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Review

Stable aromatic compounds containing heavier Group 14 elements

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Abstract

This account is devoted to the problem of aromaticity in the chemistry of heavier Group 14 elements: namely cyclic compounds including Si and Ge atoms in the ring. Three-membered, five-membered and six-membered ring systems, possessing aromatic character are described. © 2000 Elsevier Science S.A. All rights reserved.

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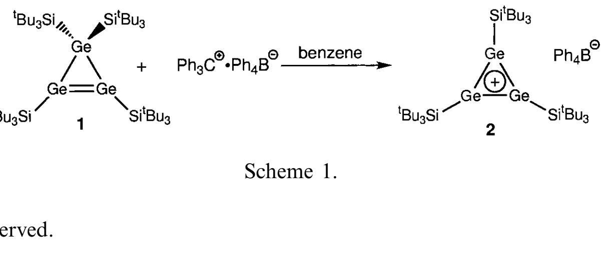
1. Introduction

Aromaticity is one of the basic concepts in chemistry [1]. After the discovery of benzene and its derivatives, the chemistry of aromatic compounds quickly became an independent, intensively studied and very important field of organic chemistry for fundamental research and industrial applications. Although aromaticity has been extensively studied for more than a century, there is still no generally acceptable definition. One of the most significant features of aromatic compounds was recognized as the existence of a cyclic structure with a delocalized system of $(4n+2)$ π-electrons. The most general point of view on aromaticity combines the geometric (bond length equality), energetic (aromatic stabilization energy) and magnetic (diamagnetic susceptibility exaltations and nucleus-independent chemical shifts) criteria [2].

Aromaticity in the chemistry of Group 14 elements heavier than carbon, sometimes called 'metalloaromaticity', is quite a new field of research, which has developed rapidly in recent years. Aromatic compounds of this type include three-, five- and six-membered ring systems, based on cyclopropenium type cations, cyclopentadienide type anions and benzene type structures, respectively. Compounds of these types will be considered in the present account from the point of view of aromaticity.

2. Three-membered ring systems

The cyclopropenium cation, possessing a Hückel-type aromatic 2 π-electron system, is the simplest and smallest aromatic compound. Due to its resonance stabilization, this compound is relatively stable despite the very large ring strain [3]. Although the chemistry of the cyclopropenium cation is well established now, heavy analogues of this compound consisting of Group 14 elements were unknown until quite recently. Theoretical calculations on the stability of $A_3H_3^+$ cations (A = C, Si, Ge, Sn, Pb), performed by Schleyer et al. [4], predicted a preference for the classical cyclopropenium cation structures with D_{3h} symmetry for the carbon and silicon cases, whereas C_{3v} hydrogen-bridged forms were expected to be favored for germanium, tin



Scheme 1.

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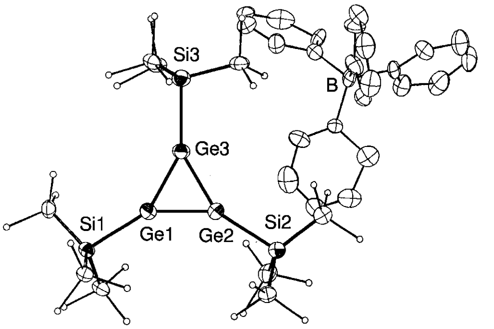


Fig. 1. Crystal structure of (^{t}Bu$_3$SiGe)$_3^+$·TPB$^-$ (**2**).

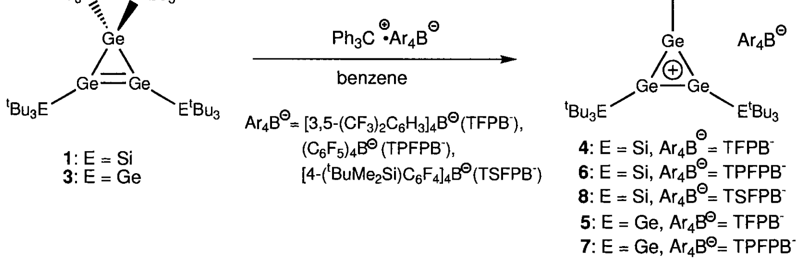
and lead. In fact, after many experimental efforts, the first free germyl cation with a 2 π-electron system was reported by Sekiguchi et al. in 1997 as a classical cyclopropenium cation type structure [5]. Tris(tri-*tert*-butylsilyl)cyclotrigermenium tetraphenylborate (**2**), [(^{t}Bu$_3$SiGe)$_3^+$·TPB$^-$] (TPB$^-$, tetraphenylborate), was prepared by the treatment of tetrakis(tri-*tert*-butylsilyl)cyclotrigermene (**1**) [6] with trityl tetraphenylborate in dry benzene and was isolated as air- and moisture-sensitive yellow crystals (Scheme 1).

The physical and spectroscopic properties of **2** are consistent with the assigned structure, which was subsequently confirmed by X-ray crystallographic analysis (Fig. 1). The three germanium atoms form an equilateral triangle (Ge–Ge distances: 2.321(4)–2.333(4) Å, and Ge–Ge–Ge bond angles: 59.8(1)–60.3(1)°). The Ge–Ge bond lengths observed for **2** are intermediate between the Ge=Ge double bond (2.239(4) Å) and the Ge–Ge single bond (2.522(4) Å) of the precursor **1**. Silicon atoms of the ^{t}Bu$_3$Si groups attached to the germanium atoms are approximately in the same plane as the three-membered ring. The distances between the germanium and boron atoms range from 6.941(3) to 9.695(3) Å. The closest distance between germanium and aromatic carbon atoms of TPB$^-$ is greater than 4 Å, well beyond the range of any significant interaction. These structural features indicate that **2** is a cyclotrigermenium ion and that it is a free germyl cation with a 2 π-electron system. The aromatic stabilization of the cyclotrigermenium ion and the charge delocalization explain the observed lack of any close interaction with the counter anion.

