ring current, which was taken as another manifestation of aromaticity.[11]

Accordingly, the NICS(1) calculations for model (unsubstituted) compounds provided negative values for heavy aromatics (Table 2).[11] In view of the magnetic criterion, such negative NICS(1) values directly point to the presence of a diamagnetic ring current, which was also demonstrated by the diamagnetic susceptibility exaltation calculations, which provided large negative Λ values for germabenzene and 2-germanaphthalene (−19.5 and −27.9), comparable with those for the parent benzene and naphthalene (−22.7 and −30.4).[11b] The values of ASE for sila- and germabenzene

Table 2: NICS(1) values calculated for the model unsubstituted heavy aromatic compounds.[a]

Arene	NICS(1)
silabenzene	−9.1
germabenzene	−9.0
1-silanaphthalene (Si-containing ring)	−9.1
2-silanaphthalene (Si-containing ring)	−9.4
2-germanaphthalene (Ge-containing ring)	−9.3
9-sila-anthracene (Si-containing ring)	−11.0

[a] Values for the parent organic derivatives: −11.1 (benzene), −11.5 (naphthalene), −13.7 (anthracene).

were estimated to be almost identical to those of the parent benzene: 34.0 and 33.8 kcal mol^{-1} versus 34.1 kcal mol^{-1}.[11a] Finally, from the viewpoint of the most fundamental criteria of aromaticity, the authors reasonably concluded that benzene, naphthalene, anthracene, and phenanthrene analogues of the heavier Group 14 elements (Si, Ge, Sn) are to a large extent aromatic.[11]

Expectedly, the heavy aromatic compounds feature red shifts in their electronic spectra compared with those of organic congeners, reflecting the decrease in the HOMO–LUMO energy gaps: 331 (**6**) and 326 nm (**9**) versus 256 nm (benzene); 378 (**7**), 387 (**5**), and 386 nm (**10**) versus 312 nm (naphthalene); 503 (**8**) and 520 nm (**11**) versus 375 nm (anthracene; Scheme 5).[11,38]

3.2. Heavy Analogues of the Cyclopentadienide Ion

The cyclopentadienide ion $[C_5H_5]^-$, which obeys Hückel's $(4n+2)$-π-electron rule, should be classified as an aromatic system, and is indeed aromatic.[5] The deprotonation of cyclopentadiene, which is known to be one of the most acidic hydrocarbons with $pK_a = 16.0$,[41] is highly thermodynamically favorable for the production of an aromatic system with all six π electrons occupying bonding orbitals (Figure 2). All spectral (IR, Raman, NMR) and crystal structure (X-ray) data indicate a planar D_{5h} geometry (with full delocalization) of the cyclopentadienide ion, for which the degree of aromaticity is smaller but still similar to that of benzene: about 80–90 % according to an estimation based on the magnetic criteria of aromaticity.[42] The cyclopentadienide ion is one of the longest-known aromatic compounds, and was synthesized for the first time by Thiele in 1901 by the reduction of cyclopentadiene with potassium in benzene.[43] Now, the number of experimental procedures for preparing derivatives of the cyclopentadienide ion (mainly, alkali-metal salts) is vast, as well as the number of their synthetic applications in main-group and, particularly, transition-metal chemistry.

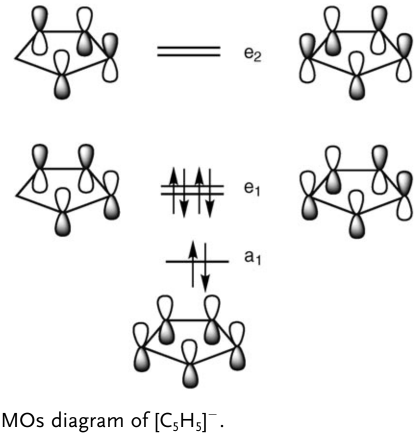
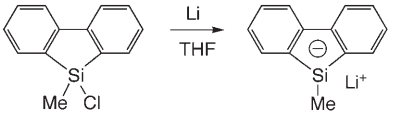


Figure 2. π-MOs diagram of $[C_5H_5]^-$.

The analogues of the cyclopentadienide ion, incorporating one heavy element of Group 14 (Si–Sn), have been extensively studied both experimentally and theoretically during the last two decades.[44] The first silacyclopentadienide ion was synthesized in 1958 by Gilman and Gorsich by the reduction of 1-chloro-1-methylsilafluorene with lithium (Scheme 6).[45]

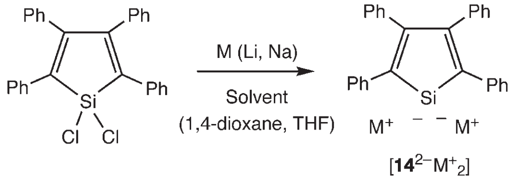


Scheme 6. Generation of a silacyclopentadienide derivative.

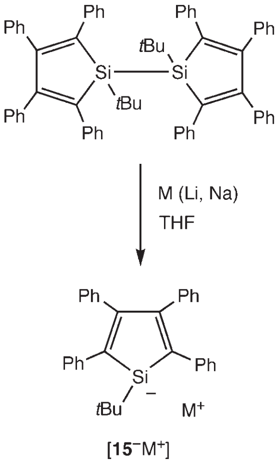
Since then, the chemistry of such silacyclopentadienide ions (and their germa- and stanna- congeners) has been considerably developed experimentally;[46] however, the fundamental question of aromaticity of such anionic species, which formally satisfy the requirements of Hückel's rule, was almost unexplored until the early 1990s. Only two theoretical papers addressing this problem were published in the mid 1980s, leading, however, to contradictory conclusions. The first one, by Gordon et al., predicted a planar C_{2v} structure for the parent silacyclopentadienide ion $[Si_5H_5]^-$ possessing about 25 % of the aromaticity of $[C_5H_5]^-$; however, these calculations utilized the low HF/STO-2G level.[47] The higher-level HF/6-31G* calculations by Damewood revealed a pyramidal C_s conformation as a minimum structure for the $[Si_5H_5]^-$ ion, whereas the planar C_{2v} structure was a transition state for the pyramidal inversion at silicon.[48] On the basis of such geometry, Damewood concluded that the degree of aromaticity of the silacyclopentadienide ion is only about 3 % that of $[C_5H_5]^-$.[48]

The story of the silacyclopentadienide ion derivatives experienced a true renaissance in the 1990s, the starting point of which was a paper published by Joo et al., which reported the generation of the 1,1-disodio-2,3,4,5-tetraphenyl-1-silacyclopentadienediide ion [$\mathbf{14}^{2-}Na^+_2$] by the reduction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene with metallic sodium in dioxane (Scheme 7; M = Na, solvent = 1,4-dioxane).[49]

The next milestone contribution was made by Boudjouk and Hong, who synthesized [$\mathbf{15}^{-}M^+$] (M = Li, Na) by cleavage of the exocyclic Si–Si bond of bis(1-*tert*-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl) with either lithium or sodium (Scheme 8).[50] Based on the tendencies of the NMR chemical shift changes upon reduction (primarily, deshielding of the skeletal Si atoms), Boudjouk proposed a significant delocalization of the negative charge over the five-membered ring and, consequently, its aromaticity.[50] Reducing a 1,1-dichloro-



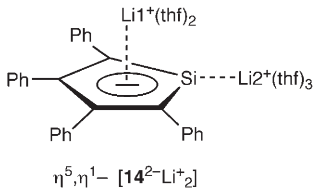
Scheme 7. Generation of [**14**$^{2-}$M$^+_2$].



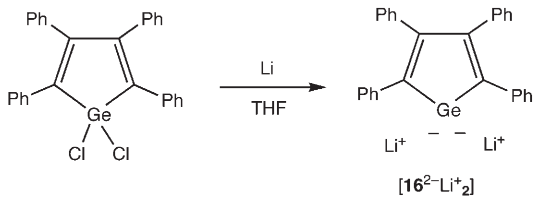
Scheme 8. Generation of [**15**$^-$M$^+$].

2,3,4,5-tetraphenyl-1-silacyclopentadiene with lithium upon sonication, Boudjouk and co-workers prepared [**14**$^{2-}$Li$^+_2$], whose aromaticity was manifested in its characteristic NMR spectral data: a large deshielding of the Si atom ($\Delta\delta = 61.7$ ppm) and shielding of the skeletal C atoms upon reduction (Scheme 7; M = Li, solvent = THF).[51] The same compound [**14**$^{2-}$Li$^+_2$] was later isolated and structurally characterized by West et al., who reported the essentially unfolded five-membered ring with an almost planar geometry around the Si atom and nearly equal C–C bond lengths (1.426–1.448 Å), implying cyclic aromatic π delocalization.[52]

The most unusual structural feature of this dianion was the mode of coordination of both Li ions: Whereas Li1 was η^5-coordinated to the five-membered ring (as would be expected for a delocalized system), Li2 was η^1-coordinated exclusively to the Si atom (Scheme 9; R = Ph). The accompanying calculations found two dilithio derivatives as the minimum structures on the PES. The first one closely corresponded to the experimental η^5-Li,η^1-Li structure, and the second one, with C_{2v} symmetry, featured both Li ions above and below the ring plane (η^5-Li,η^5-Li structure), representing an "inverse-sandwich" structure. The latter structure was more stable than the former by 21 kcal mol^{-1}, although the solvation and crystal-packing effects were not taken into consideration. The experimental realization of both above-mentioned η^5,η^1 and η^5,η^5 structures was achieved through the synthesis of the germanium compound [**16**$^{2-}$Li$^+_2$], prepared by reduction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopentadiene with lithium (Scheme 10).[53]

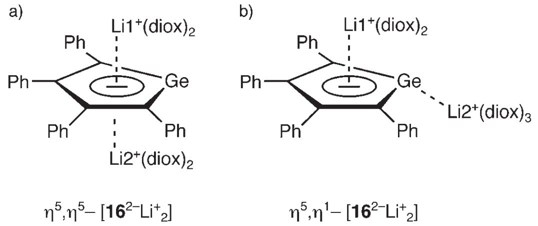


Scheme 9. Structure of [**14**$^{2-}$Li$^+_2$] in the solid state.



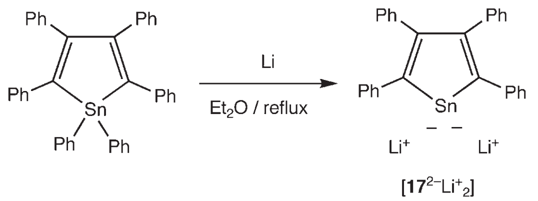
Scheme 10. Synthesis of [**16**$^{2-}$Li$^+_2$].

The dianionic derivative [**16**$^{2-}$Li$^+_2$] crystallizes in two structurally distinct forms, depending on the crystallization temperature. Crystallization from dioxane at −20 °C produced an "inverse-sandwich" η^5,η^5 structure of [**16**$^{2-}$Li$^+_2$] (Scheme 11 a) with the two Li ions situated above and below the five-membered ring. In contrast, crystallization at room temperature provided the η^5,η^1 structure of [**16**$^{2-}$Li$^+_2$] (Scheme 11 b), which closely resembles that of the above-discussed compounds [**14**$^{2-}$Li$^+_2$], the only difference between them being the geometry around the element center: pyramidal at the Ge atom in **16**$^{2-}$ [53] and nearly planar at the Si atom in **14**$^{2-}$.[52] The symmetrical η^5,η^5 structure of the model unsubstituted germacyclopentadienediide ion was calculated to be 25 kcal mol^{-1} more favorable than the η^5,η^1 structure, again similar to the above case of [**14**$^{2-}$Li$^+_2$]. Experimentally, in both the η^5,η^1 and η^5,η^5 structures of [**16**$^{2-}$Li$^+_2$] the skeletal C–C bonds are almost identical, which was also supported by calculations: This fact led the authors to a conclusion about the high degree of aromaticity of the compound, and indeed, an ASE of 13.0 kcal mol^{-1} for the model unsubstituted [GeC$_4$H$_4$]$^{2-}$ ion was calculated from the isodesmic reaction.[53] It should also be noted that the same conclusion about the cyclic π delocalization in [**16**$^{2-}$Li$^+_2$] was drawn earlier by Boudjouk and Hong on the basis of their ^{13}C NMR investigations.[54]



Scheme 11. Structures of [**16**$^{2-}$Li$^+_2$] in the solid state; diox = dioxane.

The compound [**17**$^{2-}$Li$^+_2$], the tin analogue of [**14**$^{2-}$Li$^+_2$] and [**16**$^{2-}$Li$^+_2$], was also recently prepared by Saito et al. by the reduction of either bis(1,2,3,4,5-pentaphenyl-1-stannacyclopentadienyl) or hexaphenyl-1-stannacyclopentadiene with lithium (Scheme 12).[55] Compound $[\mathbf{17}^{2-}\text{Li}^+_2]$ exists in a single structural modification of the η^5,η^5 type with nearly equivalent skeletal C–C bonds of 1.422(6)–1.446(6) Å and a planar five-membered ring, diagnostic of the delocalized aromatic nature of $[\mathbf{17}^{2-}\text{Li}^+_2]$.[55c] The supporting calculations on the actual compound $[\mathbf{17}^{2-}\text{Li}^+_2]$ revealed two minimum structures: a η^5,η^1 structure of C_1 symmetry and a η^5,η^5 structure of C_2 symmetry, the latter of which corresponds well with the experimental structure and is 20 kcal mol^{-1} more favorable than the former.



Scheme 12. Synthesis of $[\mathbf{17}^{2-}\text{Li}^+_2]$.

The delocalization of the negative charge over the entire ring was also demonstrated by the appreciable deshielding of the Sn atom upon reduction: $\Delta\delta = 251.3$ ppm (the same tendency was observed in the case of $[\mathbf{14}^{2-}\text{Li}^+_2]$).[55c] Most importantly, the ^{7}Li NMR resonance of $[\mathbf{17}^{2-}\text{Li}^+_2]$ was observed at high field ($\delta = -4.36$ ppm), typical for aromatic systems, which was also supported by the NICS(1) calculations, which provided a negative value of −5.96. The degree of aromaticity of $[\mathbf{17}^{2-}\text{Li}^+_2]$ should however be smaller than that of its silicon and germanium analogues $[\mathbf{14}^{2-}\text{Li}^+_2]$ and $[\mathbf{16}^{2-}\text{Li}^+_2]$.[55c]

After the pioneering work of Boudjouk, West, et al., some other interesting examples of anionic heterocyclic systems incorporating sila-, germa-, or stannacyclopentadiene fragments were described as possessing a greater or lesser degree of six-π-electron aromaticity on the basis of the specific structural features of the five-membered rings (planarity, cyclic C–C bond equalization, "inverse-sandwich" configuration). These examples include exclusively dianionic species (Table 3).[56–65]

In contrast, monoanions of the heavy cyclopentadienide derivatives are exclusively represented by the localized nonaromatic structures, which feature pyramidal geometries around the element centers, pronounced alternation of the cyclic C–C bonds in the five-membered rings, and specific η^1 coordination of the countercations to the elements (Table 4).[56,66–68] However, upon coordination of such monoanionic heavy cyclopentadienide ions to transition-metal fragments, a considerable π delocalization and aromatization of the five-membered rings is observed, which is manifested in a planarization at the heavy Group 14 element and equalization of the C–C bond lengths. Such a phenomenon was described for the first time by Tilley and co-workers, who prepared a variety of transition-metal complexes having either sila- or germacyclopentadienes as the cyclic polyene ligands.[69]

Table 3: Aromatic dianionic derivatives incorporating sila-, germa-, or stannacyclopentadiene fragments.

Compound	Ref.
dipotassio-2,3,4,5-tetramethyl-1-silacyclopentadienediide	[56]
dipotassio-2,3,4,5-tetramethyl-1-germacyclopentadienediide	[56b]
dilithio-3-*n*-butyl-2-phenyl-1-silaindenediide	[57]
disodio-3-*n*-butyl-2-phenyl-1-silaindenediide	[57]
dipotassio-1-silafluorenediide	[58, 59]
dilithio-2,3,4,5-tetraethyl-1-germacyclopentadienediide	[60]
(its related dianionic trimer)	([61])
dilithio-2,3-diphenyl-1-germaindenediide	[62]
disodio-2,3-diphenyl-1-germaindenediide	[62]
dipotassio-9-germafluorenediide	[63]
dilithio-3-*n*-butyl-2-phenyl-1-stannaindenediide	[64]
dipotassio-9-stannafluorenediide	[65]

Table 4: Non-aromatic anionic derivatives incorporating sila- and germacyclopentadiene fragments.

Compound	Ref.
1-lithio-1-methyl-1-silafluorenide	[66]
1,2-bis(1-lithio-3-*n*-butyl-2-phenyl-1-silaindenyl)ethane	[67]
lithio-1-tris(trimethylsilyl)silyl-2,3,4,5-tetramethyl-1-germacyclopentadienide	[56b, 68]
lithio-1-(2,4,6-trimethylphenyl)-2,3,4,5-tetramethyl-1-germacyclopentadienide	[56b]
sodio-1,2,3,4,5-pentamethyl-1-germacyclopentadienide	[56]
potassio-1-trimethylsilyl-2,3,4,5-tetramethyl-1-silacyclopentadienide	[56b]

The important experimental accomplishments in the synthesis of the heavy analogues of the cyclopentadienide ion revived a great deal of theoretical interest in the issue of aromaticity of these species.[70,71] The most considerable contribution to the problem has been made by Schleyer and co-workers in a series of papers published in the mid 1990s. Employing high-level computations, they systematically studied the analogues of cyclopentadienide ions $[C_4H_4EH]^-$ (E = C, Si, Ge, Sn, Pb) and cyclopentadienediide ions $[C_4H_4E]^{2-}$ (as well as their lithium derivatives) and found an appreciable aromaticity for these compounds.[70] Such a conclusion significantly disagreed with the earlier reported results of low-level calculations, which predicted a small,[47] or almost negligible,[48] degree of aromaticity for the silacyclopentadienide ion.

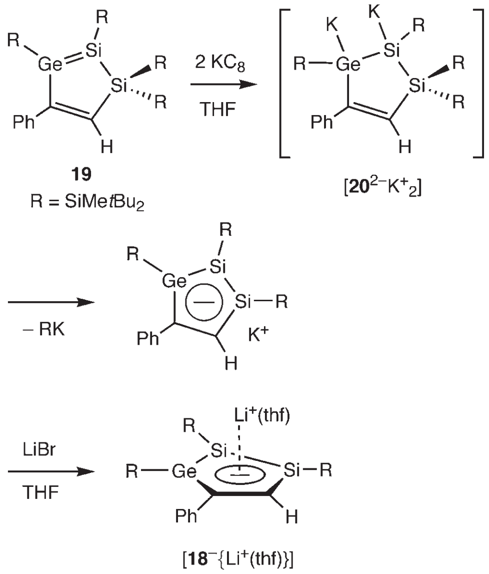
According to the work by Schleyer et al., the ASE and Λ values of $[C_4H_4SiH]^-$ were calculated to be about half the values for the parent cyclopentadienide ion $[C_5H_5]^-$.[70a] Moreover, the η^5 coordination of the Li$^+$ ion to the silacyclopentadienide ring significantly increases its aromaticity (compared with that of "naked" $[C_4H_4SiH]^-$), which was manifested in the planarization of the geometry at the Si atom, appreciable equalization of the cyclic C–C bonds, increase in the ASE of η^5-Li-silacyclopentadienide up to 80 % (compared with that for η^5-Li-cyclopentadienide), and increase in the Λ value of η^5-Li-silacyclopentadienide to as large as that for η^5-Li-cyclopentadienide (−14.1 ppm versus −14.5 ppm).[70b]

The geometric, energetic, and magnetic criteria all lead to the same conclusion: The η^5-Li-silacyclopentadienide is highly aromatic, even more than the silacyclopentadienide ion itself. Moreover, the dianion $[C_4H_4Si]^{2-}$ and its alkali-metal salts $C_4H_4SiLi_2$, $C_4H_4SiNa_2$, and $C_4H_4SiK_2$ were also found to be highly aromatic.[70c] Thus, all three derivatives are represented by the η^5,η^5 "inverse-sandwich" structures with the equalized C−C bond lengths that are diagnostic of strongly delocalized structures, and have markedly negative values of Λ, thus pointing to large aromatic ring currents which are responsible for shielding of the Li nucleus in $C_4H_4SiLi_2$ (calculated δ value of the ^{7}Li NMR resonance is $\delta = -7.7$ ppm).[70c]

The influence of the nature of the heavier Group 14 element on the degree of aromaticity of mono- and dianions was also systematically studied by Goldfuss and Schleyer.[70d] Thus, the aromaticity of C_s monoanions $[C_4H_4EH]^-$ (E = C, Si, Ge, Sn, Pb) notably decreases on going from C to Pb owing to increasing pyramidality at the element and increasing inversion barriers. Compared with pyramidal C_s geometries, the planar C_{2v} configurations were found to be significantly more aromatic; however, they were only transition structures for inversion. In contrast, the aromaticity of the dianions $[C_4H_4E]^{2-}$ and their dilithium derivatives $C_4H_4ELi_2$, for which no pyramidalization takes place, was remarkably constant for all compounds going down Group 14.[70d] The dilithium salts $C_4H_4ELi_2$ were the most aromatic among all calculated structures, even more than free dianions $[C_4H_4E]^{2-}$.

An particularly exciting analogue of the cyclopentadienide ion, the pentasilacyclopentadienide ion $[Si_5H_5]^-$, whose structure consists exclusively of heavier Group 14 elements, was computationally studied by Schleyer and co-workers.[25] Two nonplanar minimum structures of C_s and C_2 symmetry with equal energies were found on the PES, whereas the planar delocalized D_{5h} structure was 8.3 kcal mol^{-1} higher in energy. The value of ASE for C_s-symmetric $[Si_5H_5]^-$ was calculated from the isodesmic equation as 52.8 kcal mol^{-1}, which was much smaller than the 84.7 kcal mol^{-1} calculated for its carbon analogue $[C_5H_5]^-$, thus pointing to a significantly lower extent of aromaticity.[25] Nevertheless, this value was still much greater than that for the silacyclopentadienide ion $[C_4H_4SiH]^-$ (2.2 kcal mol^{-1}), which was calculated on the basis of an analogous isodesmic reaction.[48] However, experimentally such persilacyclopentadienide derivatives $[R_5Si_5]^-$, as well as their heavier analogues $[R_5E_5]^-$ (R = Ge, Sn, Pb), have never been realized and remain a very attractive target for organometallic chemists.

The closest approach to this problem was achieved by the recent accomplishment of Sekiguchi and co-workers, who reported the first analogue of the cyclopentadienide ion incorporating three heavy Group 14 elements in the ring: two Si atoms and one Ge atom.[72] This compound, [**18**$^-$Li$^+$(thf)], was prepared as bright-orange crystals in 34 % yield by the reduction of the most electronically perturbed metallacyclopentadiene **19**, which has a Si=Ge−C=C diene system,[73] with potassium graphite KC_8 and subsequent exchange of the countercation from K$^+$ to Li$^+$ by treatment with LiBr (Scheme 13).[72] The first step in the reaction is, presumably, the two-electron reduction of the Si−Ge double bond (the LUMO of **19** is largely localized on the Si=Ge π* orbital), followed by the β-elimination of tBu$_2$MeSiK. The driving force for the last step would be a release of the electrostatic repulsion between the two negative charges in [**20**$^{2-}$K$^+_2$] and formation of the six-π-electron system.



Scheme 13. Synthesis of [**18**$^-$Li$^+$(thf)].

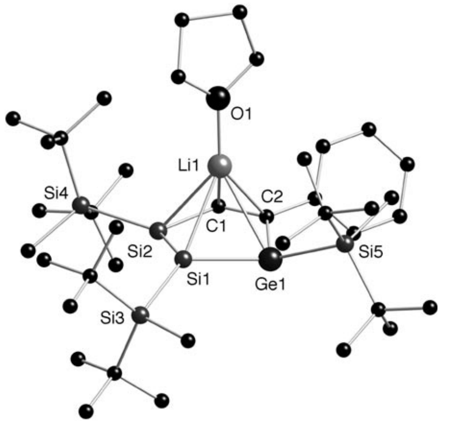


Figure 3. Crystal structure of [**18**$^-$Li$^+$(thf)] (Crystal Maker view; hydrogen atoms are not shown).