However, the problem of the TPB$^-$ is its chemical instability [7], because **2** can survive in a solution of dichloromethane only at temperatures below −78°C. [3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$B$^-$ (TFPB$^-$, tetrakis{3,5-bis(trifluoromethyl)phenyl}borate) [8], (C$_6$F$_5$)$_4$B$^-$ (TPFPB$^-$, tetrakis(pentafluorophenyl)borate) [9] and [4-(^{t}BuMe$_2$Si)C$_6$F$_4$]$_4$B$^-$ (TSFPB$^-$, tetrakis{4-[*tert*-butyl(dimethyl)silyl]-2,3,5,6-tetrafluorophenyl}borate) [10] are known to be stable borate anions. These counter anions should increase the stability of the resulting cyclotrigermenium ion. Therefore, the reaction of ^{t}Bu$_3$E-substituted cyclotrigermenes **1** (E = Si) [6] and **3** (E = Ge) [6] with Ph$_3$C$^+$·TFPB$^-$, Ph$_3$C$^+$·TPFPB$^-$, and Ph$_3$C$^+$·TSFPB$^-$, producing [(^{t}Bu$_3$EGe)$_3^+$·TFPB$^-$], [(^{t}Bu$_3$EGe)$_3^+$·TPFPB$^-$], and [(^{t}Bu$_3$EGe)$_3^+$·TSFPB$^-$] (E = Si, Ge), were examined [11]. The resulting germyl cations can survive for extensive periods without decomposition both in solution and in the solid state.

Synthesis of germyl cations was carried out under an inert atmosphere using Schlenk and high vacuum line techniques. Dry oxygen-free benzene was introduced by vacuum transfer to a mixture of (^{t}Bu$_3$Si)$_4$Ge$_3$ (**1**) and Ph$_3$C$^+$·TFPB$^-$, and the mixture was stirred at room temperature to form (^{t}Bu$_3$SiGe)$_3^+$·TFPB$^-$ (**4**), which was isolated as a yellow powder in 81% yield. The reaction of **3** with Ph$_3$C$^+$·TFPB$^-$ in benzene also proceeded to give (^{t}Bu$_3$GeGe)$_3^+$·TFPB$^-$ (**5**) in 76% yield. Similar to that of Ph$_3$C$^+$·TFPB$^-$, the reaction of **1** and **3** with Ph$_3$C$^+$·TPFPB$^-$ in benzene produced (^{t}Bu$_3$SiGe)$_3^+$·TPFPB$^-$ (**6**) (80%) and (^{t}Bu$_3$GeGe)$_3^+$·TPFPB$^-$ (**7**) (80%), respectively. The reaction of **1** with Ph$_3$C$^+$·TSFPB$^-$ produced (^{t}Bu$_3$SiGe)$_3^+$·TSFPB$^-$ (**8**) as orange crystals in 88% yield (Scheme 2).

The molecular structure of **4** is shown in Fig. 2. The three-membered ring consisting of germanium atoms is almost an equilateral triangle, as determined by the internal bond angles of 59.79(3) to 60.28(3)°. The Ge–Ge distances of the three-membered ring are almost equal, ranging from 2.3284(8) to 2.3398(8) Å (av. 2.3333(8) Å). The three silicon atoms are nearly coplanar with the central three-membered ring. The bond lengths of the Ge–Si bonds (Ge1–Si1, 2.425(1); Ge2–Si2, 2.442(1); Ge3–Si3, 2.444(1) Å) of **4** are short-



Scheme 2.

ened compared with those of **1** [6] (2.629(7) Å for the Ge–Si bond length of sp^3 Ge atom and 2.448(7) Å for the Ge–Si bond length of sp^2 Ge atoms). The perspective view appears to show a weak electrostatic interaction between the germanium and fluorine atoms. The three closest distances range from 3.823 to 5.097 Å, however, these distances are longer than the sum (3.57 Å) of the van der Waals radii for germanium and fluorine atoms [12]. Undoubtedly, CF_3 groups of the counter anion are sufficiently remote from the germanium center to preclude any covalent interaction.

X-ray diffraction data were also obtained for **8**. Due to the steric bulkiness of the $^t\mathrm{BuMe_2Si}$ group attached to the *para* positions of the phenyl rings of the borate anion, no interaction between the cation moiety and the counter anion can be found (Fig. 3). As a consequence, the skeleton of the three-membered framework forms an equilateral triangle; the Ge–Ge bond lengths are 2.3310(8) for Ge1–Ge2, 2.3315(7) for Ge1–Ge3, and 2.3349(8) Å for Ge2–Ge3, and the Ge–Ge–Ge bond angles are 60.10(2) for Ge2–Ge1–Ge3, 59.96(2) for Ge1–Ge2–Ge3, 59.94(2)° for Ge1–Ge3–Ge2. The structural features for **4** and **8** are practically the same as those of **2** [5].

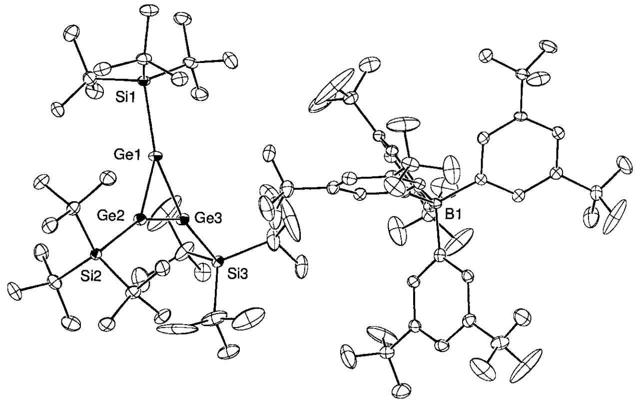


Fig. 2. Crystal structure of $(^t\mathrm{Bu_3SiGe})_3^+\cdot\mathrm{TFPB}^-$ (**4**).

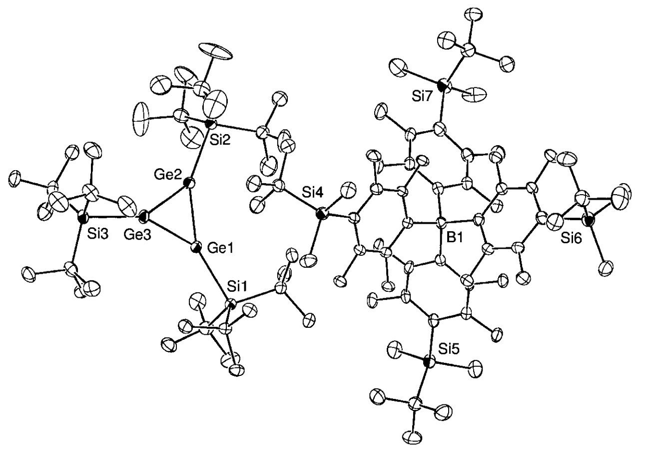
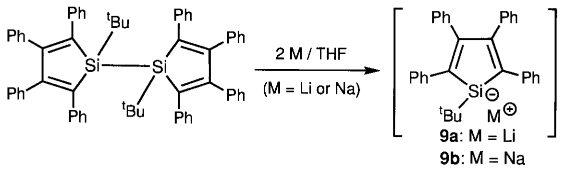


Fig. 3. Crystal structure of $(^t\mathrm{Bu_3SiGe})_3^+\cdot\mathrm{TSFPB}^-$ (**8**).



Scheme 3.

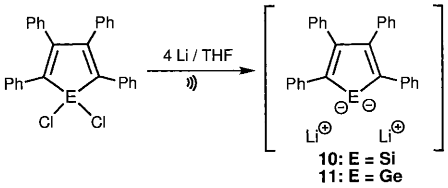
The evidence for the existence of the free cyclotrigermenium ion in solution was supported by the NMR spectroscopic data. The ^{1}H-, ^{13}C-, and ^{29}Si-NMR chemical shifts for the cyclotrigermenium moiety of **4**, **6** and **8** in CD_2Cl_2 are practically the same. For example, ^{29}Si-NMR chemical shifts of **4**, **6** and **8** are independent of the counter anion. The ^{29}Si-NMR chemical shift of **4** is also essentially the same in different solvents, appearing at $\delta = 64.0$ in CD_2Cl_2, $\delta = 64.2$ in $CDCl_3$, $\delta = 64.4$ in toluene-d_8, and $\delta = 64.5$ in Et_2O. This independence from both the counter anion and solvent clearly indicates that $(^t\mathrm{Bu_3SiGe})_3^+$ is a free germyl cation in solution.

The large downfield shifted ^{29}Si-NMR resonance of $(^t\mathrm{Bu_3SiGe})_3^+$, relative to that of the precursor **1** ($\delta = 37.2$ for $^t\mathrm{Bu_3Si}$ attached to the saturated Ge atom and 50.1 for $^t\mathrm{Bu_3Si}$ attached to the Ge=Ge double bond) [6], is due to the positive charge of the cyclotrigermenium ion. The positive charge is not localized on the germanium atoms, but is significantly transferred to the silicon centers. The atomic (Mulliken) charges on $(\mathrm{H_3SiGe})_3^+$ according to HF/6-31G* level calculations indicate a delocalization of the positive charge; -0.07 for the ring germanium atoms, $+0.64$ for the silicon atoms of the SiH_3 substituents.

3. Five-membered ring systems

There is current interest in the synthesis of heavier Group 14 element analogues of the cyclopentadienyl anion, which is well known as a classical example of a 6 π-electron aromatic compound. Recent experimental [13,15,17–24] and theoretical [2a,2b,14,16,17,19] investigations have established that aromaticity of the heavier Group 14 element analogues of the cyclopentadienyl anion strongly depends on the nature of the counter cation and substituents. Not all metallole anions and dianions are aromatic.

Although the first generation of the tetraphenylsilole dianion was described in 1990 [20], the detailed study of silole systems, which showed the tetraphenylsilole anion to be an aromatic species, was performed several years later. Thus, reduction of bis(silole) with sodium (or lithium) in THF at room temperature under ultrasonic activation produced a dark purple solution of the silole anion (Scheme 3) [13]. NMR data of this anion showed



Scheme 4.