Consideration of the structural peculiarities of [**18**$^-$Li$^+$(thf)] definitely points to its delocalized structure (Figure 3). Because the skeletal atoms in **18**$^-$ are different (two C atoms, two Si atoms, and one Ge atom), the discussion in terms of the equalization of the bonds of the cylce is meaningless in such a case. Instead, one should take into account the tendencies in the changes of these skeletal bonds upon reduction. Indeed, all double bonds of the starting compound **19**[73] are elongated to form [**18**$^-$Li$^+$(thf)][72] (Ge1−Si1: 2.250(1) versus 2.322(1) Å; C1−C2: 1.343(5) versus 1.402(2) Å), whereas all single bonds of **1** are shortened (Ge1−C2: 1.972(3) versus 1.930(2) Å; Si1−Si2: 2.364(1) versus 2.240(1) Å; Si2−C1: 1.888(3) versus 1.827(2) Å;

Figure 4). Importantly, the lengths of all the skeletal bonds in **18**$^-$ are intermediate between those of typical single and double bonds. Moreover, the planarity of the {C_2Si_2Ge} five-membered ring of the starting **19** was almost unaffected by the reduction to form anionic **18**$^-$, as was demonstrated by a comparison of the sum of their interior bond angles: 539.9° (**19**)[73] and 536.3° (**18**$^-$).[72]

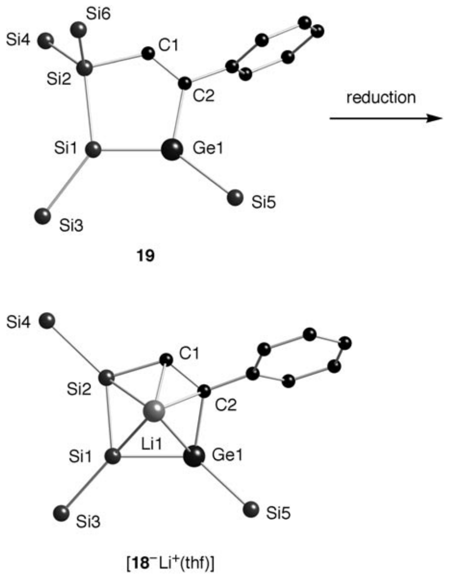
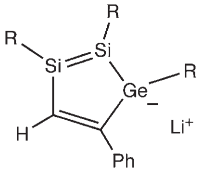


Figure 4. Structural changes upon the reduction of **19** to [**18**$^-$Li$^+$(thf)] (Crystal Maker view; hydrogen and carbon atoms of the tBu$_2$MeSi substituents, hydrogen atoms of the Ph groups, and thf molecule are not shown).

The Li$^+$ cation in [**18**$^-$Li$^+$(thf)] is characteristically η^5-coordinated to the anionic ring; thus the overall structure represents a classical "half-sandwich" complex, which is diagnostic of the cyclopentadienide derivatives of the type C_5R_5Li. Clearly, all these structural features of [**18**$^-$Li$^+$(thf)] prove the delocalization of the six-π-electron density over the entire five-membered ring, that is, the requirements of the geometrical criterion of aromaticity are definitely satisfied for [**18**$^-$Li$^+$(thf)]. Certainly, the extent of aromaticity of [**18**$^-$Li$^+$(thf)] is smaller than that of the prototypical lithium cyclopentadienide: In contrast to C_5H_5Li, in which the negative charge is equally distributed between all C atoms, one cannot assume such an even distribution of electron density over all the skeletal atoms in [**18**$^-$Li$^+$(thf)] because of their different electronegativities. Instead, the majority of the negative charge is expected to be accumulated on the Ge atom, whose pyramidalization is the most appreciable of all the skeletal atoms (the sum of the bond angles around the particular atom is shown in parentheses): Ge1 (342.89°), Si1 (350.75°), Si2 (357.03°), C1 (359.94°), C2 (359.79°).

With respect to the magnetic criterion of aromaticity, [**18**$^-$Li$^+$(thf)] should also be qualified as an aromatic compound. Thus, the NICS(1) for the model compound [**18'**$^-$Li$^+$] (H_3Si groups instead of the tBu$_2$MeSi substituents) was negative (−8.4). This value is similar to (albeit smaller than) those of the classical aromatic compounds with six π electrons: C_5H_5Li (NICS(1) = −10.3) and C_6H_6 (NICS(1) = −11.2).[72b] Accordingly, the ^{7}Li NMR resonance of [**18**$^-$Li$^+$(thf)] in toluene was observed at very high field (δ = −5.4 ppm), which is typical for the aromatic lithium cyclopentadienide derivatives.[74] Thus, the aromaticity of [**18**$^-$Li$^+$(thf)], deduced from characteristics of its crystal structure, is also preserved in toluene (or benzene) solution. For example, the η^5 coordination of Li$^+$ to the ring was manifested by the non-equivalence of all tBu groups of the silyl substituents, as well as by the NMR resonances of the skeletal Si atoms of [**18**$^-$Li$^+$(thf)] at δ = 54.4 and 69.1 ppm. These values are in between those of the typical sp^2- and sp^3-Si atoms.[75]

However, the solution structure of [**18**$^-$Li$^+$(thf)] is highly solvent-dependent: While it is aromatic in nonpolar toluene or benzene (see above), it is unable to benefit from aromatic delocalization in polar THF. This difference was clearly observed in the NMR spectra of [**18**$^-$Li$^+$(thf)] measured in [D$_8$]THF, which are totally different from those in [D$_8$]toluene. A simplified ^{1}H NMR spectrum in THF because of the breaking of η^5 coordination of the Li$^+$ ion to the five-membered ring, a large deshielding of both skeletal Si atoms (δ = 97.4 and 104.9 ppm) indicating their double-bond character,[76] and the resonance of the Li ion observed in a typical region of η^1-germyllithium compounds (δ = −0.6 ppm,[77] clearly outside the range expected for the aromatic lithium cyclopentadienide derivatives).[74] Comparing the spectral features of [**18**$^-$Li$^+$(thf)] in toluene and THF, it should be concluded that the coordination mode was changed from a delocalized η^5 coordination in nonpolar toluene to a localized η^1 coordination in polar THF. Consequently, [**18**$^-$Li$^+$(thf)] in THF acquires the properties of the localized cyclopentadienide featuring a negative charge on the Ge atom and Si=Si and C=C double bonds (Scheme 14). Thus, the heavy cyclopentadienide [**18**$^-$Li$^+$(thf)] is an aromatic compound in the solid state and in nonpolar solvents (toluene, benzene), whereas it is non-aromatic in polar THF.



R = SiMetBu$_2$

18$^-$

Scheme 14. Structure of **18**$^-$ in THF: cyclopentadienide with localized π electrons.

It should also be noted that [**18**$^-$Li$^+$(thf)] is the first monoanionic derivative of the heavy cyclopentadienide analogues whose aromaticity was reliably established both experimentally and theoretically.[72] Compound [**18**$^-$Li$^+$(thf)] thus represents an experimental realization of Schleyer's theoretical prediction about the significant aromaticity of lithium silacyclopentadienide C_4H_4SiHLi.[70b]

3.3. Heavy Analogues of the Cyclobutadiene Dianion

As was demonstrated in Section 2.2, the behavior of the small doubly positively charged systems, such as the cyclobutadiene dication with two π electrons, is greatly dictated by the severe Coulomb repulsive interaction between the two charges, which might overcome the tendency toward π delocalization and aromatic stabilization.[21a,24,25] The same trends evidently operate in the case of the doubly negatively charged cyclobutadiene dianion with six π electrons (Scheme 15; E = C), whose story is strikingly different from that of its singly negatively charged analogue with six π electrons, the cyclopentadienide ion (see Section 3.2).

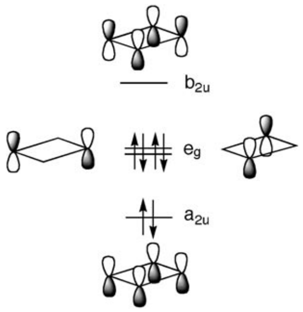
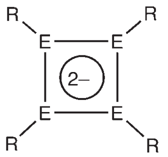


Figure 5. π-MOs diagram of $[C_4H_4]^{2-}$.

The origin of such a difference can be easily visualized in terms of the interplay between the two principal tendencies: cyclic π delocalization and thermodynamic stabilization. If the singly charged species (cyclopentadienide ion) can greatly benefit from π delocalization, resulting in the overall aromatic stabilization of the molecule, the cyclic delocalization in the doubly charged systems (cyclobutadiene dianion) has a totally opposite, destabilizing effect owing to the unavoidable mixing of the two extra electrons, which cannot be efficiently separated, resulting in a strong Coulomb repulsion. Similar to the case of the cyclobutadiene dication, such Coulomb repulsion can overcompensate for stability gained by delocalization, and consequently the trend for electron localization and separation may cause a significant departure of the cyclobutadiene dianion ring from planarity.

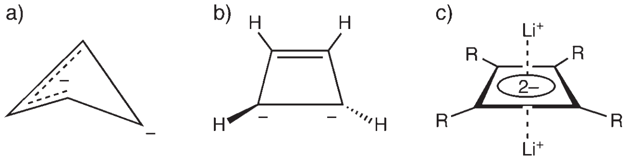
Another important reason greatly contributing to the overall destabilization of the molecule is the fact that in the planar D_{4h} structure, four out of the six π electrons are forced to occupy the nonbonding orbitals to form a pair of doubly degenerate HOMOs (Figure 5), thus giving rise to strongly repulsive 1,3-antibonding interactions; therefore, an intrinsically high reactivity of the cyclobutadiene dianion should be expected.



E = C, Si, Ge, Sn, Pb

Scheme 15. Derivatives of the cyclobutadiene dianion.

Indeed, the early calculations by Schaad et al. described the structure of the parent cyclobutadiene dianion as a puckered four-membered ring bearing one localized and one allylic-type delocalized negative charge, thus predicting a small degree of cyclic conjugation of the six π electrons (Scheme 16a).[24] More elaborate calculations by van Zandwijk et al. showed that the above conformation possesses an imaginary frequency and is actually a saddle point on the PES. The true minimum structure of the cyclobutadiene dianion is represented by one with a C=C double bond and the two negative charges located on the other two adjacent tetrahedral carbon atoms, giving an overall trapezoid shape to the four-membered ring (Scheme 16b).[78] However, as was demonstrated by Schleyer and co-workers, the introduction of the highly positive lithium ions may (and does) greatly counteract the unfavorable tendency of the Coulomb repulsion, significantly diminishing the degree of mixing of the extra electrons, which finally results in the much greater extent of cyclic delocalization and, in effect, in the overall aromatic stabilization of the system.[79] According to these calculations, $[(C_4H_4)^{2-}Li^+_2]$ has a planar "inverse-sandwich" D_{4h} structure (Scheme 16c; R = H). The experimental realization of such a theoretical prediction was accomplished recently by Sekiguchi et al. by the synthesis of a dilithium derivative of the cyclobutadiene dianion $[(Me_3Si)_4C_4^{2-}Li^+_2]$, stabilized by the four π-accepting trimethylsilyl groups, which was shown to possess a planar C_4 ring with a fully delocalized six-π-electron aromatic system (Scheme 16c; R = $SiMe_3$).[80]

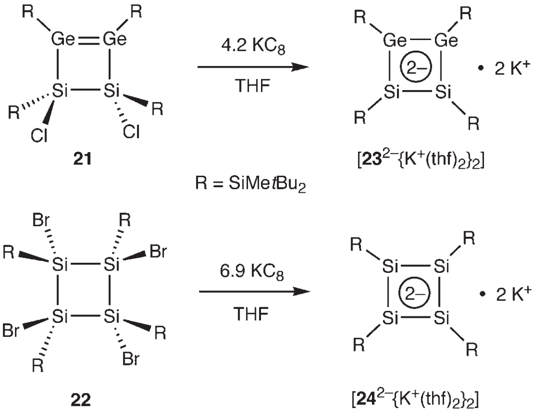


Scheme 16. Calculated structures of a), b) $[C_4H_4]^{2-}$ and c) $[(C_4H_4)^{2-}Li^+_2]$.

To the best of our knowledge no experimental studies on heavy analogues of the cyclobutadiene dianion have been reported in the literature. The only theoretical paper on the tetrasilacyclobutadiene dianion, found through the SciFinder search, predicted that the most stable structure of the unsubstituted compound $[Si_4H_4]^{2-}$ is tetrasilabicyclo[1.1.0]butane-2,4-diide of C_s symmetry, which is more stable than the planar D_{4h} configuration of the delocalized tetrasilacyclobutadiene dianion by 29.9 kcal mol^{-1}.[28]

One of the best methods for making E=E′ double bonds is the dehalogenative reduction of the 1,2-dihalogen precursors of the type E(X)−E′(X) (X = halogen) with alkali metals. For this reason, for the preparation of the heavy analogues of cyclobutadiene dianions, initially we designed the appropriate precursors: *trans*-1,2-dichloro-$^3\Delta$-1,2,3,4-disiladigermetene **21**[81] and *trans,trans,trans*-1,2,3,4-tetrabromo-1,2,3,4-tetrasiletane **22**.[72b] The formation of the target 1,2-disila-3,4-digerma- and 1,2,3,4-tetrasilacyclobutadiene dianions $[\mathbf{23}^{2-}\{K^+(thf)_2\}_2]$ and $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$ was smoothly achieved by the reduction of **21** or **22** with potassium graphite KC_8 (4.2 and 6.9 equiv, respectively) in THF (Scheme 17).[82] The heavy cyclobutadiene dianions $[\mathbf{23}^{2-}\{K^+(thf)_2\}_2]$ and $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$ were isolated as emerald-green crystals in reasonable yields of 70 and 73 %.

The crystal structures of both $[\mathbf{23}^{2-}\{K^+(thf)_2\}_2]$ and $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$[82,72b] (Figure 6) are remarkably different from that of the above-mentioned carbon analogue $[(Me_3Si)_4C_4^{2-}Li^+_2]$ featuring D_{4h} symmetry.[80a] First, both four-membered $\{Si_2Ge_2\}$ and $\{Si_4\}$ rings of $[\mathbf{23}^{2-}\{K^+(thf)_2\}_2]$ and $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$ significantly depart from planarity, being markedly puckered with folding angles of 43 and 34°. Consequently, both K^+ ions, which are located above and



Scheme 17. Synthesis of $[\mathbf{23}^{2-}\{K^+(thf)_2\}_2]$ and $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$.

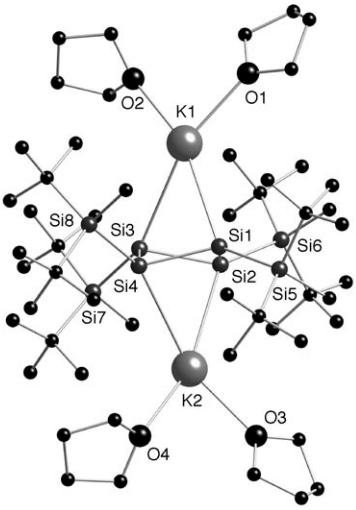
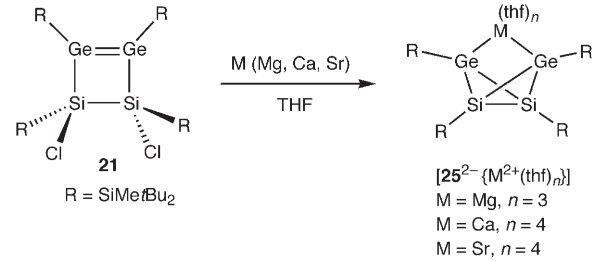


Figure 6. Crystal structure of $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$ (Crystal Maker view; hydrogen atoms are not shown).

below the $\{Si_4\}$ ring, prefer η^2 coordination (at the 1,3- and 2,4-positions of the ring) instead of the η^4 coordination anticipated for the fully delocalized planar D_{4h} structure. Despite the homonuclear constitution of the four-membered ring, the skeletal Si–Si bonds in $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$ are not identical: Two of them, Si1–Si4 and Si2–Si3, are equal (2.3301(8) and 2.3300(8) Å), whereas one, Si1–Si2, is shorter (2.2989(8) Å) and the other, Si3–Si4, is longer (2.3576(8) Å). The overall shape of the $\{Si_4\}$ ring therefore represents a folded trapezoid. The bulky silyl substituents are bent away from the coordinated K^+ ions, thus occupying the alternating up-and-down positions, and the skeletal Si atoms are appreciably pyramidalized: The sum of the three Si-Si-Si bond angles around the Si1(Si2) and Si3(Si4) atoms is 341 and 326°, respectively. Such a geometry for both $[\mathbf{23}^{2-}\{K^+(thf)_2\}_2]$ and $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$ very closely approaches the one predicted by Schaad et al., but the electron distribution is different from that calculated in $[C_4H_4]^{2-}$.[24] Certainly, such a folded configuration of both $[\mathbf{23}^{2-}\{K^+(thf)_2\}_2]$ and $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$ results from the significant Coulomb repulsion of the two negative charges, which cannot be outbalanced by the spatially remote potassium cations, a conclusion that is well-supported by recent calculations.[83]

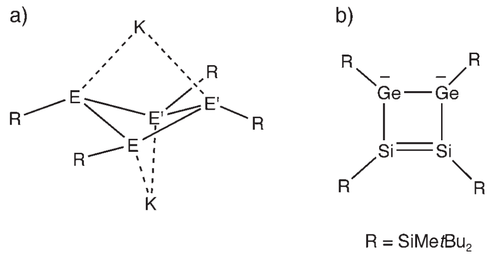
The analysis of these structural features of both $[\mathbf{23}^{2-}\{K^+(thf)_2\}_2]$ and $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$ leads to a definite conclusion, that the structural peculiarities of both derivatives certainly do not fit the geometrical criteria of aromaticity in its classical sense: ring planarity, cyclic bond equalization (anticipated at least for homonuclear $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$), η^4 coordination to the counterion expected for the aromatic cyclobutadiene dianion in its D_{4h} conformation. The requirement of the magnetic criterion of aromaticity[6] is also not fulfilled. The NICS(1) calculation on model compounds for both $[\mathbf{23}^{2-}\{K^+(thf)_2\}_2]$ and $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$ (Me_3Si groups instead of the tBu_2MeSi substituents) provided positive values of $+4.3$ and $+6.1$, indicating the absence of a diatropic ring current. It should thus be concluded that the heavy cyclobutadiene dianion derivatives are non-aromatic species, at least in the solid state.

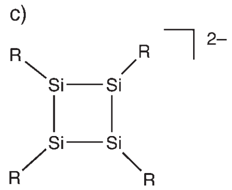
However, the extent of the π delocalization and, consequently, aromaticity strongly depend on the nature of the counterions. Smaller cations could approach the cyclobutadiene dianion ring more closely and therefore more effectively counteract the Coulomb repulsion of the two negative charges, giving an overall stabilization of the system. According to our preliminary results, both dilithium and disodium derivatives of tetrasilacyclobutadiene dianion $[\mathbf{24}^{2-}\{M^+(thf)_2\}_2]$ ($M = Li$, Na) show η^4 coordination of both M atoms (close to the "inverse-sandwich" structure) and a markedly more planar $\{Si_4\}$ ring than that in the $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$.[84] Moreover, the reduction of **21** with the alkaline-earth metals Mg, Ca, and Sr (instead of the alkali metals Li, Na, K) resulted in the formation of completely different products, the Mg, Ca and Sr salts $[\mathbf{25}^{2-}\{M^{2+}(thf)_n\}]$ ($M = Mg$, $n = 3$; $M = Ca$, $n = 4$; $M = Sr$, $n = 4$),[85] whose structures very closely resemble the one predicted as a minimum structure for $[Si_4H_4]^{2-}$ (Scheme 18).[28] In effect, this reaction clearly demonstrates the decisive influence of the nature of the metal on the structure of the final product.



Scheme 18. Synthesis of $[\mathbf{25}^{2-}\{M^{2+}(thf)_n\}]$.

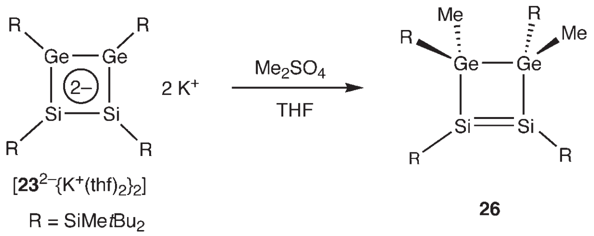
Interestingly, whereas the solid-state structures of both $[\mathbf{23}^{2-}\{K^+(thf)_2\}_2]$ and $[\mathbf{24}^{2-}\{K^+(thf)_2\}_2]$ are virtually identical (Scheme 19a), their solution structures are appreciably different, which was clearly manifested in their ^{29}Si NMR spectra.[82,72b] Thus, the resonances of the skeletal Si atoms in $[\mathbf{23}^{2-}K^+_2]$ were observed at low field ($\delta = 113.7$ ppm), characteristic of doubly bonded Si atoms,[75] thus pointing to the most important contribution of the resonance structure in





Scheme 19. Structures of the heavy cyclobutadiene dianions $\mathbf{23}^{2-}$ and $\mathbf{24}^{2-}$ a) in the solid state (E = Si, E′ = Si, Ge) and b), c) in solution.

Scheme 19b with both negative charges located on the more electronegative Ge atoms. Indeed, methylation of [$\mathbf{23}^{2-}$\{K$^+$(thf)$_2$\}$_2$] with Me_2SO_4 proceeded exclusively at the Ge atoms to form the $^1\Delta$-1,2,3,4-disiladigermetene **26** as the only product (Scheme 20).[82,72b] This observation corroborates



Scheme 20. Methylation of [$\mathbf{23}^{2-}$\{K$^+$(thf)$_2$\}$_2$] with Me_2SO_4: formation of $^1\Delta$-1,2,3,4-disiladigermetene **26**.

well with the common postulate that the electronegativity difference favors electron localization, overcoming the trend of cyclic π delocalization and, consequently, making the molecule non-aromatic.[78] In contrast, in the all-Si version [$\mathbf{24}^{2-}$\{K$^+$(thf)$_2$\}$_2$] the resonances of the skeletal Si atoms were observed at $\delta = 17.0$ ppm, which is definitely outside the range of the doubly bonded Si atoms, thus indicating a more important degree of delocalization of negative charges in [$\mathbf{24}^{2-}$\{K$^+$(thf)$_2$\}$_2$] corresponding to the resonance structure in Scheme 19c. The solution structures of both [$\mathbf{23}^{2-}$\{K$^+$(thf)$_2$\}$_2$] and [$\mathbf{24}^{2-}$\{K$^+$(thf)$_2$\}$_2$] do not depend on the polarity of the solvent, as they are identical in polar THF and nonpolar toluene.

By comparing with the theoretical predictions, it can be realized that the resonance structure in Scheme 19b for [$\mathbf{23}^{2-}$\{K$^+$(thf)$_2$\}$_2$] closely resembles the localized 1,2-dianionic cyclobutene-type structure found by van Zandwijk et al.,[78] whereas the resonance form in Scheme 19c for [$\mathbf{24}^{2-}$\{K$^+$(thf)$_2$\}$_2$] has more similarities to the planar D_{4h} structure calculated for [$(C_4H_4)^{2-}Li^+_2$] by Schleyer et al.[79] Two factors concerning the possibility of synthesizing the heavy analogues of planar aromatic cyclobutadiene dianion derivatives should be considered: 1) the preparation of the homonuclear four-membered ring of identical Group 14 elements (to avoid the undesirable electron localization resulting from the difference in electronegativities) and 2) the use of the smaller countercations (preferably Li$^+$), which are more capable of forming covalent bonding with the skeletal atoms.

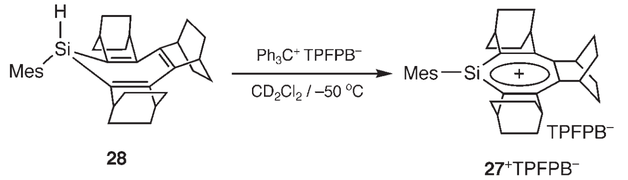
3.4. Heavy Analogues of the Tropylium Ion

The synthesis of the first stable cycloheptatrienylium derivative, tropylium bromide by Doering and Knox in 1954, clearly demonstrated the predictive power of Hückel's $(4n+2)$-π-electron rule.[86] The tropylium ion, whose six-π-electron aromaticity was predicted by this rule, was indeed very stable and can be prepared through a variety of experimental procedures.[87] Furthermore, the tropylium ion became a very familiar species for organic mass spectrometry specialists, who often observed the abundant formation of tropylium ion upon ionization of toluene.[88] Both experimental (X-ray crystallography)[89] and theoretical[90] studies concluded that the tropylium ion possesses a planar D_{7h} structure with equal C–C bond lengths of 1.400(2) Å (X-ray)[89b] and 1.405 Å (calculations)[90a] in the ground state, which pointed to the delocalization of its π electrons and, consequently, its aromaticity.