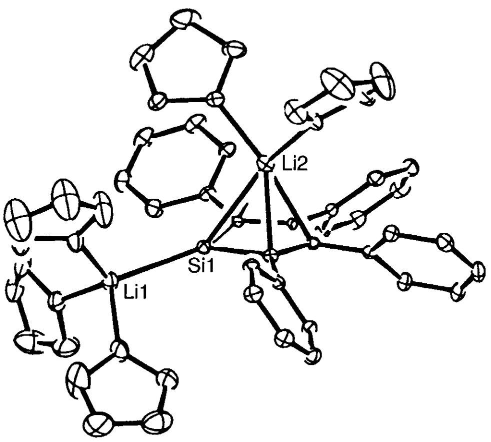


Fig. 4. Crystal structure of $Li_2[(PhC)_4Si]\cdot 5$ THF (**10**) (Ref. [17]). Reprinted with permission from the Journal of American Chemical Society.

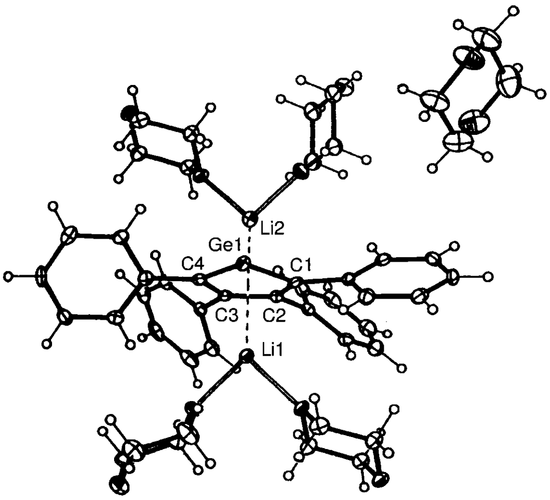


Fig. 5. Crystal structure of $Li_2[(PhC)_4Ge]\cdot 5$ dioxane (**11a**) (Ref. [19]). Reprinted with permission from VCH Publishers.

evidence for an appreciable charge transfer from the silicon atom into the ring. The most significant observation is deshielding of the silicon atom; a downfield shift in ^{29}Si-NMR of **9b** by $\delta = 22.5$, compared with the starting bis(silole). This fact, and also the shielding of the C_α and C_β atoms of the five-membered ring, indicate an appreciable delocalization of the negative charge in the ring, that is, significant aromatic character of the silole anion species. These tendencies have been well reproduced by theoretical calculations of the chemical shifts for the parent compound $[SiC_4H_5]Li$ [14].

Silole dianion **10**, which was generated by the reaction of dichlorotetraphenylsilole with lithium in THF under ultrasonic activation [15], has a large downfield shift ($\Delta\delta = 61.7$) in the ^{29}Si-NMR relative to the starting dichlorosilole (Scheme 4). As in the previous case, upfield shifts of the C_α and C_β atoms of the cyclopentadienide ring were observed. All of these NMR data gave the strong evidence for the significant aromatic nature of the silole dianion **10**, which is also supported by calculations [16] showing that the silole dianion species is more aromatic than isoelectronic phosphole and thiophene systems and even approaches the aromaticity level of the cyclopentadienyl anion. Further proof for this suggestion was obtained from the X-ray crystallography data [17], which showed the silole ring in **10** to be planar with nearly equal C–C distances, as is expected for a delocalized system (Fig. 4).

However, the arrangement of the two lithium atoms was quite different from the calculated structure [17]; one of the lithium atoms is η^5-coordinated to the silole ring, whereas another one is η^1-bonded to the silicon atom, although theory predicted a symmetrical η^5-η^5 structure to be thermodynamically more favorable by 21 kcal mol^{-1}. Such a contradiction may be a result of solvation of lithium ions by THF as well as crystal packing forces, which could reverse the stability order. In contrast, the aromatic 18-crown-6 complex of $[Me_4C_4Si]K_2$, which was prepared by the reaction of the corresponding dibromosilole with potassium metal in THF in the presence of 18-crown-6 [18], adopts the 'inverse sandwich' structure in the solid state with η^5-η^5 coordination of both potassium atoms. It is interesting that germole dianion **11** [19], for which a delocalized structure was established on the basis of the ^{13}C-NMR spectrum [21], exhibited two different types of Li-coordination, as was shown by X-ray crystallography. Crys-

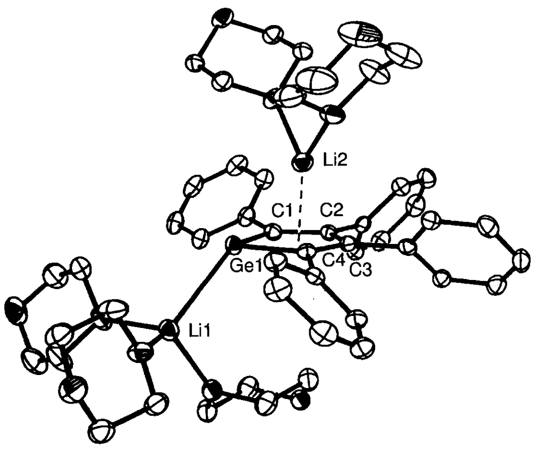
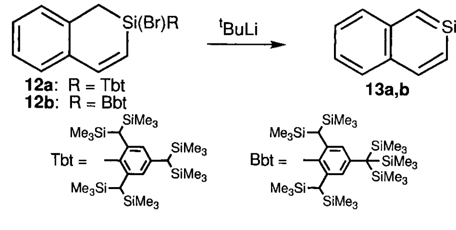


Fig. 6. Crystal structure of $Li_2[(PhC)_4Ge]\cdot 5.5$ dioxane (**11b**) (Ref. [19]). Reprinted with permission from VCH Publishers.