The analogues of the tropylium ion of heavier Group 14 elements have still not been synthesized as stable derivatives. The early gas-phase experiments by Beauchamp and co-workers claimed that of the two observed distinct $[C_6SiH_7]^+$ isomers, the silatropylium ion and the hypothetical silabenzene cation, the former was thermodynamically more stable than the latter, similarly to the carbon analogues.[91] However, in a later study Jarek and Shin disproved that statement, indicating that the most stable $[C_6SiH_7]^+$ isomer is $[(\eta^4\text{-}C_6H_6)SiH^+]$, not the silatropylium ion.[92] This contradiction was rationalized by the high-level computations of Radom et al., who showed that the silatropylium ion is destabilized relative to the silabenzyl cation by 9.1 kcal mol^{-1}, a tendency that is opposite to that in carbon chemistry, where among the $[C_7H_7]^+$ isomers the tropylium ion is more stable than the benzyl cation by 7.6 kcal mol^{-1}.[93] The calculated structure of the planar C_{2v} silatropylium ion exhibited C–C bond alternation; however, the degree of its electron delocalization or aromaticity was not discussed.[93]

Experimentally, the closest approach to the synthesis of silatropylium ion derivatives was demonstrated by Komatsu and co-workers, who employed a modification of the seven-membered ring of the silatropylium ion with a rigid σ framework by annelation with bicyclo[2.2.2]octene units.[94] Such a silatropylium ion derivative, $\mathbf{27}^+$TPFPB$^-$ bearing a bulky mesityl (Mes) group on the Si atom, was prepared from the corresponding silepin **28** by the classical "hydride-transfer reaction" with $Ph_3C^+TPFPB^-$ in CD_2Cl_2 at $-50\,^\circ C$ by utilizing the general tendency of the stronger C–H versus Si–H bonds (Scheme 21).[94a]

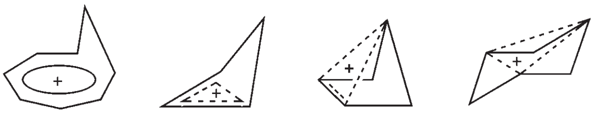
The aromaticity of the silatropylium ion $\mathbf{27}^+$ is manifested in the low-field resonance of the Si atom at $\delta = 142.9$ ppm, as



28

27$^+$TPFPB$^-$

Scheme 21. Synthesis of **27**$^+$TPFPB$^-$.



29$^+$ **30**$^+$ **33**$^+$ **38**$^+$

Scheme 22. The most important homoaromatic systems.

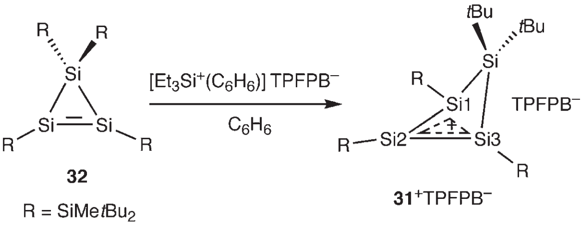
well as by appreciable deshielding of all skeletal carbon atoms, indicating significant delocalization of the positive charge over the entire seven-membered ring. The requirement of the magnetic criterion of aromaticity is also satisfied for **27**$^+$: The NICS(1) for the model unsubstituted $[C_6SiH_7]^+$ was calculated to be −7.3 (for comparison, the NICS(1) for the tropylium ion is −10.7). However, the evident drawback of such a synthetic approach was the instability of the silatropylium ion **27**$^+$. After being generated at low temperature, it can survive only at temperatures below −50 °C, whereas at higher temperatures it undergoes an unavoidable reaction with the solvent through a chlorine abstraction reaction. No other examples of a silatropylium ion or any other heavier Group 14 elements containing tropylium ions, either stable or metastable, have been reported to date.

4. Homoaromaticity of Group 14 Organometallics

Homoaromaticity is generally attributed to the cyclic compounds in which the conjugated system is formed by bypassing a saturated unit (typically, a CH_2 group).[3] Despite the interruption of the cyclic conjugation, such systems can still benefit from the stabilization effects of aromaticity; however, the overall stabilization is reduced, compared to normal aromatics, owing to the poorer orbital overlap. The term "homoaromatic" was introduced for the first time in 1959 by Winstein.[95] Since then, the concept of homoaromaticity has been widely accepted in organic chemistry,[5,96] and homoaromaticity was well-recognized in cationic systems in which delocalization of the positive charge was considered as an important driving force for homoaromaticity.[96d] However, this is not the case in anionic and neutral systems, for which the application of homoaromaticity remains highly controversial.[96d] The key compound among the cationic homoaromatic systems is the homotropylium ion **29**$^+$, synthesized for the first time in 1962 by Pettit and co-workers by treatment of cyclooctatetraene with $SbCl_5$/HCl in nitromethane (Scheme 22).[97] The homotropylium ion, comprehensively studied both experimentally and computationally, is considered as the prototypical homoaromatic system, serving as a reference species relative to which the properties of other homoaromatic compounds can be estimated.[5]

Cyclobutenylium ion **30**$^+$, the homoaromatic analogue of the very stable aromatic cyclopropenylium ion, is the simplest homoaromatic system, one of the best-studied among other homoconjugated compounds (Scheme 22). It was prepared by Olah et al. by the treatment of 3-acetoxycyclobutene with $HOSO_2F$ under superacidic conditions (SbF_5/SO_2ClF, −78 °C).[98] The NMR spectra (particularly the ^{13}C NMR spectrum) of **30**$^+$ were consistent with its homoaromatic structure,[98] which was also supported by calculations that well-reproduced the structural and spectral features of **30**$^+$.[99] However, the overall stabilization of **30**$^+$ is less than that of the homotropylium ion **29**$^+$. The homoaromatic stabilization energy of **30**$^+$ is about 40 % that of **29**$^+$.[5]

The all-Si version of the cyclobutenylium ion, homocyclotrisilenylium ion **31**$^+$, was recently prepared by Sekiguchi et al. in the form of **31**$^+$TPFPB$^-$.[100] The synthesis was achieved smoothly by the oxidative demethylation of cyclotrisilene **32** with the $[Et_3Si]^+$ cation in benzene, which produced **31**$^+$TPFPB$^-$ as yellow crystals in 91 % yield (Scheme 23). Control experiments with deuterium-labeled cyclotrisilene [D$_6$]-**32** showed that the Me group was abstracted from one of the tBu$_2$MeSi substituents on the skeletal sp^3 Si atom, accompanied by the formation of an intermediate silyl cation, and followed by its isomerization to homocyclotrisilenylium ion **31**$^+$TPFPB$^-$. The crystal structure determination showed that **31**$^+$ lacks any observable interactions with the counteranion or solvent, and is thus a truly free cation in the crystalline state (Figure 7). Similar to its carbon analogue, the homocyclopropenylium ion,[96d] homocyclotrisilenylium ion **31**$^+$ adopts a significantly puckered (46.6°) geometry with a short nonbonding Si1−Si3 interatomic distance of 2.692(2) Å, consistent with its homoaromaticity (Figure 8).[100]



32

R = SiMetBu$_2$

31$^+$TPFPB$^-$

Scheme 23. Synthesis of **31**$^+$TPFPB$^-$.

Typically for homoaromatic systems, a significant amount of the positive charge is built up at the central Si2 atom of the homoaromatic system, which was clearly manifested by its greatly low-field-shifted resonance at $\delta = +315.7$ ppm (for comparison, the chemical shifts of the terminal Si1 and Si3 atoms of the homoaromatic system were observed at a much higher field: $\delta = +77.3$ ppm). In full agreement with the homoaromatic composition of **31**$^+$, the geometry around its three Si atoms (Si1, Si2, and Si3), constituting a cationic portion, was perfectly planar (sp^2-hybridized), whereas the environment around the by-passed atom Si4 was pronoun-

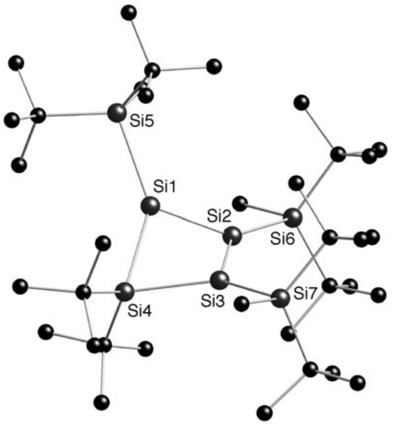


Figure 7. Crystal structure of **31**$^+$ (Crystal Maker view; TPFPB$^-$ and hydrogen atoms are not shown).

cedly pyramidal (sp^3-hybridized; Figure 7). Moreover, the lengths of the Si–Si bonds of the cationic portion of **31**$^+$ (Si1–Si2 2.240(2) Å, Si2–Si3 2.244(2) Å) are intermediate between those of typical Si–Si single and double bonds.[100]

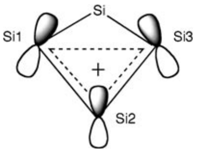
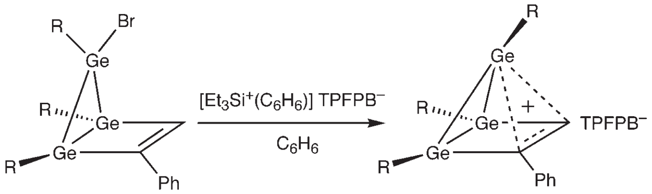


Figure 8. HOMO of the homocyclotrisilenylium ion, calculated for the model compound $[(H_3SiSi)_3SiMe_2]^+$ (Me and H$_3$Si substituents are not shown) at the B3LYP/6-31G(d) level.

The homoconjugated bishomocyclopropenylium ion **33**$^+$, folded by about 90° (Scheme 22), was calculated to be more stable than its planar less-strained conformer by 6 kcal mol^{-1};[101] nevertheless the parent bishomocyclopropenylium ion remains unknown experimentally.[96d] In contrast, its numerous 3,5-bridged derivatives have been widely studied both experimentally and computationally. For example, the recently reported crystal structures of such compounds showed elongation of the C1–C2 double bond (ca. 1.41 Å) and tilting of the C4 atom toward the C1=C2 bond, resulting in a significant shortening of the C1–C4 and C2–C4 interatomic distances (ca. 1.75–1.88 Å).[102] Such structural features strongly support the homoaromaticity of these systems.

The number of stable heavy analogues of bishomocyclopropenylium systems is limited to only one example, whose crystal structure was recently reported by Sekiguchi et al.[103] Compound **34**$^+$TPFPB$^-$ was synthesized by oxidative debromination of the bromide precursor **35** with the $[Et_3Si]^+$ ion in benzene and isolated as pale yellow crystals in 61 % yield (Scheme 24). The positive charge, developed on the bridging Ge atom upon debromination, is effectively stabilized by the intramolecular through-space interaction with the endocyclic C–C double bond, thus forming a bishomocyclopropenylium system (Figure 9). Quite parallel to the case of carbon bishomocyclopropenylium derivatives (see above), both the Ge3–C1 and Ge3–C2 interatomic distances are rather short (2.415(7) and 2.254(7) Å), whereas the C1–C2 double bond is appreciably elongated (1.411(9) Å), unambiguously indicating the through-space π(C=C)→4p(Ge) homoconjugation.



35
R = Si*t*Bu$_3$

34$^+$ TPFPB$^-$

Scheme 24. Synthesis of **34**$^+$TPFPB$^-$.

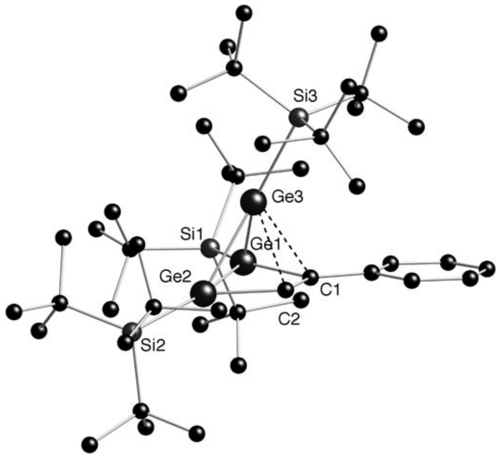
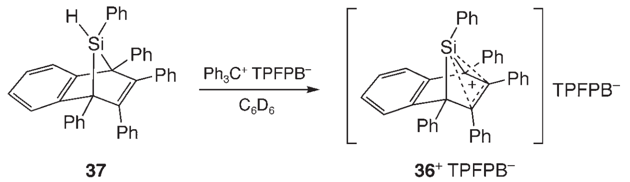


Figure 9. Crystal structure of **34**$^+$ (Crystal Maker view; TPFPB$^-$ and hydrogen atoms are not shown).

As a result, the Ge3 atom is significantly tilted toward the C=C bond to form a highly folded bicyclic structure with an interplanar angle of 67°. The formation of such three-center, two-electron bonding was also predicted by an NBO calculation, which showed the important electron deficiency of the occupied π(C=C) orbital (1.28 electrons) and appreciable electron occupancy of the vacant 4p(Ge) orbital (0.42 electrons).[103] Consequently, the bond orders (Wiberg bond indices, WBI) of the Ge3–C1, Ge3–C2, and C1–C2 bonds were computed as 0.37, 0.46, and 1.39, respectively. Furthermore, the NICS(1) calculated at 1 Å above the center of the imaginary Ge3-C1-C2 triangle was negative (−11.0), thus confirming the homoaromaticity of **34**$^+$. Interestingly, in contrast to expectations based on the partial delocalization of the positive charge on the olefinic C1 and C2 atoms in **34**$^+$, they were actually strongly shielded upon oxidation ($\Delta\delta(C1) = -29.8$, $\Delta\delta(C2) = -54.5$), which was explained by their partial rehybridization from sp^2 to sp^3.

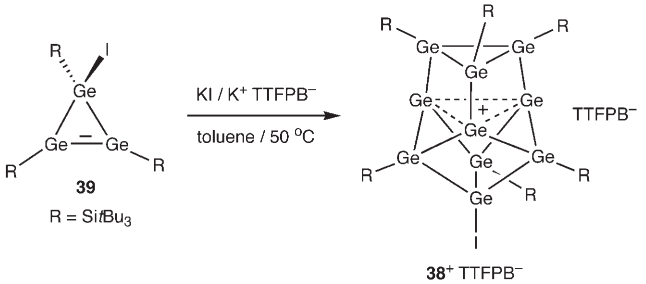
The silicon version of the bishomocyclopropenylium systems has still not been realized experimentally, although the intermediate formation of the 7-silanorbornadienylium ion derivative **36**$^+$TPFPB$^-$, generated from the corresponding 7-silanorbornadiene **37** by reaction with Ph$_3$C$^+$TPFPB$^-$, was recently discussed by Müller et al. (Scheme 25).[104] In sharp contrast to the 7-norbornadienylium ion, which is one of the most stable carbocations, **36**$^+$TPFPB$^-$ could not be detected even at −60 °C, rearranging at room temperature into the π-type complex [PhSi$^+$/1,2,3,4-tetraphenylnaphthalene]. How-



Scheme 25. Generation of transient **36**$^+$TPFPB$^-$.

ever, the transient **36**$^+$ ion can be effectively intercepted by Lewis bases such as acetonitrile or diethyl ether to produce the corresponding silylnitrilium or silyloxonium ions, as identified by NMR spectroscopy.[104]

The trishomocyclopropenylium ion **38**$^+$ (Scheme 22) was one of the first proposed homoaromatic species, having been classified as homoaromatic by Winstein as early as 1959.[95a] The homoaromaticity of this compound was convincingly demonstrated by the following investigations. Cremer and coworkers pointed out the equality of the homoconjugative interatomic C–C distances (1.82 Å) and the even distribution of the positive charge over all three homoconjugative C atoms.[101] The closest approach to the trishomocyclopropenylium system of the heavier Group 14 elements was reported by Sekiguchi et al. in 2002.[105] An unusual trishomoaromatic cationic {Ge$_{10}$} cluster compound **38**$^+$TTFPB$^-$ was prepared by the thermolysis of the iodide precursor **39** in the presence of excess KI in toluene at 50 °C for one week and was isolated as brown crystals in 37 % yield (Scheme 26).



Scheme 26. Synthesis of trishomoaromatic cationic cluster **38**$^+$TTFPB$^-$.

The structure of **38**$^+$TTFPB$^-$ is interesting, and represents a metal-rich cluster in which six (out of ten) Ge atoms carry silyl substituents and one Ge atom has an iodo substituent, whereas the remaining three Ge atoms are tricoordinate ("naked"). The interatomic distances between the three "naked" Ge atoms are virtually identical (3.2642(15), 3.2622(17), and 3.2542(15) Å), and are thus much longer than the normal Ge–Ge single-bond lengths but still in the range of the metallic Ge–Ge bond lengths in Zintl anions of the type [Ge$_9$]$^{3-}$.[106] This observation definitely points to a homoconjugative interaction between the three central Ge atoms to make a trishomoaromatic cationic system.

This conclusion was firmly supported by theoretical calculations. The trishomocyclotrigermenylium structure of the model [Ge$_{10}$H$_7$]$^+$, representing a global minimum on the PES, features three-center, two-electron bonding between the three Ge atoms inside the central core of the cluster with an even distribution of the positive charge over these Ge atoms. This {Ge$_3$} bonding is clearly seen in the HOMO of [Ge$_{10}$H$_7$]$^+$, and is manifested through the in-phase interaction of the p(Ge) orbitals (Figure 10). The Ge–Ge homoconjugative distances were calculated to be 3.423 Å with a bond order (WBI) of 0.288. The energetic and magnetic criteria of aromaticity were also satisfied with cluster **38**$^+$TTFPB$^-$: The ASE value for [Ge$_{10}$H$_7$]$^+$ is highly exothermic (−19.2 kcal mol^{-1}) and the NICS(0) is significantly negative (−26.4), consistent with the large homoaromatic stabilization of [Ge$_{10}$H$_7$]$^+$.[105]

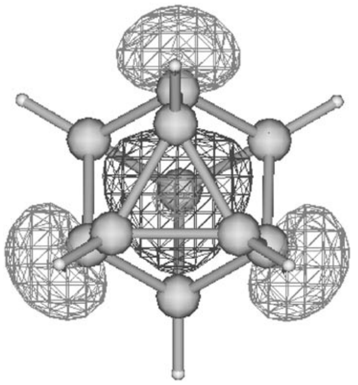


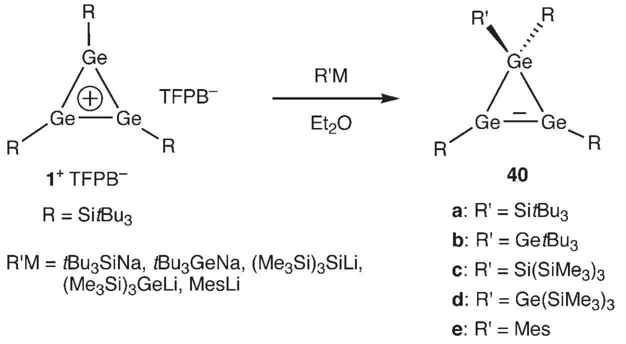
Figure 10. HOMO of the model cationic cluster [Ge$_{10}$H$_7$]$^+$ (calculated at the MP2/6-31G(d)//B3LYP/6-31G(d) level).

5. Reactivity and Applications of Group 14 Organometallics with Two and Six π Electrons

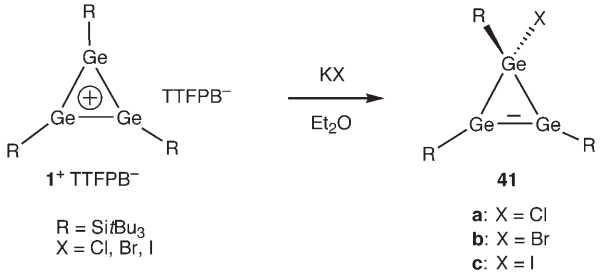
The chemistry of the heavy aromatics of Group 14 is rich and diverse, similar to that of its carbon aromatic congeners. Many reactions with nucleophiles (for cationic heavy aromatics), electrophiles (for anionic heavy aromatics), and a variety of addition and cycloaddition reactions (for neutral heavy aromatics) have been reported in recent years. The limited space of this review does not allow us to describe all of them in detail; instead we focus only on the most important examples of reactivity.

An example of the reactivity of two-π-electron heavy aromatic compounds is the interaction of cyclotrigermenylium derivative **1**$^+$TFPB$^-$ with different nucleophiles (*t*Bu$_3$SiNa, *t*Bu$_3$GeNa, (Me$_3$Si)$_3$SiLi, (Me$_3$Si)$_3$GeLi, MesLi), which provides a simple and effective approach for the synthesis of novel unsymmetrically substituted cyclotrigermenes **40a–e** in high yields (Scheme 27).[107] Interestingly, the (Me$_3$Si)$_3$Si-substituted cyclotrigermene **40c**, prepared by this method, featured an unprecedented example of *cis*-bent geometry around the Ge–Ge double bond[108] as a consequence of the steric and electronic effects of the bulky and electropositive (Me$_3$Si)$_3$Si substituent.

On the other hand, the reaction of **1**$^+$TTFPB$^-$ with potassium halides KX (X = Cl, Br, I) in diethyl ether resulted in the formation of halogen-substituted cyclotrigermenes **41a–c** (Scheme 28), in which the halogen atoms have undergone unique room-temperature migration over the entire

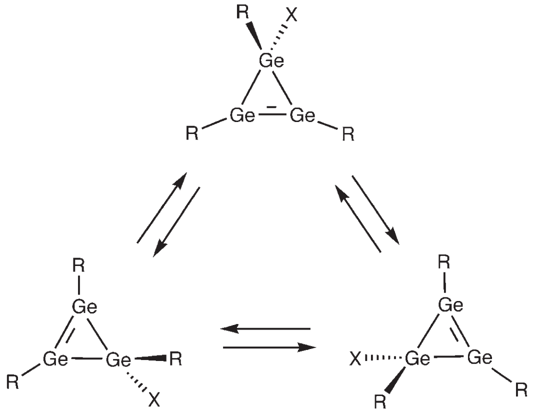


Scheme 27. Synthesis of unsymmetrically substituted cyclotrigermenes **40 a–e**.



Scheme 28. Synthesis of halogen-substituted cyclotrigermenes **41 a–c**.

{Ge_3} skeleton, as shown by dynamic ^{1}H NMR spectroscopy (Scheme 29).[109] Both Br- and I-substituted cyclotrigermenes **41 b** and **41 c** revealed an unusual *cis*-bent geometry around the Ge=Ge bond, which was realized in terms of significant π(Ge=Ge)→σ*(Ge–X) through-space orbital interaction (Figure 11).



Scheme 29. Halogen migration over the {Ge_3} skeleton of cyclotrigermenes **41 a–c**.

The reactivity of the neutral heavy six-π-electron aromatic compounds—benzene and its analogues (numerous addition and cycloaddition reactions, as well as thermal and photochemical transformations)—has been comprehensively described by Tokitoh in his latest reviews.[11]

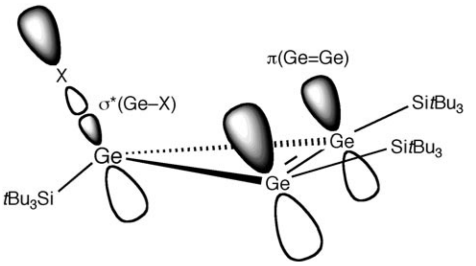
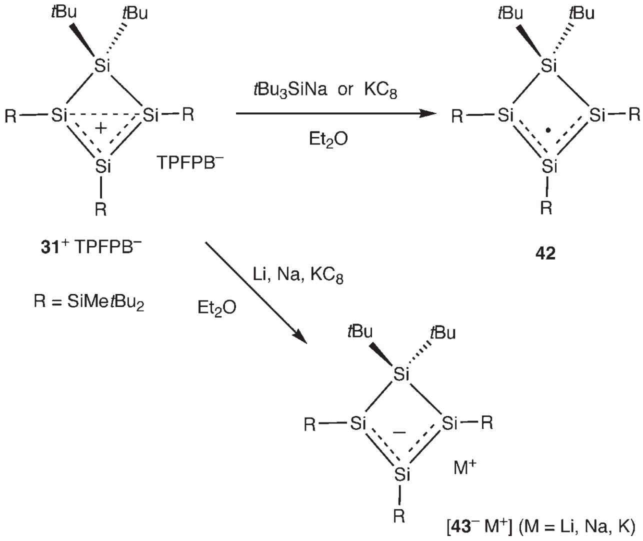


Figure 11. π(Ge=Ge)→σ*(Ge–X) interaction in halogen-substituted cyclotrigermenes.