Scheme 5.

tallization of **11** from dioxane at − 20°C produced yellow crystals of the symmetrical η^5-η^5 structure $Li_2[(PhC)_4Ge]\cdot 5$ dioxane **11a** (Fig. 5), whereas crystallization at room temperature produced orange crystals of $Li_2[(PhC)_4Ge]\cdot 5.5$ dioxane **11b** (Fig. 6) with the η^1-η^5 structure. In both structures **11a** and **11b**, the π-electrons are highly delocalized on germole ring, which leads to a nearly planar five-membered ring and equal C–C bond lengths. Such structures are in good agreement with the calculated geometries for the model compound $Li_2(H_4C_4Ge)$ [19].

Quite recently, some new examples of aromatic silole- and germole-based anionic species have been reported. Thus, reduction of dichlorosilaindane with lithium or sodium metals cleanly produced the corresponding lithium and sodium salts of the silaindenyl dianion, which has aromatic character in the five-membered ring according to ^{13}C- and ^{29}Si-NMR data [22]. X-ray analysis also revealed η^1-η^5 coordination of lithium atoms to the five-membered ring as was previously found for silole and germole dianions. An unusual example of the tetraethylgermole dianion coordinated with three lithium cations, in which two lithium atoms are η^5-coordinated and one lithium atom is η^1-coordinated with the germole ring $[\eta^5\text{-Li}\cdot\text{TMEDA}][\eta^5\text{-Li}]_{1/2}[\eta^1\text{-Li}]_{1/2}$-$[Et_4C_4Ge]$, has been described [23]. This compound also exhibits significant aromatic character, according to ^{13}C-NMR and X-ray data. Some examples of transition metal complexes, incorporating silole or germole units as ligands, have also been reported as having an aromatic character [24,25].

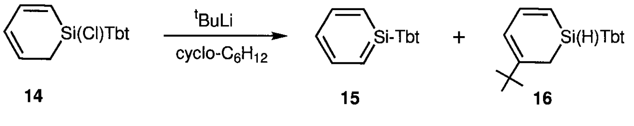
4. Six-membered ring systems

4.1. Silicon-containing benzene and naphthalene

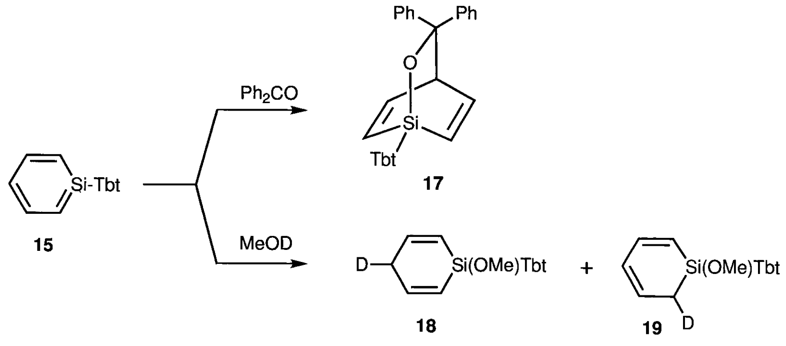
Silaaromatic compounds such as sila- and disilabenzenes have been proposed as highly reactive intermediates during several last decades [26], although no direct evidences have been reported. The closest approach for a ‘stable’ silabenzene was reported by Märkl et al., who synthesized 1,4-di-*tert*-butyl-2,6-bis(trimethylsilyl)silabenzene [27]. However, this compound was stable only below − 100°C. Nevertheless, numerous theoretical calculations of sila- and disilabenzene molecules [28] have predicted a delocalized structure and considerable aromaticity (∼ 80% of benzene aromaticity from the energy criterion [29]). That gave a chance for synthetic chemists to prepare stable silaarenes by the introduction of very bulky substituents, which could suppress the high reactivity of silaarenes. In fact, this approach was successfully realized by the Tokitoh and Okazaki group, who reported the stable 2-silanaphthalene [30] in 1997 and stable silabenzene [31] in 2000. These compounds were synthesized using kinetic stabilization as a result of using extremely bulky Tbt (2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl) [32] and Bbt (2,6-bis-[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]-phenyl) [33] groups. For the synthesis of 2-silanaphthalene **13** [30,34], the corresponding bromosilane **12** was selected as a possible precursor. Treatment of bromosilanes **12** with an equivalent amount of ᵗBuLi in hexane resulted in the formation of the expected 2-silanaphthalenes **13a**,**b** as colorless crystals, which were characterized by low-field ^{29}Si-NMR resonances (**13a**: $\delta = 87.3$, **13b**: $\delta = 86.7$) (Scheme 5).

2-Silanaphthalenes are moisture-sensitive, but very thermally stable in the solid state or even in solution up to 100°C. Aromaticity of 2-silanaphthalenes was evaluated on the basis of NMR, UV and Raman spectra [34]. Thus, for example, it is well known that the coupling constants of two adjacent atoms can serve as a good index for the estimation of the bond order [35]. Values of about 50 Hz are typical for Si–C single bonds [35], whereas values of 83–85 Hz were reported for Si=C double bonds [36]. For 2-silanaphthalene **13a**, J_{Si-C1} and J_{Si-C3} were found to be 92 and 76 Hz, respectively; both values are much larger than those for Si–C single bonds, therefore it is reasonable to suggest double bond character for these Si–C bonds as in the case of naphthalene. 2-Silanaphthalene **13a** exhibits three absorption maxima at 267 (ε 20 000), 327 (ε 7000) and 387 (ε 2000) nm in hexane. Despite the red shift, these bands clearly correspond to the *E*1, *E*2 and *B* bands of naphthalene. 2-Silanaphthalenes are not only aromatic compounds, but they also contain the silene fragment in the molecule. Indeed, despite the great steric congestions, the Si=C double bond still has enhanced reactivity. Thus, 2-silanaphthalene smoothly undergoes addition of D_2O and MeOH. Cycloaddition reactions with benzophenone, mesitonitrile oxide and 2,3-dimethyl-1,3-butadiene produced the corresponding adducts.

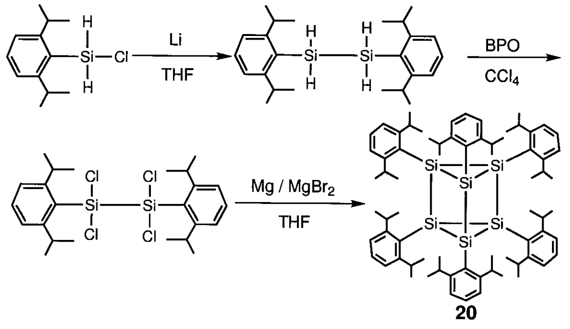
Another representative of stable silaaromatic compounds — the simplest arene analogue: silabenzene,



Scheme 6.



Scheme 7.



Scheme 8.

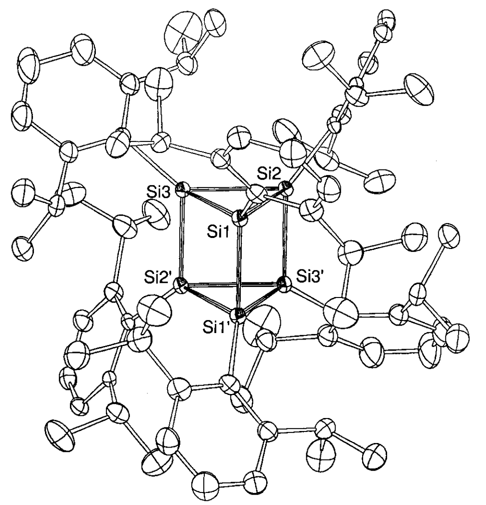


Fig. 7. Crystal structure of hexasilaprismane (**20**).

was prepared quite recently by using the same protecting Tbt group [31]. Reaction of **14** with ^{t}BuLi in cyclohexane afforded two products, one of them was identified as silabenzene **15** (^{29}Si-NMR: $\delta = 92.5$ in cyclohexane-d_{12}) together with silacyclohexadiene **16** (Scheme 6).

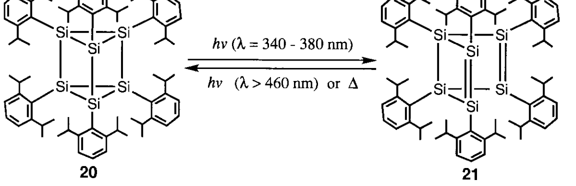
Silabenzene **15** was trapped by benzophenone to afford $[4+2]$ cycloadduct **17** (Scheme 7). Such behavior is quite different from that of 2-Tbt-2-silanaphthalene **13a**, which reacted only as an isolated Si=C double bond system and does not exhibit any diene type reactivity [30,34]. Silabenzene **15** also reacted with methanol to form a mixture of two adducts **18** and **19** in a 3:2 ratio.

The aromatic character of silabenzene **15** was established by NMR data [31]. Thus, the ^{29}Si-NMR resonance of silabenzene **15** ($\delta = 92.5$) is close to that of the above mentioned aromatic 2-silanaphthalene **13a** ($\delta = 87.3$). The coupling constant $^1J_{\text{SiC}}$ value (83 Hz) of silabenzene **15** for a Si–C bond in the ring lies between the two $^1J_{\text{SiC}}$ values for 2-silanaphthalene **13a** (92 and 76 Hz). The $^1J_{\text{SiC}}$ value of silabenzene **15** is also almost the same as that of Brook's silene $(Me_3Si)_2Si{=}C(Ad)OSiMe_3$ (84 Hz) [36]. The Si–C bond length in the ring was calculated to be 1.777 Å, which is intermediate between Si–C single and Si=C double bond lengths and similar to the average calculated value of the two Si–C bond lengths of 2-silanaphthalene (1.750 and 1.791 Å).

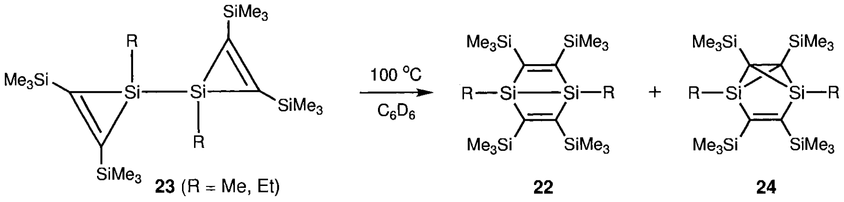
4.2. Silicon-containing benzene valence isomers

There are some examples of the silicon-containing Dewar benzenes (hexasila-Dewar benzene and 1,4-disila-Dewar benzene). Hexasila-Dewar benzene was obtained upon the photochemical isomerization of hexasilaprismane **20** [37], which in fact is also a hexasilabenzene valence isomer. The compound **20** was prepared by the dechlorinative coupling reaction of tetrachlorodisilane $RSiCl_2{-}SiCl_2R$ or $RSiCl_3$ ($R = 2,6\text{-}{}^iPr_2C_6H_3$) with $Mg{-}MgBr_2$ in THF [37] (Scheme 8). Hexagermaprismane derivatives, which are valence isomers of hexagermabenzene, were also synthesized [38].