The chemistry of the heavy cyclopentadienide analogues primarily concerns the reactivity of dilithio-2,3,4,5-tetraphenyl-1-silacyclopentadienediide [$\mathbf{14}^{2-}Li^+_2$], which was treated with 1,1-dichloro-2,3-diphenylcyclopropene to form a stable biradical,[110] with 2-adamantanone to produce a novel silene[111], and with diphenylcyclopropenone to form the dilithium salt of 2,3,5,6-tetraphenyl-1,4-hydroquinone.[112] The dimerization of the 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide ion in THF solution at room temperature produced an unusual tricyclic diallylic dianion isolated in the form of its dilithium salt,[113] whereas the reaction of dilithio-2,3,4,5-tetramethyl-1-silacyclopentadienediide with diphenylcyclopropenone resulted in the formation of a silaspirotropylidene derivative.[114]

The synthetic application of the homoaromatic systems of the heavier Group 14 elements is limited to a couple of interesting examples. The one-electron reduction of $\mathbf{31}^+$ with either tBu$_3$SiNa or KC_8 in diethyl ether produced the cyclotetrasilenyl radical **42**, the first one in the series of stable silicon-centered free radicals (Scheme 30).[115] Further reduction of $\mathbf{31}^+$ with an excess of metallic Li, Na, or KC_8 yielded the lithium, sodium, or potassium salts of cyclotetrasilenide ion [$\mathbf{43}^-M^+$] (M = Li, Na, K; Scheme 30).[116] The X-ray analysis of its lithium derivative [$\mathbf{43}^-Li^+$(thf)] showed a



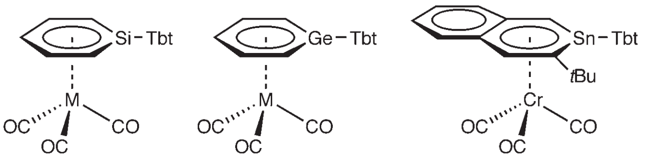
Scheme 30. One- and two-electron reduction of $\mathbf{31}^+$: formation of cyclotetrasilenyl radical **42** and cyclotetrasilenide $\mathbf{43}^-$.

cyclotetrasilene structure, in which the Li cation intramolecularly coordinates to a Si–Si double bond.

The most important application of the heavy Group 14 aromatic compounds is undoubtedly associated with their use as novel cyclic polyene ligands for next-generation transition-metal complexes. In modern organometallic chemistry carbocyclic polyene ligands, such as η^3-C_3R_3 cyclopropenyls, η^4-C_4R_4 cyclobutadienes, η^5-C_5R_5 cyclopentadienyls, η^6-C_6R_6 arenes, η^7-C_7R_7 cycloheptatrienyls, and η^8-C_8R_8 cyclooctatetraenes, have found widespread utilization for the synthesis of a huge number of transition-metal complexes.[117] However, their heavier counterparts with Si, Ge, Sn, and Pb atoms were unknown until the mid 1990s, when Tilley et al. reported the synthesis of the first transition-metal complexes with heavy cyclopentadienyl ligands. Since then, there has been growing interest in such a highly promising field of organometallic chemistry, resulting in the synthesis of approximately two dozen hybrid transition-metal–main-group-element complexes. We briefly describe them here.

The heavy cyclopropenyls η^3-E_3R_3 (E = Si, Ge, Sn, Pb) as ligands for transition-metal complexes are still unknown, although they were theoretically predicted to be feasible synthetic targets. Thus, several complexes of Groups 9 (Co, Rh, Ir) and 10 (Ni) metals bearing η^3-E_3H_3 fragments (E = Si, Ge) as π ligands were calculated to be minimum structures, in which there was significant ligand-to-metal electron donation, thus making η^3-E_3H_3 cationic ligands.[118] The η^3-Si_3H_3 ligand was even calculated to be capable of forming sandwich-type complexes with main-group elements, such as boron and carbon, as the central atoms with stabilization by charge transfer from the ligand to the central atom.[119]

The neutral heavy aromatic compounds synthesized by Tokitoh and co-workers (Section 3.1) have recently found a promising application as η^6-C_5ER_6 (E = Si, Ge) and η^6-C_9ER_8 π-arene ligands (E = Sn) for complexes of Group 6 metals (Cr, Mo).[39,120,121] The complexation smoothly proceeded upon the ligand-exchange reaction of stable silabenzene **6**,[33] germabenzene **9**,[36] and 2-stannanaphthalene **13**[39] with the transition-metal complexes $[M(CH_3CN)_3(CO)_3]$ (M = Cr, Mo) in either benzene or THF solvents to produce the corresponding [(η^6-silabenzene)M(CO)$_3$] (**44a,b**),[120] [(η^6-germabenzene)M(CO)$_3$] (**45a,b**),[121] and [(η^6-2-stannanaphthalene)Cr(CO)$_3$] (**46**)[39] complexes in good yields (Scheme 31). As further examples of heavy aromatic compounds of this type, the remarkable sila- and 1,4-disilabenzene complexes of ruthenium recently synthesized by Tilley and co-workers should also be mentioned.[122]



44
a: M = Cr
b: M = Mo

45
a: M = Cr
b: M = Mo

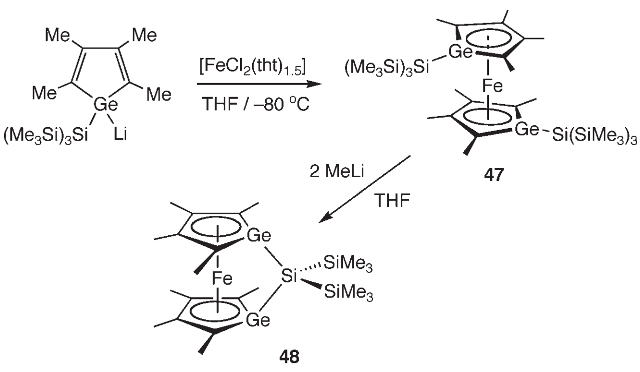
46

Scheme 31. Transition-metal complexes **44**–**46** with heavy neutral π-arene ligands.

As mentioned above, the heavy cyclopentadienyl compounds η^5-C_4ER_5 and η^4-C_4ER_6 (E = Si, Ge) were the first heavy cyclic polyenes utilized as ligands for transition-metal complexes by Tilley et al. Several complexes featuring either sila- or germacyclopentadienyl ligands have been reported in the past decade (Table 5).[69] An interesting complex, [{η^5-$C_4Me_4GeSi(SiMe_3)_3$}$_2$Fe] (**47**), with the two germacyclopentadienyl ligands sandwiching the central Fe atom (a heavy analogue of ferrocene) was also recently prepared by Tilley et al. by the coupling reaction of germacyclopentadienide ion $Li^+[C_4Me_4GeSi(SiMe_3)_3]^-$ with $[FeCl_2(tht)_{1.5}]$ in THF at low temperature (Scheme 32).[123] The reaction of complex **47** with MeLi surprisingly produced a novel ferrocenophane-type complex, *ansa*-[$(Me_3Si)_2Si(\eta^5$-$GeC_4Me_4)_2Fe$] (**48**; Scheme 32).

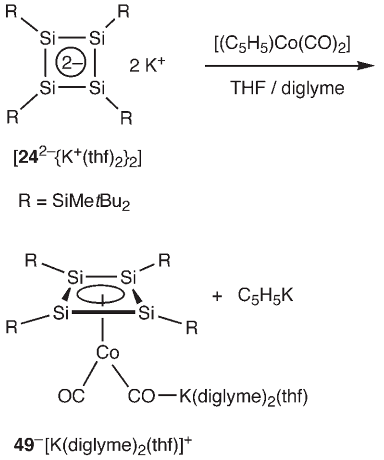
Table 5: Transition-metal complexes with sila- or germacyclopentadienyl ligands.

Complex	Ref.
[(η^5-C_5Me_5)Ru{η^5-$C_4Me_4GeSi(SiMe_3)_3$}]	[69a]
[(η^5-C_5Me_5)(η^5-$C_4Me_4SiSiMe_3$)$HfCl_2$]	[69c,d]
[(η^5-C_5Me_5)(η^5-$C_4Me_4GeSiMe_3$)$HfCl_2$]	[69c]
[{(η^5-C_5Me_5)(η^5-C_4Me_4Ge)$HfMe_2$\{Li(thf)\}}$_2$]	[69d]
[(η^5-C_5Me_5)(η^5-$C_4Me_4GeSiMe_3$)$HfMe_2$]	[69d]
[(η^5-C_5Me_5)(η^4-$C_4Me_4GeMeEt$)HfMe]	[69d]
[(η^5-C_5Me_5)(η^4-C_4Me_4GeMe*t*Bu)HfMe]	[69d]
[(η^5-C_5Me_5)(η^4-$C_4Me_4GeMePh$)HfMe]	[69d]
[(η^5-C_5Me_5)(η^5-$C_4Me_4SiSiMe_3$)$ZrCl_2$]	[69d]
ansa-[{η^4-$C_4Me_4Ge[Rh(PMe_3)_3H]$(η^5-$C_5Me_4CH_2$)}$HfMe_2$]	[69e]
[(η^5-C_5Me_5)(η^5-$C_4Me_4Ge[Rh(dmpe)_2]$)$HfMe_2$]	[69e]
[(η^5-C_5Me_5)(η^5-$C_4Me_4Ge[Ir(dmpe)_2]$)$HfMe_2$]	[69e]
[{(η^4-$C_4Me_4GeMeCl$)$TaCl_3(Et_2O)_x$}$_2$] ($x = 0.5$–1.0)	[69f]
[(η^4-$C_4Me_4GeMeCl$)$TaCl_3(PPh_3)$]	[69f]
[(η^4-$C_4Me_4GeMeCl$)$TaCl_3$(CNXyl)]	[69f]
[(η^4-$C_4Me_4GeMeCl$)$TaCl_3$(CNXyl)$_2$]	[69f]
[(η^4-$C_4Me_4GeMeCl$)$TaCl_3$(py)$_2$]	[69f]
[(η^5-C_5H_5)(η^4-$C_4Me_4GeMeCl$)$TaCl_2$]	[69f]



Scheme 32. Synthesis and reactivity of the heavy ferrocene **47**.

The heavy η^4-E_4R_4 cyclobutadienes (E = Si, Ge) as novel ligands for transition-metal complexes have quite recently become synthetically accessible,[72b,82] which is in marked contrast to the well-established chemistry of η^4-C_4R_4 transition-metal complexes.[124] Only two examples of the complexes featuring tetrasilacyclobutadiene ligands have been synthesized:[125] the anionic cobalt complex $[\{\eta^4\text{-}(t\mathrm{Bu_2MeSi})_4\mathrm{Si_4}\}\mathrm{Co(CO)_2}]^-[\mathrm{K(diglyme)_2(thf)}]^+$ ($\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$)[126] and the neutral iron complex $[\{\eta^4\text{-}(t\mathrm{Bu_2MeSi})_4\mathrm{Si_4}\}\mathrm{Fe(CO)_3}]$ (**50**).[127] The cobalt complex $\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$ was prepared by the reaction of tetrasilacyclobutadiene dianion dipotassium salt $[\mathbf{24}^{2-}\{\mathrm{K^+(thf)_2}\}_2]$[72b,82] with an excess of $[(\mathrm{C_5H_5})\mathrm{Co(CO)_2}]$ in THF and quantitatively isolated as orange crystals after addition of diglyme (Scheme 33).[126]



$[\mathbf{24}^{2-}\{\mathrm{K^+(thf)_2}\}_2]$

R = SiMe*t*Bu$_2$

$\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$

Scheme 33. Synthesis of $\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$.

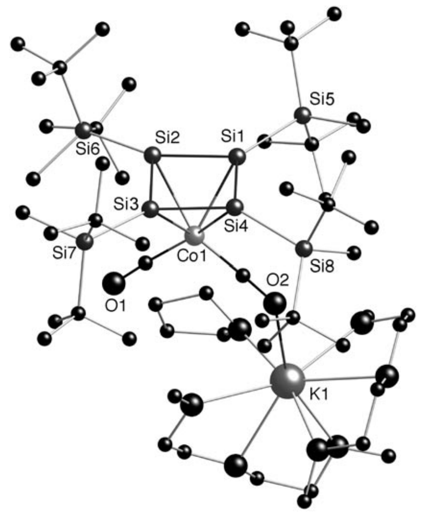
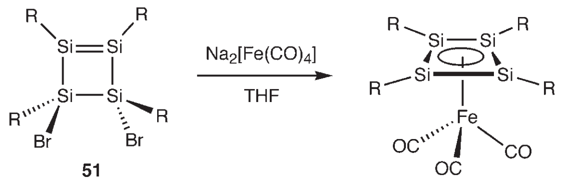


Figure 12. Crystal structure of $\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$ (Crystal Maker view; hydrogen atoms are not shown).