Hexasilaprismane was isolated as orange crystals, which are quite stable in the solid state even upon



Scheme 9.



Scheme 10.

prolongated exposure to air. The structure of hexasilaprismane was established by X-ray crystallography [37], which showed that the molecule has a slightly distorted prism structure with two triangular and three rectangular units (Fig. 7).

Irradiation of hexasilaprismane **20** at low temperature with light of wavelength 340–380 nm caused the formation of three new absorption bands at 335, 455 and 500 nm in UV–vis spectrum, attributable to hexas-ila-Dewar benzene **21** (Scheme 9). Such isomerization is reversible and upon irradiation of hexasila-Dewar benzene **21** with light of wavelength longer than 460 nm, starting hexasilaprismane **20** was regenerated. Hexasila-Dewar benzene **21** is stable at − 150°C, but gradually reverted to hexasilaprismane **20** upon warming up [39]. The half-life is $t_{1/2} = 0.52$ min at 0°C in 3-methylpentane. The activation parameters for the isomerization were estimated as $E_a = 13.7$ kcal mol^{-1}, $\Delta H^{\ddagger} = 13.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -17.8$ cal K^{-1} mol^{-1}.

Disila-Dewar benzene **22** was generated by the thermolysis of bis(silirene) **23** at 100°C in C_6D_6 together with 2,5-dimethyldisilabenzvalene **24**, which is another valence isomer [40] (Scheme 10). The structure of 1,4-disila-Dewar benzene was established by X-ray crystallography, which showed that the central Si–Si bond length is short (2.244–2.248 Å) in comparison with 1,2-disilacyclobutenes (2.344–2.359 Å) [41], and even disilacyclopropane (2.272 Å) [42].

5. Conclusion

Great success has been achieved quite recently in the synthesis and characterization of aromatic compounds containing heavier Group 14 elements, although even just a few years ago such compounds would have been considered inaccessible. The aromatic nature of these compounds has been established by physico–chemical methods and supported by theoretical calculations, bringing a new important impact on our understanding of the question of aromaticity. The number of aromatic compounds of heavier Group 14 elements is still very limited and significant progress can be expected in this chemistry in the near future.

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References

[1] For general reviews, see: (a) P.J. Garratt, Aromaticity, Wiley, New York, 1986. (b) V.I. Minkin, M.N. Glukhovtsev, B.Y. Simkin, Aromaticity and Antiaromaticity, Electronic and Structural Aspects, Wiley, New York, 1994.
[2] (a) P.v.R. Schleyer, P.K. Freeman, H. Jiao, B. Goldfuss, Angew. Chem. Int. Ed. Engl. 34 (1995) 337. (b) B. Golgfuss, P.v.R. Schleyer, Organometallics 16 (1997) 1543. (c) P.v.R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N.J.R.v.E. Hommes, J. Am. Chem. Soc. 118 (1996) 6317. (d) P.v.R. Schleyer, H. Jiao, N.J.R.v.E. Hommes, V.G. Malkin, O.L. Malkina, J. Am. Chem. Soc. 119 (1997) 12 669.
[3] (a) R. Breslow, J. Am. Chem. Soc. 79 (1957) 5318. (b) R. Breslow, C. Yuan, J. Am. Chem. Soc. 80 (1958) 5991. (c) R. Breslow, Pure Appl. Chem. 28 (1971) 111.
[4] E.D. Jemmis, G.N. Srinivas, J. Leszczynski, J. Kapp, A.A. Korkin, P.v.R. Schleyer, J. Am. Chem. Soc. 117 (1995) 11 361.
[5] A. Sekiguchi, M. Tsukamoto, M. Ichinohe, Science 275 (1997) 60.
[6] A. Sekiguchi, H. Yamazaki, C. Kabuto, H. Sakurai, S. Nagase, J. Am. Chem. Soc. 117 (1995) 8025.
[7] S.H. Strauss, Chem. Rev. 93 (1993) 927.
[8] S.R. Bahr, P. Boudjouk, J. Org. Chem. 57 (1992) 5545.
[9] J.C.W. Chien, W.-M. Tsai, M.D. Raush, J. Am. Chem. Soc. 113 (1991) 8570.
[10] (a) L. Jia, X. Yang, A. Ishihara, T.J. Marks, Organometallics 14 (1995) 3135. (b) L. Jia, X. Yang, C.L. Stern, T.J. Marks, Organometallics 16 (1997) 842.
[11] (a) M. Ichinohe, N. Fukaya, A. Sekiguchi, Chem. Lett. (1998) 1045. (b) A. Sekiguchi, N. Fukaya, M. Ichinohe, Phosphorus Sulfur Silicon Relat. Elem. 59 (1999) 150–151. (c) A. Sekiguchi, N. Fukaya, M. Ichinohe, Y. Ishida, Eur. J. Inorg. Chem. (2000) 1155.
[12] A. Bondi, J. Phys. Chem. 68 (1964) 443.
[13] J.-H. Hong, P. Boudjouk, J. Am. Chem. Soc. 115 (1993) 5883.
[14] B. Golgfuss, P.v.R. Schleyer, Organometallics 14 (1995) 1553.
[15] J.-H. Hong, P. Boudjouk, S. Castellino, Organometallics 13 (1994) 3387.
[16] B. Golgfuss, P.v.R. Schleyer, F. Hampel, Organometallics 15 (1996) 1755.
[17] R. West, H. Sohn, U. Bankwitz, J. Calabreze, Y. Apeloig, T. Müller, J. Am. Chem. Soc. 117 (1995) 11 608.
[18] (a) W.P. Freeman, T.D. Tilley, G.P.A. Yap, A.L. Rheingold, Angew. Chem. Int. Ed. Engl. 35 (1996) 882. (b) W.P. Freeman,