51

R = SiMe*t*Bu$_2$

50

Scheme 34. Synthesis of (tetrasilacyclobutadiene)tricarbonyliron complex **50**.

This ligand-exchange reaction, accompanied by the fast elimination of $\mathrm{C_5H_5K}$, is rather curious because it involves elimination of the innocent $\mathrm{C_5H_5}$ ligand, which typically plays a purely spectator role, instead of the loosely bound and easily removable CO groups. The evident reason for such a preference for elimination of the $\mathrm{C_5H_5}$ ligand is the fact that the starting tetrasilacyclobutadiene dianion $\mathbf{24}^{2-}$ is heavily overloaded with two negative charges and strongly favors the loss of one electron, which can be favorably removed in the form of an aromatic $\mathrm{C_5H_5}$ anion. The spectral data of $\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$ indicated a significant π back-donation from the Co 3d orbitals to the $\{\mathrm{Si_4}\}$ fragment. As expected, upon complexation the four-membered ring of the $\{\mathrm{Si_4}\}$ ligand became significantly flatter; consequently, its geometry is best described as rectangular-planar (folding angles 2.8 and 4.8°), which is in sharp contrast to the highly folded structure of the starting non-aromatic tetrasilacyclobutadiene dianion $\mathbf{24}^{2-}$ (folding angle 34°) (Figure 12).[126] The cyclic Si–Si bond lengths are intermediate between those of typical Si–Si single and double bonds, ranging from 2.2570(9) to 2.3154(8) Å.

The iron complex **50** was obtained in 42 % yield as pale yellow crystals by treatment of 3,4-dibromo-1,2,3,4-tetrakis(di-*tert*-butylmethylsilyl)cyclotetrasilene **51** with an excess of $\mathrm{Na_2[Fe(CO)_4]}$ in THF at room temperature (Scheme 34).[127] Again, appreciable $3d(\mathrm{Fe})\rightarrow\pi^*(\mathrm{Si_4})$ π back-donation was suggested on the basis of the greatly high-field-shifted resonance of the skeletal Si atoms at $\delta = -15.8$ ppm (calculated by the GIAO method, the value for the model $\mathrm{Me_3Si}$-substituted complex is $\delta = -21.9$ ppm). Similar to the above case of the Co complex $\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$, the tetrasilacyclobutadiene ring in **50** is η^4-coordinated to the transition-metal center and nearly planar (folding angle 1.8°), whereas the cyclic Si–Si bond lengths (2.2610(7)–2.2802(7) Å) fit well within the range of typical Si–Si single-bond (av 2.34 Å) and double-bond (av 2.20 Å) lengths (Figure 13).

However, in contrast to the Co complex $\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$, which features a rectangular-shaped $\{\mathrm{Si_4}\}$ ligand,[126] the $\{\mathrm{Si_4}\}$ skeleton in the Fe complex **50** has a nearly regular square shape,[127] diagnostic of transition-metal cyclobutadiene complexes.[124a,c] Such a striking difference in geometry of the tetrasilacyclobutadiene ligand in $\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$ and **50** was attributed to partial delocalization of the negative charge over the $\{\mathrm{Si_4}\}$ ligand in $\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$, as observed in the lower values of the CO stretching vibrations in $\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$ (1870 cm^{-1}) in comparison with those in **50** (1922 and 1973 cm^{-1}), implying stronger π back-donation from the transition-metal center to the CO groups in the case of $\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$. Another important influence affecting the overall geometry of the $\{\mathrm{Si_4}\}$ ligand is the spatial orientation of the CO groups, which are located directly below the two opposite skeletal Si–Si bonds in $\mathbf{49}^-[\mathrm{K(diglyme)_2(thf)}]^+$, resulting in their elongation and,

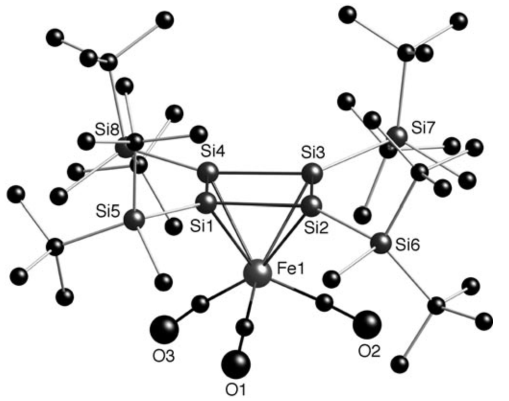


Figure 13. Crystal structure of **50** (Crystal Maker view; hydrogen atoms are not shown).

consequently, a preference for the rectangular form for the {Si_4} ligand.

Likewise, in the parent complex [$(H_4C_4)Fe(CO)_3$], one of the most important ligand-to-metal bonding interactions in **50** (Me_3Si-substituted model) occurs between the singly occupied π orbitals of the tetrasilacyclobutadiene ligand and the d_{xz} and d_{yz} orbitals of the Fe atom, resulting in the formation of two pairs of doubly degenerate bonding (HOMO−1, HOMO) and antibonding (LUMO, LUMO+1) orbitals (Figure 14). As expected, the HOMO and LUMO levels of the model complex [{$(Me_3Si)_4Si_4$}$Fe(CO)_3$] are higher and lower than the corresponding levels of the hypothetical carbon analogue [{$(Me_3Si)_4C_4$}$Fe(CO)_3$], giving rise to a markedly smaller HOMO–LUMO energy gap for the silicon version [{$(Me_3Si)_4Si_4$}$Fe(CO)_3$] (4.61 eV) compared to that of the carbon analogue [{$(Me_3Si)_4C_4$}$Fe(CO)_3$] (5.64 eV). The appreciable energy increase in the HOMO level of the Si complex results in a stronger π-donating ability of the {Si_4} ligand (compared with that of the {C_4} ligand) and, accordingly, enhanced π back-donation from the Fe atom to the CO ligands. The potential aromaticity of **50** was verified by an NICS(1) calculation, which gave a negative value of −12.5 (for the Me_3Si-substituted model), thus pointing to an assignment of this complex to the class of three-dimensional organometallic aromatic complexes similar to the parent complex [$(H_4C_4)Fe(CO)_3$].

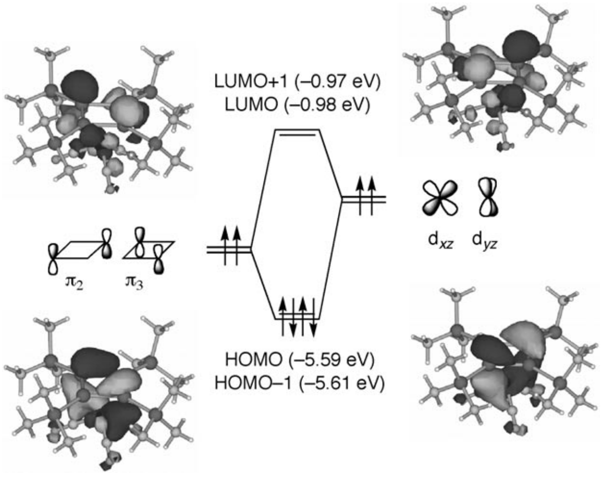


Figure 14. Frontier MOs of **50** (calculated for the model complex with Me_3Si groups instead of tBu_2MeSi substituents at B3LYP/6-31G(d) for H, C, O, and Si and at LANL2DZ for Fe).

6. Summary and Outlook

The concept of aromaticity is one of the oldest and most fundamental in organic chemistry. The study of aromatic compounds covers almost two centuries, since the milestone discovery of the first aromatic compound, benzene, by Faraday. The number of experimental accomplishments in this field is vast, and a modern theory of aromaticity, with the invaluable support of sophisticated computational methods, provides a rather satisfactory insight into the nature of aromaticity. Particular emphasis has been given to the definition of aromaticity as a peculiar phenomenon from the viewpoint of various criteria, which have allowed a more reliable assignment of organic compounds to the classes of either aromatic or non-aromatic compounds.

In contrast, the field of the heavy congeners of aromatic compounds, containing Group 14 elements heavier than carbon, is still waiting for comprehensive investigation. Considered as fleeting, unstable (and even undetectable) intermediates just several decades ago, the heavy aromatic species have turned into a class of real compounds that can be isolated, stored for an indefinite period, and even structurally characterized. Now, the heavy aromatic derivatives are becoming readily available and synthetically extremely useful organometallic reagents.

However, the chemistry of such compounds is very far from completion, and much still remains to be done. For example, the stable derivatives of the heavy analogues of the two-π-electron cyclobutadiene dication, as well as those of the six-π-electron cycloheptatrienylium (tropylium) ion and cyclooctatetraene dication, are still unknown experimentally. Moreover, aromatic compounds consisting of all heavy Group 14 elements, representing a particular interest from the viewpoint of inorganic-ring aromaticity, have been prepared only in the case of cyclopropenylium ion and cyclobutadiene dianion species. Undoubtedly, tetrasilacyclobutadiene dications, pentasilacyclopentadienide ions, hexasilabenzene compounds, and heptasilatropylium ions (as well as their heavier homologues with Ge, Sn and, possibly, Pb atoms) are among the most desirable synthetic targets for the near future.

Apart from the synthetic achievements, one should also expect major breakthroughs in the theory of heavy (organometallic) aromaticity, which is vastly different from its organic counterpart (indeed, carbon is very different from its heavier neighbors in Group 14). There are few serious theoretical studies related to this topic, and new theoretical insights based on high-level computations using the appropriate model compounds would be very welcome.

We also predict a greatly increasing interest in the chemistry of transition-metal complexes with heavy aromatic compounds as novel cyclic polyene ligands. Apart from its inherent synthetic and theoretical interest, such promising chemistry would also be highly attractive in applied sciences for the design of new advanced materials.

Addendum

Several remarkable papers have been published since our manuscript was accepted for publication. The novel sila-aromatic compound, 9-silaphenanthrene, kinetically stabilized by the bulky Tbt group on the Si atom, was synthesized by Tokitoh and co-workers.[128] The full account describing details of the synthesis and reactivity of the stannacyclopentadienide and stannacyclopentadienediide [$\mathbf{17}^{2-}\mathrm{Li}^{+}_{2}$] derivatives was published by the group of Saito.[129] The same group has also recently reported an interesting example of an aromatic dilithium dibenzopentalenediide bearing $i\mathrm{Pr}_3\mathrm{Si}$ substituents on the five-membered rings.[130] An unusual reaction of dilithio-2,3,4,5-tetraphenyl-1-silacyclopentadienediide [$\mathbf{14}^{2-}\mathrm{Li}^{+}_{2}$] with 1,3-dienes producing spirosilacyclopentadienes and elemental lithium was reported by West and co-workers.[131] Transition-metal derivatives featuring either η^6-germabenzene (Cr (**45a**), Mo (**45b**), W complexes) or η^5-germabenzene (Ru complex) ligands have been prepared by the group of Tokitoh.[132] The first ferrocene derivative [$(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Fe}\{\eta^5\text{-}(\mathrm{CPh})(\mathrm{CH})\mathrm{Si_2Ge}(\mathrm{SiMe}t\mathrm{Bu_2})_3\}$] incorporating *three* heavy Group 14 elements (two Si and one Ge) in one of the cyclopentadienyl rings was synthesized by Sekiguchi and co-workers.[133]

Abbreviations

ASE	aromatic stabilization energy
Bbt	2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl
dmpe	1,2-bis(dimethylphosphino)ethane
GIAO	gauge independent atomic orbital
Λ	diamagnetic susceptibility exaltation
NICS	nucleus independent chemical shift
PES	potential energy surface
Py	pyridine
RE	resonance energy
Tbt	2,4,6-tris[bis(trimethylsilyl)methyl]phenyl
THT	tetrahydrothiophene
TFPB$^-$	tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
TPB$^-$	tetraphenylborate
TPFPB$^-$	tetrakis(pentafluorophenyl)borate
TSFPB$^-$	tetrakis{4-[*tert*-butyl(dimethyl)silyl]-2,3,5,6-tetrafluorophenyl}borate
TTFPB$^-$	tetrakis(2,3,5,6-tetrafluorophenyl)borate
WBI	Wiberg bond index
Xyl	2,6-dimethylphenyl

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