T.D. Tilley, L.M. Liable-Sands, A.L. Rheingold, J. Am. Chem. Soc. 118 (1996) 10 457.

[19] R. West, H. Sohn, D.R. Powell, T. Müller, Y. Apeloig, Angew. Chem. Int. Ed. Engl. 35 (1996) 1002.

[20] W.-C. Joo, J.-H. Hong, S.-B. Choi, H.-E. Son, J. Organomet. Chem. 391 (1990) 27.

[21] J.-H. Hong, P. Boudjouk, Bull. Chem. Soc. Fr. 132 (1995) 495.

[22] S.-B. Choi, P. Boudjouk, P. Wei, J. Am. Chem. Soc. 120 (1998) 5814.

[23] S.-B. Choi, P. Boudjouk, J.-H. Hong, Organometallics 18 (1999) 2919.

[24] W.P. Freeman, T.D. Tilley, A.L. Rheingold, J. Am. Chem. Soc. 116 (1994) 8428.

[25] J.M. Dysard, T.D. Tilley, J. Am. Chem. Soc. 120 (1998) 8245.

[26] For reviews on silaaromatic compounds, see: (a) G. Raabe, J. Michl. Chem. Rev. 85 (1985) 419. (b) G. Raabe, J. Michl, The Chemistry of Organic Silicon Compounds, in: S. Patai, Z. Rappoport (Eds.), Wiley, New York, 1989, pp. 1102–1108. (c) A.G. Brook, M.A. Brook, Adv. Organomet. Chem. 39 (1996) 71.

[27] G. Märkl, W. Schlosser, Angew. Chem. Int. Ed. Engl. 27 (1988) 963.

[28] (a) Y. Apeloig, The Chemistry of Organic Silicon Compounds, in: S. Patai, Z. Rappoport (Eds.), Wiley, New York, 1989, pp. 151–166. (b) Y. Apeloig, M. Karni, The Chemistry of Organic Silicon Compounds, in: Z. Rappoport, Y. Apeloig (Eds.), Wiley, New York, 1998, vol. 2, part 1, pp. 1–102 (Chapter 1).

[29] M.S. Gordon, P. Boudjouk, F. Anwari, J. Am. Chem. Soc. 105 (1983) 4972.

[30] N. Tokitoh, K. Wakita, R. Okazaki, S. Nagase, P.v.R. Schleyer, H. Jiao, J. Am. Chem. Soc. 119 (1997) 6951.

[31] K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, Angew. Chem. Int. Ed. 39 (2000) 634.

[32] R. Okazaki, N. Tokitoh, T. Matsumoto, Synthetic Methods of Organometallic and Inorganic Chemistry, in: W.A. Herrmann (Ed.), Thieme, New York, 1996, vol. 2 (N. Auner, U. Klingebiel, Eds.), pp. 260–269.

[33] (a) N. Kano, N. Tokitoh, R. Okazaki, Organometallics 17 (1998) 1241. (b) N. Tokitoh, T. Sasamori, R. Okazaki, Chem. Lett. (1998) 725.

[34] K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, P.v.R. Schleyer, H. Jiao, J. Am. Chem. Soc. 121 (1999) 11 336.

[35] H.-O. Kalinowski, S. Berger, S. Braun, Carbon-13 NMR Spectroscopy, Wiley, New York, 1986, p. 600.

[36] A.G. Brook, F. Abdesaken, G. Gutekunst, N. Plavac, Organometallics 1 (1982) 994.

[37] A. Sekiguchi, T. Yatabe, C. Kabuto, H. Sakurai, J. Am. Chem. Soc. 115 (1993) 5853.

[38] A. Sekiguchi, C. Kabuto, H. Sakurai, Angew. Chem. Int. Ed. Engl. 28 (1989) 55.

[39] A. Sekiguchi, T. Yatabe, S. Doi, H. Sakurai, Phosphorus Sulfur Silicon Relat. Elem. 93-94 (1994) 193.

[40] Y. Kabe, K. Ohkubo, H. Ishikawa, W. Ando, J. Am. Chem. Soc. 122 (2000) 3775.

[41] (a) J. Belzner, H. Ihmels, B.O. Kneisel, R. Herbst-Irmer, J. Chem. Soc. Chem. Commun. (1994) 1989. (b) K. Tamao, K. Nagata, M. Asahara, A. Kawachi, Y. Itoh, M. Shiro, J. Am. Chem. Soc. 117 (1995) 11 592.

[42] S. Masamune, S. Murakami, H. Tobita, D.J. Williams, J. Am. Chem. Soc. 105 (1983) 7776.